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CONTENTS

Pages

Editor/Members of the Editorial Board…………………………………………………………. III

Preface………..……………………………………………………………………………VII

Acknowledgments………………………………………………………………………...VIII

Organizing Committee Members……………………………………………………… IX

International Advisory Board Members……………………………………………….. X

Scientific Committee Members…………………………………………………………… XIII

Messages……………………………………………………………………………………… XVII
- Message from Dr. Suat İ.Günsel, Honorary President of the Conference
- Message from Prof.Dr. Hüseyin Gökçekuş, President of the Conference

Opening Speeches…………………………………………………………………………….. XIX

- Prof. Dr. Ümit Hassan, Rector of Near East University, TRNC
- Prof.Dr. Hüseyin Gökçekuş, President of the Conference & Organizing Committee, TRNC
- Rahmi Koç, Honorary Chairman & Founding Member of TURMEPA, TURKEY
- Eşref Cerrahoğlu, Chairman of Executive Board of TURMEPA, TURKEY
- Cemal Bulutoğluları, Mayor, Turkish Municipality of Lefkoşa, TRNC
- Asım Vehbi, Minister of Environment and Natural Resources, TRNC
- Tahsin Ertuğruloğlu, Leader of the National Unity Party(UBP), TRNC
- Assoc. Prof.Dr. Turgay Avcı, Deputy Prime Minister & Minister of Foreign Affairs of TRNC
- Türkekul Kurttekin, Turkish Ambassador to Lefkoşa, TRNC
- Ferdi Sabit Soyer, Prime Minister of TRNC
- Prof. Dr. Ekmeleddin İhsanoğlu, OIC Secretary General
- Mehmet Ali Talat, President of TRNC

Final Report of the International Conference On Environment: Survival and Sustainability... XXXIX

List of Papers and Posters……………………………………………………………………XLIII

Papers and Posters

Volume 1: MT-1: Business and Environment : Redefining Interests……………………….……………..… 1

Volume 2: MT-2: Conservation and Management of Biodiversity ……….……………………. 187

Volume 3: MT-3: Cultural Heritage and Environmental Factors……………….……………………. 769

Volume 4: MT-4: Economics, Development and Sustainability…………….…………….....……. 1043

Volume 5: MT-5: Energy and Development: New and Renewable Energy……………………… 1673
MT-6: Environment and Health……………………………………………………… 1953

Volume 6: MT-7: Environmental Awareness, Education, and Lifelong Learning……………….. 2369
MT-8: Environmental Knowledge and Information Systems…………………….…….. 2615
MT-9: Environmental Law and Ethics……………………………………….…………. 2807
MT-10: Environmental Organizations: Roles, Problems and Prospects……….…….. 2895

Volume 7: MT-11: Environmental Science and Technology…………………………...….….. 2923
MT-12:Global Warming: How Much of A Threat?... 3607

Volume 8: MT 13 -Green Factor In Politics……….……………..……………………………….. 3785
MT-14: Integrated Water Resources Management…………..………………………. 3847

Volume 9: MT-15: International Relations and Environmental Issues…………………………..… 4367
MT-16: Literature and Environmental Awareness…………………………………… 4527
MT-17: Natural and Man-Made Disasters: Emerging Link and Challenges……….... 4587
MT-18: Pesticides In The Environment and Food Commodities…………………….. 4741
MT-19: The Role of Media : Problems and Challenges……………………………….. 4809

Volume 10: MT-20: Seas, Ecological Balance, and Sustainable Environment…………………… 4915
MT-21: Social and Psychological Dimensions of Environmental Issues……………. 5117

Index………………………………………………………………………………………..I

Brief Information About Near East University…………………………………………..…XI

Brief Information About Turkish Republic of Northern Cyprus…………………………...XV

PREFACE

Creating a sustainable and a healthy environment is one of the most important global issues facing mankind today. Therefore, serious consideration should be given to environmental problems and concerted efforts should be made worldwide in order to respond and prevent present and future environmental risks and challenges.

The International Conference on Environment: Survival and Sustainability (ESS 2007) organized by the Near East University between the dates 19 and 24 February 2007 was held in Lefkosa, Turkish Republic of Northern Cyprus. The main objective of this multidisciplinary conference was to gather scientists from all over the world to discuss the overall issue of the environment, to find out sustainable solutions for environmental problems and to identify areas for future collaboration in this matter. The conference brought together 2,052 participants from 108 different countries. During the conference a total of 1,463 papers were presented under 21 different subtopics, representing various scientific disciplines. The topics included environmental law and ethics, environmental knowledge, technology and information systems, media, environmental awareness, education and lifelong learning, the use of literature for environmental awareness and the effects of the green factor in politics and in international relations.

The Scientific Committee of International Conference ESS2007 evaluated all of the 1,463 papers and selected among them 610 papers to be included in The Proceedings of Environment: Survival and Sustainability. The readers will notice the wide range of topics represented by the papers included in the Conference Proceedings.

It is hoped that this book will serve to contribute to increase in awareness towards various environmental issues as well as drawing more attention to the urgency of international cooperation and collaboration in pursuing sustainable environmental management.

Prof. Dr. Hüseyin Gökçekuş
President of the Conference and the Organizing Committee
Vice Rector of the Near East University
Lefkoşa-TRNC
18 February 2009

ACKNOWLEDGMENTS

The Organizing Committee of the ESS2007 Conference would like to extend its sincere appreciation to Dr. Suat Günsel, the Founding Rector of the Near East University, to Prof. Dr. Ekmeleddin İhsanoğlu, General Secretary of the Organization of Islamic Conference and to Prof. Dr. Walter W. Kofler, President of ICSD/IAS for their significant support and encouragement in the conference.

Appreciation is also extended to the chairpersons, the keynote speakers and the presenters of papers in the conference.

We are deeply grateful for the members of the editorial board who have carefully read and recommended the papers for publishing.

We also wish to express our gratitude to numerous individuals for their valuable contribution to the editing process.

Prof. Dr. Hüseyin Gökçekuş
President of the Conference and the Organizing Committee
Vice Rector of the Near East University
Lefkoşa-TRNC

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Message from the Honorary President of the Conference

The interaction between humans and their environment has entered a critical stage as the delicate balance between them has become more fragile making it difficult for the nature in many areas to renew itself. All this poses a variety of serious challenges for us all. The main challenge before us is no less than redefining our entire relationship with our environment. At this critical juncture, I feel excited and take pride in once again hosting such a distinguished group of scientists, researchers, journalists, and students from all over the world at our university addressing such a critical global concern. I look forward to welcoming you all in Turkish Republic of Northern Cyprus.

Yours truly,
Dr. Suat İ. Günsel
Founding Rector of the Near East University

Message from President of the Conference

It gives me the utmost pleasure in welcoming you all to the International Conference " Environment: Survival and Sustainability" here at the Near East University in Turkish Republic of Northern Cyprus to be held at 19-24 February 2007.
The conference aimed at bringing together more than 2,000 scholars and researchers from over 90 countries around the world to discuss environmental issues from a variety of perspectives; underline the importance of the need for urgency in taking steps by the international organizations, states, local authorities and non-governmental organizations to move to a sustainable environment/development model; and thereby makes its contribution to worldwide debate effort on strengthening the bridge between theory and practice in meeting environmental threats/challenges.
Since our last international conference on environment, "Environmental Problems of the Mediterranean Regions", worldwide environmental disasters as well as local ones have multiplied and environmental degradation and pollution has continued. While major strides have been made in the world in analyzing, understanding and informing the public about the environmental challenges we are facing, we still have a long way to go. Our way of life is still far from a sustainable model and our environment continues to degrade and deteriorate due to human activities. The consequences can be seen in worldwide environmental disasters as well as locally in our daily lives.
This is going to be our third international conference on Environment organized by our young university since it was established in 1988.

Yours sincerely,
Prof. Dr. Hüseyin Gökçekuş
Vice Rector of the Near East University

OPENING SPEECHES

Prof. Dr. Ümit HASSAN
Rector of Near East University, TRNC

His Excellency, the Prime Minister of the Turkish Republic of Northern Cyprus,

His Excellency Secretary General Organization of the Islamic Conference,

Distinguished guests, colleagues, ladies and gentlemen,

On behalf of the Founding Rector and the Near East University, I take this opportunity to wish you all a warm welcome for a fruitful conference. It is a great pleasure for me to be a participant at this international conference.

The International Conference on Environment, Survival and Sustainability is a new and most important sequel to a chain of international conferences organized by the Near East University. I trust the conference will provide participants with an opportunity to discuss, to show and to express the related problems and share their experiences. I believe that we will have a most beneficial scientific medium taking the battles into consideration between theoretical analysis and experimental observations and studies.

It is evident that this balance of methods and techniques will have to create a high level of scientific contribution. In other words, the conference will strengthen the bridge between theory and practice in meeting environmental threats, and emphasize the urgent need for coordination and integration among all bodies towards a more sustainable environment. I would like to take this opportunity to proudly emphasize and announce the accomplishments of the Near East University in fulfilling the requirements in founding the School of Medicine as a subsequent step following the School of Pharmacology and the School of Dentistry which will start to function properly in this coming academic year. Within this context, I would like to inform you that the technological means and the academic staff needed by such schools are at the highest level at the Near East University. Our conception of the Technopark being different from the practices of other universities is solely aimed at using our efforts and resources in developing the necessary infrastructure for establishing a Medical School which will be in the service of the island. From a social-psychological perspective, I believe this will enhance the perception of people regarding the dimensions on the management of health issues of the islanders, and for us this would be a moral boost. Considering the significant intellectual and moral capacity of the participants, I simply think that we all want to declare that each and every soul on this planet has the right for survival and to be included amongst the fittest.

Thank you, thank you all.

Prof. Dr. Hüseyin GÖKÇEKUŞ
President of the Conference & Organizing Committee
Vice Rector of Near East University

Your Excellency, President of the Turkish Republic of Northern Cyprus,
Your Excellencies, Distinguished Scientists and Participants,
Ladies and Gentlemen, Members of the World Press

On behalf of the NEU, I would like to welcome you all to the "Environment: Survival and Sustainability" Conference organized by Near East University in LEFKOŞA.

Today, it has been understood that environmental problems with their cumulative characteristics are closely interrelated with many economic, social, cultural, political and administrative parameters, which are naturally interrelated with academic insight.

Near East University was established in 1988 and has since then grown to become one of the fastest developing universities in the region setting itself the strategic goal of joining the "top 500 universities in the world."

Near East University is a member of the European University Association, the International Association of Universities and the Federation of the Universities of the Islamic World.
The University has over 3,000 staff, of which 900 are academic personnel. 17,000 students from 44 different countries are attending 12 faculties and 50 departments at the university. There are 14 dormitories with a capacity of 4,000; and several new dormitories are under construction. Nearly 50% of the students receive scholarships. This figure includes full scholarships, partial support given to students who are in need of financial help, and to those students with sportive accomplishments.

The University has to date organized 12 international conferences and congresses and many local and regional conferences, seminars and panel discussions on a variety of subjects.

The Near East University is honored to host this world conference which has surpassed in scope and content the conferences it has organized before.

Around 2,000 participants from more than 100 countries in the world are present here to discuss environmental issues from a variety of perspectives.

Turning back to the cumulative characteristic of the environmental problems, it is clear that ecological deterioration is the most important problem resulting from regional conflicts, demographic outburst, consumption of natural resources, starvation, degradation of the environment, dwindling fresh water supplies, natural mega-disasters like typhoons, earthquakes, and landslides. Hunger and malnutrition are a direct result of a lack of access to/or exclusion from productive resources, such as land, the forests, the seas, water and technology. As such, this problem is gradually gaining weight in international and national environmental politics, because all these are threatening the common future of humanity. This has refocused the world's attention on the urgency of researches and practical steps on environmental issues. These issues require global solutions in accordance with their global characteristics.

In the EU programme called "*Environment 2000: Our Future, Our Choice"* 4 major topics have been selected as priority targets.
Climate Change
Biological Diversity
Environment and Health
Management of Natural Resources and Waste
Sustainable development is the solution that leads towards a strategy that will consider the environmental problems for future generations.

Most important guidelines for Sustainable Development are:
-Demographic control.
-Reforestation.
-Protection of agricultural areas.
-Energy saving.
-Development of renewable energy sources.
-Improvement in the implementation of existing legislation.
-Integrating environmental concerns into other policies.
-Working in cooperation with the business.
-Educating people to change their unfriendly behaviors towards the environment.
-Environmental accounting in land-use planning and management decisions.

Global Environmental strategy is a must.

ENVIRONMENT DOES NOT UNDERSTAND POLITICS.
IT HAS NO BOUNDARIES OR BORDERS.

The main message of our Conference will contribute to the worldwide debate and create a multi-disciplinary discussion forum where experts from various disciplines will be able to discuss environmental issues in 21 fields such as culture, biodiversity, health, education, business and economy, environmental technology, climate change and energy among others.

Dear Guests,
Environment: Survival and Sustainability Conference is going to give you all an opportunity to get to know Near East University. The Grand Library collection has reached to more than 500,000 while 52 million articles are accessible through electronic databases. The Grand Library is fully computerized and linked to many major world libraries and research institutions throughout the world. It is open 24 hours a day, serving not only the university but the whole community. In other words the Grand Library functions as a national library.

It is my pleasure to extend our gratitude to the members of the Scientific Committee and the International Advisory Board whose active role raised the scientific level of this conference and also increased the number of participants. Unfortunately, some of the Scientific Committee members withdrew due to non scientific letters they received.

In my opinion, as pointed above

SCIENCE HAS NO BORDERS and NO BOUNDARIES.
IT IS OF THE HUMANS and FOR THE HUMANS.

Coming to our SLOGAN:
RIO 1992
Johannesburg 2002
Nicosia 2007
We do not have much time to lose.

On behalf of the Organizing Committee, I would like to extend our special and sincere thanks to our Founding Rector Dr. Suat Günsel, whose basic aim is to provide generous support for the improvement of continental lifestyle capabilities of the island.

We extend our gratitude to Islamic Development Bank and to the Secretary General of Islamic Conference Organization, Prof. Ekmeleddin İhsanoğlu for their invaluable contributions.

I would like to convey our thanks to the government of Turkish Republic of Northern Cyprus for their support.

Our special thanks go to the Organizing Committee Members and the students who worked day and night for the success of this conference.

Last but not least, we would also like to extend our gratitude to H.E. Mr. Ban KI-MOON Secretary General of the United Nations, for his kind moral support.

I believe this conference will scientifically contribute to the solutions of environmental problems, and hope you will enjoy your stay in our beautiful country.

Thank you.

Rahmi KOÇ
Honorary Chairman & Founding Member of TURMEPA, TURKEY

Mr. President, Mr. Prime Minister, Your Excellencies, distinguished guests, Ladies and Gentlemen

I would like to express my gratitude to Mrs. Sıdıka Atalay for inviting us here for this very important international conference today. As founder of TURMEPA, The Turkish Marine Environmental Protection Association, I would like to share my views with you regarding our activities and accomplishments in Turkey. Why and how did I found TURMEPA? You can call it luck, you can call it coincidence. I was the Chairman of the Turkish-Greek Business Council for six years. During this period, every effort that I made to get the two countries' businessmen to cooperate failed. The Greeks never said no, but they never got their act together either. Again on one occasion in Athens, though I had great enthusiasm to continue to join forces for an interesting project, unfortunately I was very disappointed by their lack of response. At the end of the meeting just before we had lunch, the late shipping Tycoon, George Livanos, who was sitting at the very back of the conference room, called me and said, "Look here, I've been following you and your efforts for sometime and see that you are not getting anywhere and are becoming frustrated. If you really want the Greeks and Turks to cooperate in one area, that will be the environment." He also said, "I founded HELMEPA, Hellenic Marine Environmental Turkish Association, called TURMEPA and let them two cooperate to keep our seas clean. So in 1994, 24 friends believed in the cause and we founded TURMEPA, the first NGO specifically dedicated to keeping the seas clean. At that time, HELMEPA was already eleven years ahead of us and the World Bank had been gathering data on Turkish seas and marine life from HELMEPA. Soon, I found out that this was a long term project and would at least need one generation's commitment. During our efforts, we learned that there are four very important points. Point number one: It's more economical to keep our waters clean than to clean them after polluting them, this was very important. The second important point: the subject is a major undertaking and cannot be done by one association alone and requires a nationwide awareness of the problem. Our third finding was that it needed education; education is most important in achieving our goal. The last important point was international collaboration that is a must as the environment does not have borders, does not have barriers, religion, race or different languages and no politics are involved. With these four points in mind, we first trained teachers in primary schools in coastal areas and then distributed hundreds and thousands of books to these students and pupils. We also held a drawing competition with the subjects of clean seas, we made films for television and cinemas, we used newspaper advertising to get our messages across, and we worked with several universities to test water quality. In the 30 years, from 1960 to 1990 the number of species in the Marmara Sea, believe it or not, came down from 148 to only 14. Now they are coming back. We have started to see dolphins in the Bosphorus and this is good news because when dolphins come, other marine life generates itself. We set up a data room to collect and store information about marine life, our seas, inland waters and currents.

We learned to our surprise again that only 10% of sea pollution comes actually from shipping. The risk comes from domestic and industrial waste; therefore, we set up a system to monitor waste being dumped in our seas. Clean seas are of most importance to tourism which is a major source of revenue for our economy. Therefore to this end, we collaborated with sea side hotels, holiday villages, restaurants and cafes to ensure their compliments with environmental regulations. We then hoisted our TURMEPA flag on their premises. When they did so in the summer months, we put together a team of students to collect garbage from boats and yachts free of charge, we set up garbage containers in coastal areas where garbage can be deposited by banks, businesses, industries and then collected by municipal authorities. Our financing is usually organized on a project basis. With all this said and done, Ladies and Gentlemen, our efforts are still only a drop in the ocean if awareness is not felt by our citizens. Therefore, we are constantly telling the public at large that we have ignited a spark, which we must still help to spread throughout the country.

I am happy to say that the Turkish government and its Ministers, especially the Ministry of Transportation, our Governors, Mayors, academicians and businessmen have realized that clean seas are one of the most important issues we are facing. Clean seas mean life and oxygen. Polluted seas not only kill marine life but also tourism and give third world nation appearance.

I am delighted that I am joined today by our Chairman Eşref Cerrahoğlu, who is himself a ship owner and our Board Member Mr. İbrahim Yazıcı who is himself a sailor, and our General Secretary Levent Ballar who never stops coming up with a new project.

Before I finish, I would like to ask our Chairman, who made contacts yesterday, to give good news to our Cypriot friends.

Thank you for bearing with me.

Eşref CERRAHOĞLU
Chairman of Executive Board of TURMEPA, TURKEY

Mr. President, Mr. Prime Minister, Ladies and Gentlemen,

My Honorary Chairman addressed TURMEPA's activities. I am very pleased and honored to announce our work carried out in North Cyprus. Today, we will be opening a branch of TURMEPA in Girne, and more importantly, we will open a sea and shore observation center in Girne in partnership with the Municipality of Girne and the Near East University, and before the summer of 2009, our training and education program will start.

I would like to thank Mrs. Sıdıka Atalay for accepting the coordination of TURMEPA activities in North Cyprus, and I am confident that we will have all the backing of our President and our Prime Minister, and the people of Northern Cyprus.

Thank you.

Cemal BULUTOĞLULARI
Mayor, Turkish Municipality of Lefkoşa, TRNC

Honorable President, Prime Minister, Secretary General of the Islamic Conference and distinguished guests,

Welcome to Lefkoşa.

The habitat mentioned and diversity of living creatures are shrinking everywhere due to an increase in the fragmentation of landscape. The situation in Cyprus is heading towards a formidable shortcoming in terms of environmental resources. In Cyprus, we have already started to see the danger. There is a great need to improve the diversity and human health on the island. Despite the efforts put forward on these specific issues and existing threats, we still need to stress the fact that deeper collaboration is needed amongst the developing nations.

The conclusion that will be reached at the end of ESS 2007 conference will be a torch light for our municipality and we shall consider balanced use of sources in the future services and activities for Lefkoşa. I wish you all a fruitful conference during your stay in Lefkoşa and North Cyprus.

Thank you.

Asım VEHBI
Minister of Environment and Natural Resources, TRNC

His Excellency, the President of the Turkish Republic of Northern Cyprus,
His Excellency, the Secretary General of the Islamic Conference Organization,
Honored guests,

I would like to welcome you all to our conference on Environment, Survival and Sustainability here in the Near East University in the Turkish Republic of Northern Cyprus. Northern Cyprus is honored to host you with this international conference. I believe that the conference will be an important recognition of the issue of this week's environmental topics which concern not only Cyprus but also the whole world. This conference is bringing together almost 1,500 academicians from more than 100 different countries and there are 21 major topics that reflect all areas of environment such as business and environment, environment and health, global warming and a lot of others.

With the industrial revolution in the late 18th century, human beings started to change the global environment. Prior to industrialization the only unsustainable loses from human economic activities were forest cover topsoil. Most societies were relatively based on small and simple technologies using limited amounts of energy with limited territorial area, but the industrial revolution in Europe has changed this. After the revolution, large scale exploitation of fossil fuels enabled the human societies to consume natural resources, the potential of which seemed limitless. Most of our environmental problems today have a global dimension precisely because of the process of development initiated by the industrial revolution. After the 2nd World War, the world population increased rapidly. With this increase, the world started to use more fossil fuels, but these human activities effected the world adversely and we started to loose biodiversity in the environment. It is stated that every year we are losing at least 50 different species of live hood and every year a vast coverage of agricultural land has been lost due to unplanned development and soil erosion. The forests of the world are declining every year. Waste management of all kinds of waste is another problem including domestic waste and hazardous waste. Societies are producing more waste and waste amounts are increasing every year. The uncontrolled dumping of waste is still continuing specially in developing countries and polluting the soil, air and water resources.

Water shortage is another important problem. The amount of drinkable and usable water is decreasing while we are polluting these resources. Almost two weeks ago, IPCC released the draft project from its fourth assessment report where it puts forward that our climate is changing mainly because of inter human induced efforts. Global atmospheric concentrations of carbon-dioxide, methane and nitrous-oxide have increased as a result of human activities and now far exceed pre industrial values determined from many thousands of years. The global increases in carbon-dioxide concentration are due to primarily fossil use and land use change while those of methane and nitrous-oxide are primarily due to agriculture. The net result of these effects is a global average temperature rise of 6^{o}C in the last century. When we compare its greenhouse gas emissions within those other developed countries, Cyprus as an island may not have significant effects on the global warming but on the other hand, we may be one of the most effected countries from this problem. According to different United Nations scenarios, the temperature of the island may increase 2 to 4 degrees Celsius in the following century. It is also foreseen that we may have serious water problems and shortages in the near future due to increasing water demand and up to 40% decreases in the precipitation values according to the climate model predictions. Another effect of the climate change expected for Cyprus is an increasing loss of productive land leading to the desertification of the island. We have also been facing serious environmental issues like other developing countries such as problems in waste, waste water management, copper mining related problems such as the CMC and a lot of others. To solve these problems and harmonize with the European Union, the present government of the Turkish Republic of Northern Cyprus has agreed to form a separate ministry for environment: The Ministry of Environment and Natural Resources. The main mission of the ministry is to protect the environment in Northern Cyprus and ensure the sustainable use of its natural resources as well as to preserve its cultural heritage. The role of the ministry is to develop and implement the government’s environmental policies in order to achieve its mission in environmental protection, sustainable use of natural resources and preservation of cultural heritage. In particular, our responsibilities include establishing coordination between different ministerial departments internally and with other ministries externally, mainly with Turkey, the European Union and others on issues of sustainability and environmental protection. We have also started to develop necessary policies and legislation. We are reviewing and endorsing different policies and legislation, submitting draft legislations to our Parliament for discussion and approval. We communicate with the media and the public on environmental issues. We provide support for environmental education in all levels of the education system. The environmental policy concerns of the Turkish Republic of Northern Cyprus should be based on economic prosperity and social coherence, taking into consideration the following three key elements.

The first one is sustainable development. Social and economical development will take place in a way that preserves our natural and cultural heritage and resources. The second one is to follow the European Union rules and standards on environmental protection. Our laws will be harmonized with the European Union environmental legislation and policies to protect and preserve our environment and the health and life of our people. The third element will be the establishment of the environmental governments’ partnership model among the administration, all sectors of the economy and our people through processes which will both inform about environmental issues and standards and involve people in the associated decision making processes.

Before I finish my words, I would like to express the importance of sustainable development. All of the problems I have mentioned show us that we have to develop in an environmentally sustainable way. We have to protect the environment and preserve our natural and cultural heritage while we are developing.

I would like to thank all of the participants who came from other countries and also I would like to thank the Near East University for this wonderful organization and their great team for their outstanding efforts. I hope that this conference will shed light on most of our regional and global environmental problems.
Thank you.

Tahsin ERTUĞRULOĞLU
Leader of the National Unity Party(UBP), TRNC

Distinguished contributors, participants and honorable guests,

It is indeed an honor for all of us here in the Turkish Republic of Northern Cyprus to welcome you in a country that supposedly does not exist. Your presence here in the name of knowledge and academic freedom, and above all, in the name of service to humanity will hopefully give a valuable lesson to those who tried so desperately to prevent your participation and contributions to this conference.

Dear friends, you shall be subject to further propaganda and will be delivered misinformation about the circumstances here upon your return to your respective countries. The challenging spirit that you have, the spirit of not bothering about those that stand in the way of knowledge, friendship and partnership and service merit will guarantee the success of this most valuable conference.

In closing, I wish to thank the Near East University for working so hard and for so long in making today a reality.

I wish to thank you all for being with us here today. I wish the conference every success.

Thank you.

Assoc. Prof. Dr. Turgay AVCI
Deputy Prime Minister & Minister of Foreign Affairs of TRNC

Your Excellency, Mr President,

Your Excellency, Prime Minister,

Honorable Secretary General of the Organization of the Islamic Conference Prof. Dr. Ekmeleddin İhsanoğlu,

Your Excellencies, distinguished participants, Ladies and Gentlemen,

Today is the day. It is the day of pride and success, the day of international victory. It gives me great pleasure and honor to address a conference of which timing is very important, and welcome you all to the Turkish Republic of Northern Cyprus.

I also would like to thank the Near East University, particularly to its Founder Rector and Honorary President, Dr. Suat İ. Günsel, and the Rector, Prof. Dr. Hüseyin Gökçekuş, and many others who have patiently and continuously carried out efforts to bring this very important conference into life. A thousand papers from over 100 countries are going to be presented today. I, myself being an academician for 15 years before being a politician, know the importance of presenting a paper in such a conference. I know the excitement, the feeling, the success of presenting, asking questions and the feeling of success at the end of such a conference. I have participated in many conferences internationally. I have presented many papers in many countries. It is a great feeling; it is a great pleasure. I know your feelings and I know the success and pleasure that you will get at the end of the conference. Even under normal circumstances, conferences and organizing conferences would have been a drowning task, but in a country like this which is under an inhuman political, economical and cultural isolation and embargoes due to Greek Cypriot's political blackmail and pressure, it is much more difficult to organize such events. It is very much appreciated that you have stood up against these immoral efforts by putting science and survival of global environment first in the line rather than politics. The future of our world and of our children needs courageous scientists, thinkers and writers like you who are able to transit between politics and political pressures wherever they are fighting for the survival of humanity and the global environment. The bounties and rich resources of our planet have given their best to civilizations throughout the past, but we have reached a point in time and technology that our activities have exceeded the life saving abilities of the earth. The global challenges and the level of distraction we have caused are too great now.

The issue of globalization of environment and conservation is the most crucial and urgent issue that the whole of mankind face today. The survival and sustenance of our environment and biodiversity has importance for our future, and just opened our commitment to fight and fight hard for our world. Businessmen, scientists, intellectuals, artists, politicians, indeed the whole of humanity, must stand and strengthen our struggle in this issue. The results of this conference must provide us with the strategies of sustainable environmental management through the development of environment friendly technologies and legislation. We must also show the way for social survival to all global citizens, local governments and non-governmental organizations, and because of this, we have a very challenging but at the same time a noble task. In this context, we also strongly believe that institutions from primary schools to universities throughout the world should make in learning the most important attempts to teach about the environment and to train about the protection of environment. I am pleased to inform you that we have a coalition government in the Turkish Republic of Northern Cyprus and we have a Ministry called the Ministry of Environment and Natural Resources. My friend who spoke a few minutes ago is in charge of this ministry. With these thoughts in mind, I would once more like to take this opportunity to thank Near East University and its Honorary President Dr. Suat İ. Günsel for organizing and hosting the Environment, Survival and Sustainability Conference and wish you success in your deliberations.

I thank you for being here in the Turkish Republic of Northern Cyprus and I am sure you will enjoy your stay here and you will remember us and tell the rest of the world the Turkish Republic of Northern Cyprus is a place to be, a place to visit and a place to enjoy.

Thank you.

Türkekul KURTTEKIN
Turkish Ambassador to Lefkoşa, TRNC

Mr. President, Mr. General Secretary of the Organization of the Islamic Conference, Ministers, Members of the Parliament, Distinguished Party Members, Members of the Organizing Committee, Members of the Media,

Let me first comment on the Near East University for organizing this conference and express my pleasure that I have the opportunity to say a few words about the conference.

From my perspective, the conference is significant for a variety of reasons. Firstly, a very important topic will be addressed throughout the conference. It reminds me the 1972 United Nations Conference on the Human Environment held in Stockholm, the 1992 Earth Summit or the United Nations Conference on Environment and Development held in Rio, and the 2002 World Summit on Sustainable Development held in Johannesburg.

The world constituted combined efforts by the international Community to face a common challenge, that is, the protection and preservation of the environment while achieving developmental objectives in the rapidly changing world. In spite of these efforts, the challenge stays pretty much alive. We, the human beings, have disturbed the balances of nature and the environment. However, we have no luxury for skepticism. A few minutes ago, we heard about the cooperation between TURMEPA and HELMEPA from Mr. Rahmi Koç which proved to us that if there is a will this challenge will be gradually met. You, experts from various disciplines, from academy, various policy makers and executives responsible for the implementation in many countries will be discussing ways to overcome this challenge. Major topics of discussion in the conference show the multi dimensional character and the magnitude of that, and the outcome of your discussions and your deliberations will contribute to the efforts to increase world awareness on this important challenge, and I hope it provides useful material for the decision makers by strengthening the bridge between theory and science.

Secondly, the meaning of this conference in my opinion reflects the severity faced by the Turkish Republic of Northern Cyprus with its people and its institutions. Environment, the problems, economic and industrial development are interrelated issues. The importance of minimizing the environmental damage while achieving sustainable development is widely realized in the Turkish Republic of Northern Cyprus, which is a country going through a remarkable development in the recent year with a growth rate approaching 14% in 2005 and with an increase of 7% in 2006. The increasing public awareness in the Turkish Republic of Northern Cyprus about institutional measures such as the establishment of the Ministry of Environment and Natural Resources constitutes a good, encouraging example. Thirdly, this international conference, which we were told is the 12th of its type organized by Near East University, demonstrates the important role of universities in the Turkish Republic of Northern Cyprus. As many of you have mentioned, education was amongst the fields falling within the problems of the community in the 1960’s. The progress achieved by the Turkish Cypriots in this field is commendable and demonstrates the unacceptability of the isolation the Turkish Cypriot people have been subjected to for many years. Even in such circumstances, the Turkish Cypriots have been demonstrating their will and determination to move ahead and to combine forces with the international community to face the common challenges to humanity.

Let me conclude by hoping that this conference will create more awareness around the world and in this respect, the recognition of the Turkish Cypriot People will no more remain unattended. Let me also wish all the distinguished participants of this conference every success and express my sincere hope that your deliberations will contribute to the combined efforts to give a better world to the next generations.

Thank you.

Ferdi Sabit SOYER
Prime Minister of TRNC

His Excellency, Mr. President,
His Excellency, General Secretary of the Organization of the Islamic Conference,
His Excellency, Minister and Members of Parliament and the very important scholars who have came to our country for this conference,

I would like to greet and welcome you all.

Today is the beginning of a meaningful conference where very important environmental issues will be discussed in this conference hall. As you can see, all the flags in this hall symbolize a different color and a different history of all the nations, and as we also know, the colors of nature are reflected by these flags in this beautiful atmosphere. If nature had been just one color, just yellow or just green, the richness and beauty of living would not be seen and people would not have even been able to fall in love. This colorful atmosphere reflects also the dynamism of human beings. Also, this dynamism provides the humans with the ability to find and change everything in nature which they need. It is because of this developing dynamism that human beings take what already exists in nature and turn it to their benefit. Although there are many differences among all nations we should still cooperate together to protect nature. I strongly believe that this conference will bring very important conclusions. I also believe that although the Turkish Republic of Northern Cyprus and Turkish Cypriot society have been isolated both politically and economically, this conference will have very important outcomes. We want to be recognized in the world with our nation, with our national identity. This conference also gives out this message to the world.

I would like to thank the Near East University, the valuable Rectors, and Scholars for participating in such a conference. I would also like to thank and welcome once again the valuable scientists for coming to our country.

Thank you.

Prof. Dr. Ekmeleddin İHSANOĞLU
OIC Secretary General

Your Excellency Mr. President, Mr. Prime Minister, distinguished scholars, Ladies and Gentlemen,

I sincerely greet you all. It gives me great pleasure to be with you here. It is a great pleasure to be at the opening ceremony of this important event: The International Conference on Environment, Survival and Sustainability organized by the Near East University. I am grateful to Near East University for their kind invitation which has enabled me to address such a distinguished gathering. I would also like to thank you all who have worked hard, took part in preparation and realization of this project.

Let me share with you my honest feelings. I am not a newcomer to this island and I have heard a lot about Near East University and I have also heard of its good reputation. Some of my friends' sons and daughters were here as students. I have heard all the facts and data about the universities. I am really impressed.

His Excellencies, Ladies and Gentlemen,
I am not an expert on environment issues but the convening of this important conference is very timely as the subject matter has become a very serious global matter. We read all the reports on a daily basis about the dangers of climate change. Climate change and environmental degradation affect the whole world. Meanwhile we hear the frequent comments of the world leaders about the lack understanding and cooperation on environmental issues which might lead us towards the destruction of our planet and humanity. Global pandemics, deforestation and natural disasters are only a few of the issues that presently affect the globe. All these problems are at the heart of sustainable development that we all need to achieve. We find ourselves helpless today when we see rich nations of the world continuing to load the atmosphere with carbon-dioxide; compromising the well being of human race and pushing our planet to an unknown future. It is obvious that these acts have contributed to a rapid change of climate which has caused global warming, rising sea levels, extreme droughts, erosion of soil, loss of the forests and extinction of the species. Sadly, most of the environment degradation is severely affecting the developing world. Its population is facing severe droughts and dry rivers, while some other areas are facing excess floods, rainfalls, mud slides and loss of properties. I am just back from a long trip to Indonesia and I have seen the negative side of the phenomena there. Ladies and Gentlemen, the catastrophes have also negatively affected ecological imbalance. Hence, they have been posing a serious threat to the genetic pool with ramped out breaks of disasters and leading to more poverty in the undeveloped parts of the world. Recognizing the important role played by the environment in the development and in the progress of its member states, the OIC ten year plan of action, a joined action development for the Muslim world to face the challenges of the 21st century, was developed by the 3rd Extraordinary Summit convened in Mecca in 2005 and attended by all heads of state from 57 OIC countries.

In this context, I would like to bring to your attention the fact that the heads of state present in this Summit in December 2005 made a very strong appeal to all OIC member states and their institutions on the issue and were able to coordinate their environmental policies and positions in the international environmental issues so as to prevent any adverse effects of such policies on their economical development.

Following the adoption of the OIC ten year plan of action, I have organized several meetings with the OIC institutions and stakeholders in the framework of the implementation of the OIC ten year plan of action. The OIC General Secretariat itself is committed to the world capacity and policies to contribute to the global efforts to counter the environmental challenges. The OIC also notes with pleasure that the majority of its many initiatives and activities reflect the facts of important organizations such as UNEP and our parties to various international conventions on environment in particular to the protocol. Joining such conventions reflect the fact that the OIC member states are giving their attention to the international laws and requirements. Such devotion shall certainly provide us with a solid basis for our future efforts suggested by the OIC ten year activity program.

I would like to praise the Near East University for providing the opportunity for the conference participants to address a wide range of crucial issues such as redefining the business of conservation and management of biodiversity, culture heritage and environmental factors, economics, development and sustainability, energy and development, environment and health, the threat of global warming, ecological balance and sustainable environment and social and psychological dimensions of the environmental issues.

Mr. President, Your excellencies, Ladies and Gentlemen,

I am of the view that the environment issue can be viewed from at least two major perspectives: The perspective of science and technology and the perspective of effects and impacts of environment on economic development. The important contributions and inputs from science and technology to ensure sustainable development cannot be denied. However, environmental challenges that we are talking about are mostly trans-boundary ones and cannot be faced with individual efforts of the nations. The very nature of these challenges require that these states should combine their efforts and facilities together. In this context, the OIC member states are called upon by the conclusions of various OIC gatherings and decisions to join hands to collaborate and to synergize their efforts in performing and undertaking research and development to reduce some of the environmental effects and challenges faced by them. Assessing the effects of environmental challenges on economical development also requires regional and global cooperation and coordination. In the domain of sustainable development perspective, one should address the quality and sustainability of our natural resources, the threat of global environmental changes on ecosystems, quality of life in our cities, impact of the use of energy which is essential to our economies and to the way of life. We should be making use of the technologies available with the view of reconciling economical development with environmental sustainability. The achievements of all mentioned goals require coordination, harmonization and synergizing of our entire actions. In other words, we need to follow up very closely all our activities to monitor their progress, to evaluate and assess the impacts and to take recognition of all possible shortcomings.

Naturally, addressing you today in one of the heavenly parts of the world, I cannot emphasize as much as I would like to the importance of environmental studies and undertakings aimed at the protection of the Mediterranean Sea and its ecological diversity.

Ladies and Gentlemen, as I value the timely initiative of organizing this conference on an issue of great relevance for my organization and for our member states considering the excellent academics and research qualities and standards of the Turkish Cypriot Universities, I would also like to mark an appeal from this platform to the universities and scientific institutions around the world particularly those based in the OIC.
Thank you.

Mehmet Ali TALAT
President of TRNC

Distinguished guests, dear participants,

As you may have expected, I will not make many remarks about environment or raise much concern about the environment. My remarks will be mainly political but in the concerns of the environment. Possibly you can claim that environmental concerns should cause an impact to unify humanity because the solutions to environmental problems can only be found by cooperation. So, this unifying factor must be a point of consideration, and we, the Turkish Cypriots know the importance of this fact. We know the importance of being unified with the international community because we are under severe isolation on all aspects of life including environmental issues. My Prime Minister mentioned about the lack of cooperation between the two sides. We are under continuous pressure from our neighbors. Everywhere in the world, we are in a struggle against this isolation issue and try to be unified with the world, and I wish that this conference will give fruitful results to the scientific life and to humanity.

Thank you for your participation and I wish you all success.

FINAL REPORT OF THE INTERNATIONAL CONFERENCE ON ENVIRONMENT: SURVIVAL AND SUSTAINABILITY

Environment is a subject that must be brought to the top of international agendas if the threats to sustainability and survival are to be countered. It cannot continue to be seen as something to be added on to the plans of commercial enterprises or as a minor component of poverty-alleviation programs. Economic development cannot eliminate poverty without conserving natural resources and maintaining ecosystem services. Nor can productive activity ignore the significant effects of resource extraction and waste generation. Environment must be the central focus of national and international programs at all levels.

The International Conference on Environment: Survival and Sustainability, held at the Near East University, Nicosia, Northern Cyprus 19-24 February 2007, dealt with environmental threats and proposed solutions at all scales. The 21 themes addressed by the conference fell into four broad categories:

1.Threats to Survival and Sustainability

Global warming and other climate changes pose a major threat to natural and human systems throughout the world. Major impacts addressed ranged from dieback of tropical forests to altered ecosystem functions in temperate and boreal systems, changes in sea level and in polar and alpine systems, as well as impact on water supply, agriculture and extreme weather events. Pesticides threaten natural ecosystems and human health. Health is also threatened by diseases, pollution and many forms of environmental degradation. Natural and human-made disasters interact to threaten societies in many ways.

2.Technological Advances towards Survival and Sustainability

Environmental science and technology are advancing rapidly, but are not in themselves sufficient to counter the growing threats to environment. Important areas include integrated water management, new and renewable energy sources, and conservation and management of biodiversity.

3.Activities and Tools for Social Change

Activities and tools that can be applied to move society towards greater sustainability were emphasized at the conference. These included environmental law and ethics, environmental knowledge and information systems, media, environmental awareness, education and lifelong learning, the use of literature for environmental awareness, the green factor in politics, international relations and environmental organizations.

4.Defining Goals for Sustainable Societies

The new directions that societies must take include considerations of economics, development and sustainability, redefinition of the interests of business, incorporating cultural heritage, the seas, ecological balance and sustainable environment, and the social and psychological dimensions of environmental issues.

The breadth of the issues addressed at the conference made clear the need for greatly increased interdisciplinary and international collaboration if survival and sustainability are to be achieved. The exchanges at the conference represent a step in this direction.

Cyprus is getting an equal share from these developments and 51 species are under a threat of extinction. Out of 10 regional mini-hotspots within the principal foci in the Mediterranean, and also considering that Cyprus is island number two with a rich plant diversity and narrow endemism, there is a need for protection of its biodiversity.

The matter of global sustainable development actually has a connotation for change of life styles. This calls for
-interactions and understanding of people the world over,
-fair and equitable distribution of benefits derived from resources,
-conservation of biodiversity and protection of our resources,
-the water use efficiency is very important as the availability of water is becoming scarce,
-we need more international collaboration and research for wider and reliable speculation,
-management of plans and their implementation to save the critical aspects of our heritage and environment,
-cooperation of scientific disciplines is necessary to address the situation,
-countries must work together and minimize the impact of borders on science and maximize the benefit for all mankind,
-in order to obtain global sustainability, the curses of over-consumerism should be overcome by an appeal to social and spiritual values,
-for making the world a happy home for everyone, transfer of knowledge has to take place across nations,
-environment and sustainability have to be treated globally, not just locally, before time runs out.

About 2,052 participants from 108 countries from all around the world joined us to make 1,413 presentations and discuss environmental issues from a variety of perspectives.

Global Environmental Strategy is a Must.
As I mentioned on the first day of the conference,
“ENVIRONMENT DOES NOT UNDERSTAND POLITICS”.
“IT HAS NO BOUNDARIES OR BORDERS”.

This Conference has contributed to the worldwide debate and tried to create a multi-disciplinary discussion forum where experts from various disciplines were able to discuss environmental issues in 21 different fields.

Thanks to the 2,052 participants from all over the world for making this interdisciplinary conference a success. Their active role raised the scientific level of this conference.

I believe this conference has scientifically contributed to the solutions of environmental problems, and hope you have enjoyed your stay in our beautiful country.

Thank you

Prof. Dr. Hüseyin Gökçekuş

LIST OF PAPERS AND POSTERS

VOLUME 1

MT-1: BUSINESS AND ENVIRONMENT : REDEFINING INTERESTS

SUSTAINABLE INDUSTRIAL GROWTH: STRATEGIES AND IMPLEMENTATION
Jurgis Kazimieras Staniskis – LITHUANIA (*Oral*)..1

INHERENT PARADOXES IN THE INTERNATIONAL REGULATION OF INDUSTRIAL ECOLOGY: CAN SUCH LEGISLATION BE CONSIDERED SUSTAINABLE FOR THE ELECTRONICS INDUSTRY?
Julian Scott Yeomans, Yavuz Gunalay – CANADA -TURKEY (*Oral*) 11

NEW DETERMINATION OF INTERESTS IN THE FUTURE OF RELATIONSHIP BETWEEN THE ENVIRONMENT AND BUSINESS
Zehra Gül – TURKEY (*Oral*) 21

THE ROLE OF THE ENVIRONMENTAL AUDIT FOR THE REINFORCEMENT OF THE ECONOMIC AND ENVIRONMENTAL CONDITIONS OF THE ORGANISATIONS
Maria da Conceição da Costa Marques – PORTUGAL (*Oral*)..37

ENVIRONMENTAL COMMUNICATION AS A REDEFINING POSSIBILITY
Pernille Almlund – DENMARK (*Oral*) 53

INNOVATIVE TECHNOLOGIES IS NOT SUPPORTING ENVIRONMENTAL: SOCIAL AND ECONOMIC SUSTAINABILITY OF THE DEVELOPING COUNTRIES OF THE EASTERN WORLD
Saeed A.K. Lodhi, G. R. Mughal, Zakia Shoab – PAKISTAN (*Oral*) 67

NEW RULES OF BUSINESS CONDUCT: AN INVESTIGATION ABOUT SUSTAINABILITY ISSUES IN THE CHEMICAL SECTOR
Saime Önce, Nuray Tokgöz – TURKEY (*Oral*) 83

THE DEVELOPMENT OF THE FOREIGN TRADE AS ONE OF THE ESSENTIAL CONDITIONS FOR THE GROWTH OF ECONOMY IN LITHUANIA
Rasa Glinskienė, Daiva Beržinskienė, Birutė Darškevičiūtė – LITHUANIA (*Oral*) 95

INFLATION TARGETING POLICY AS A MONETARY POLICY INSTRUMENT IN DEVELOPING COUNTRIES
Serdar Altınok, Hakan Acet, Murat Çetinkaya, Abdulkadir Develi – TURKEY (*Oral*) 111

ENVIRONMENT-TRADE RELATIONSHIP AND CE-THE CASE OF EU AND TURKEY
Ayşegül Samsunlu – TURKEY (*Oral*) 121

THE ROLE, RESPONSIBILTY AND IMPACT OF BUSINESS IN DEVELOPING ECO-EFFICIENT TECHNOLOGIES AND BIO-TRADE
R. Esra Demirdogen – TURKEY (*Oral*) 129

THE RELATIONSHIPS BETWEEN MACROECONOMIC INDICATORS AND BANKING PERFORMANCES OF TURKEY AND THE EU COUNTRIES
Gülhayat Gölbaşı Şimşek, Seher Arıkan Tezergil – TURKEY (*Oral*) 143

CLIMATE CHANGE AND BUSINESS STRATEGY
Olivier Boiral – CANADA (*Oral*) 169

BUSINESS AND THE ENVIRONMENT - INTERPRETATION AND METHOD APPLICATION OF PUBLIC INVOLVEMENT
Slavka Sufi-Mićić – BOSNIA AND HERZEGOVINA (*Oral*) 181

VOLUME 2

MT-2: CONSERVATION AND MANAGEMENT OF BIODIVERSITY

DATA INVENTORY AND MONITORING IN THE COASTAL DUNES OF KAZANLI / TÜRKİYE A CASE STUDY FOR CONSERVATION PLANNING
K. Tuluhan Yılmaz, Süha Berberoğlu, Halil Çakan, Hakan Alphan, Yüksel İzcankurtaran –TURKEY (*Invited)* 187

SEASONAL GROWTH EFFECT ON HYDRAULIC CHARACTERISTICS OF THE MANGROVE EXOECARIA SP IN BATTICALOA, SRI LANKA
Printhan Manoharan, V. Nimie – SRI LANKA (*Oral)* 199

CULTURAL PERSPECTIVE AND BIODIVERSITY CONSERVATION IN UPLAND MOUNTAINS ECOSYSTEMS OF WESTERN GHATS OF INDIA: CHALLENGES & OPPORTUNITIES
Archana Godbole – INDIA (*Oral)* 221

A POPULATION STUDY OF JOHANNESTEIJSMANNIA LANCEOLATA (ARECACEAE) IN MALAYSIA
Rozainah Mohamad Zakaria – MALAYSIA (*Oral)* 231

PHYSIOLOGICAL GENETIC BASIS OF RESISTANCE OF SOME DURUM WHEAT (T.DURUM DESF.) VARIETIES TO DROUGHT
Mehraj Abbov – AZERBAIJAN (*Oral)* 237

CONSERVATION AND MANAGEMENT OF CROCUS spp.
Hasan Vurdu, İ. Sevinç Kravkaz – TURKEY (*Oral)* 241

SUSTAINABILITY OF THE LIVE BIRD TRADE IN TANZANIA: QUOTAS AND HARVESTS
Thade Clamsen, Charles Mlingwa – TANZANIA (*Oral)*...249

BIODIVERSITY CONSERVATION ISUES IN ANTHROPIZED MARSHLANDS A TWO YEAR STUDY OF INSULA MARE A BRĂILEI
Liliana Vasiliu-Oromulu, V. Sanda, Viorica Honciuc, Sanda Maican, Minodora Stănescu, M. Falcă, Cristina Munteanu, Cristina Fiera, M. Dumitru, Daniela Răducu – ROMANIA (*Oral)* 255

NATIONAL APPROACH TO THE CONVENTION ON BIOLOGICAL DIVERSITY
Ş. Doğanay Yayım – TURKEY (*Oral)* 263

SCRUTINIZING THE GEOPHYTES IN TERMS OF BIODIVERSITY
Nilüfer Seyidoğlu, Murat Zencirkıran – TURKEY (*Oral)* 271

VEGETATION AS A BIOTIC INDICATOR OF SOIL AND WATER QUALITY IN AKARCAY BASIN (TURKEY)
Ahmet Serteser, Yılmaz Icaga – TURKEY (*Oral)* 277

SHORT TERM EFFECTS OF ROYAL JELLY ON SPERM QUALITY IN OF JUVENILE RAINBOW TROUT (ONCORHYNCHUS MYKISS W., 1792).
Faruk Aral, Erdinç Şahinöz ,Zafer Doğu – TURKEY (*Oral)* 287

EVALUATION OF ALGAL FLORA OF THE INFRALITTORAL ZONE AT A NORTH CYPRUS MARINE ECOSYSTEM
Mehmet Öztürk , Ergün Taşkın, Oğuz Kurt , Salih Gücel TURKEY, NORTHERN CYPRUS - (*Oral)* 295

DETERMINATION OF SOME REPRODUCTION CHARACTERISTICS IN MASTACEMBELUS MASTACEMBELUS (Bank & Solender, 1794) LIVING IN ATATURK DAM LAKE.
Erdinç Şahinöz, Zafer Doğu, Ramazan Şevik, Faral Aral – TURKEY (*Oral)* 305

CONSERVATION OF BIODIVERSITY IN AGRICULTURAL LANDSCAPE BY SUSTAINABLE LAND USE IN CONDITIONS OF SW SLOVAKIA
Alexander Fehér – SLOVAKIA (*Oral*) 313

SOME ECOLOGICAL CHARACTERISTICS OF AGROPYRON TRICHOPHORUM IN SUMMER RANGELANDS IN THE NORTH OF IRAN (MAZANDARAN)
Ghasem ali Dianati Tilaki – IRAN (*Oral*) 325

THE PHYLOGENETIC AND BIOGEOGRAPHIC ANALYSIS OF HERACLEUM L. (UMBELLIFERAE) OBSERVED FROM ITS DNA SEQUENCE DATA
Meltem Maras , Aysel Kekıllıoglu – TURKEY (*Oral*) 329

CITRIC-ACID AND WATER-PRESOAKING ENHANCE SEED GERMINATION OF SCOTS AND ANATOLIAN BLACK PINE
Derya EŞEN, Oktay Yıldız, Aslıhan Kabtan – TURKEY (*Oral*) 339

ANALYSIS OF POLYMORPHISM AT THREE MILK PROTEIN GENES IN NATIVE CATTLE BREEDS OF TURKEY AND THEIR USE FOR MANAGEMENT
Havva Dinc, Evren Koban, Ebru Saatci, Emel Ozkan, Mesude Iscan, Inci Togan – TURKEY (*Oral*) 345

THE USE OF CAMERA TRAPS FOR DETERMINING THE PRESENCE OF MEDIUM AND LARGE SIZED MAMMALS IN MARMARIS, TURKEY
Anıl Soyumert, Oksal Macar, Behzat Gürkan – TURKEY (*Oral*) 353

THE EFFECTS OF LAND USE ON BIOMASS AND CATABOLIC DIVERSITY OF SOIL MICROBIAL COMMUNITIES
Mohammad Asghari Pour, A. Rahmani – IRAN (*Oral*) 359

CONSERVATION AND MANAGEMENT OF BIODIVERSITY: AN INDIAN PERSPECTIVE
Pranav Vyas, Subramanya Sirish Tamvada – INDIA (*Oral*) 369

EFFECT OF CONSERVATION ON PLANT DIVERSITY IN SEMIARID REGION OF IRAN H.R.
Naseri , Gh. Zehtabian , H. Azarnivand , S. Yousefi Khangah – IRAN (*Oral*) 379

THE RECOGNITION OF PLANT ASSOCIATIONS AND COMPOSITION ELEMENTS OF SANGCHAL FORESTS OF MAZANDARAN, IRAN
Rouhi-Moghaddam Einollah, Moslem Akbarinia , Seyed Gholamali Jalali, Seyed Mohsen Hosseini – IRAN (*Oral*) 387

THE LANDSCAPE IMPLEMENTATIONS THREATENING BIODIVERSITY IN URBAN AREAS: SOME SAMPLES OF EASTERN BLACK SEA REGION
Mustafa Var, Emrah Yalçınalp, Müberra Pulatkan – TURKEY (*Oral*) 393

THE EFFECTS OF PLANTATION ON BIODIVERSITY AND REGENERATION OF WOODY SPECIES
Leila Vatani, Moslem Akbarinia – IRAN (*Oral*) ....
399

MAPPING THE BIODIVERSITY OF LAND SNAILS IN TURKEY: A PRELIMINARY STUDY
Ümit Kebapçi, M. Zeki Yildirim – TURKEY (*Oral*) 411

A DISCUSSION PAPER ON PROBLEMS, ROOT CAUSES AND SUSTAINABLE USE OF PAKISTAN WETLAND'S BIODIVERSITY
Muhammad Naeem Khan, Zulfiqar Ali, Muhammad Akhtar – PAKISTAN (*Oral*) 421

THE MANAGEMENT OF THE MARINE BIODIVERSITY IN GALLIPOLI PENINSULA NATIONAL HISTORICAL PARK, CANAKKALE-TURKEY
Şükran Cirik, Yeşim Büyükateş, Mehmet Akbulut, Herdem Aslan, Özgür Emek İnanmaz, Ekrem Şanver Çelık, Suat Ateş, Özgür Cengız, emine ş. Okudan, İlknur Ak, Ali İşmen, Çiğdem Yığın, Füsun Erkan Yurdabak, Muhammet Türkoğlu, Uğur Özekıncı, Özcan Özen, Deniz Anıl Odabaşı, Fikret Çakır, Pınar İşmen, Sezginer Tunçer, Mustafa Alpaslan, Alkan Öztekın, Serkan Özden – TURKEY (*Oral*) 439

SALINITY EFFECTS ON GROWTH AND STOMATAL BEHAVIOUR IN STRAWBERRY PLANTS
Ece Turhan, Atilla Eris – TURKEY (*Oral*) 453

ANTIOXIDATIVE ENZYME ACTIVITIES IN ONION (ALLIUM CEPA L.) GENOTYPES
Ece Turhan, Hatice Gulen, Ahmet Ipek, Atilla Eris – TURKEY (*Oral*) 459

CLUSTERING OF SOME LOCAL COMMON BEAN PHASEOLUS VULGARIS L.) GENOTYPES BASED ON CARBOHYDRATE METABOLISM
Nezihe Koksal, Ece Turhan, Ahmet Ipek, Hatice Gulen, Atilla Eris – TURKEY (*Oral*) 467

THE NEED FOR CONSERVATION OF AFROMONTANE RAINFORESTS WITH THE OCCURRENCE OF WILD COFFEA ARABICA POPULATIONS IN ETHIOPIA
Feyera Senbeta, Tadesse Woldemariam, Manfred Denich, Sebsebe Demissew – ETHİOPİA (*Oral*) 475

DOCUMENTING AND COMPARING PLANT SPECIES DIVERSITY BY USING NUMERICAL AND PARAMETRIC METHODS IN KHAJE KALAT, NE IRAN
H. Ejtehadi, R. Soltani, H. Zahedi Pour – IRAN (*Oral*) 487

ENVIRONMENT EFFECT ON HETEROSIS EXPRESSION
M. Sehabi, L. Mekliche – ALGERİA (*Oral*) 493

EXPERIENCES WITH FAST GROWING FOREST TREE SPECIES
S. Ayan, A. Sıvacıoğlu – TURKEY (*Oral*) 501

FRAMEWORK FOR EVALUATION OF BIODIVERSITY SERVICES: PROBLEMS AND PROSPECTS
Nandkishor More – INDIA (*Oral*) 515

CONSERVATION OF BIOLOGICAL DIVERSITY IN THE WORLD AND IN TURKEY
Zuhal Dilaver – TURKEY (*Oral*) 521

SHOULD (EUROPEAN) TREES HAVE STANDING? IMPROVING ACCESS TO THE COMMUNITY JUDICATURE THROUGH IMPLEMENTATION OF THE AARHUS CONVENTION
Grainne Gilmore – IRELAND (*Oral*) 529

IN VITRO SHOOT REGENERATION OF IRONWORT (SIDERITIS STRICTA BOISS & HELDR.)
Dudu Özkum, Rukiye Tıpırdamaz – NORTHERN CYPRUS, TURKEY (*Oral*) 537

BIODIVERSITY OF THE SPECIES BELONGING TO TRIGONELLA L.
Z. J. Mammadova – AZERBAIJAN (*Oral*) 545

ALLELOPATHIC PROCLIVITIES OF TREE LEAF EXTRACTS ON SEED GERMINATION AND GROWTH OF WHEAT AND WILD OATS
Muhammad Azim Khan – PAKISTAN (*Oral*) 551

PLANT DIVERSITY AND SUSTAINABLE USE OF GRASSLANDS IN ÇANAKKALE-TURKEY AND THEIR ROLE IN EROSION CONTROL
Hakan Hakyemez, Altıngül Özaslan Parlak, Sezgin Çelik, Ahmet Gökkuş
TURKEY*(Poster)*...557

ECOLOGY OF CENTAUREA SOLSTITIALIS SUBSP. SOLSTITIALIS L.
Sezgin Çelik, Kürşat Özkan, Ersin Yücel – TURKEY *(Poster)* 565

INVESTIGATION ON GROWING UP OF HELIANTHUS ANNUUS L SEEDS WHICH WERE EXPOSED BY MAGNETIC FIELD
Sevil Yalçın, Ersin Karabacak, İsmet Uysal – TURKEY *(Poster)* 571

THE FIRST RECORD OF MACROBRACHIUM NIPPONENSE
Saeid Gorgin – IRAN *(Poster)* 581

BIOLOGICAL CONTROL OF AQUATIC PLANTS USING GRASS CARP: IMPLEMENTATIONS IN TURKEY
Mine Uzbilek Kırkagac – TURKEY *(Poster)* 587

INTERACTIONS BETWEEN DROUGHT STRESS AND LEAF ROLLING OF CTENANTHE SETOSA (ROSC) EICHLER
Neslihan Saruhan, Asım Kadioglu, Rabiye Terzi, Aykut Sağlam, Nihal Kutlu – TURKEY *(Poster)* 595

THE FLORISTIC AND FAUNISTIC (LEPIDOPTERA) INVESTIGATION OF ANAMUR HIGHPLATEAUS (ABANOZ-AKPINAR)
Ayşe Everest, Yusuf Hüseyinoğlu – TURKEY *(Poster)* 611

A KARYOLOGICAL STUDY ON MATTHIOLA
Esra Martin, Ahmet Duran, Murat Ünal, Ayşe Özdemir – TURKEY *(Poster)* 621

TRAGACANTHIC ASTRAGALUSES, A GOOD CUSHION PLANT IN ENVIRONMENTAL SUSTAINABILITY AND RURAL DEVELOPMENT
Mohammad Reza Naghavizadeh – IRAN *(Poster)* 627

CYTOTAXONOMIC INVESTIGATIONS ON THE SPECIES C. CHRYSANTHUS(HERBERT) HERBERT
Feyza Candan, Teoman Kesercioğlu – TURKEY *(Poster)* 637

NUTRITION (N.P.K) OF OAK (Q.CASTANEIFOLIA) SEEDLING IN DIFFERENT LIGHT INTENSITIES
Gh. A. Jalali, M. Ghanbari Motlagh, M. Tabari – IRAN *(Poster)* 641

NATURAL OR MANMADE RESTORATIONS OF PLANT COVER OF SPOIL MATERIALS IN ROMANIA
Mihaela Paucă-Comănescu, Marilena Onete – ROMANIA *(Poster)* 645

ECOTOXICOLOGAL EFFECT OF SOME DIFFERENT ALKALINE METAL SALTS (NACL, KNO3) AND STRONG ACID (HCL, H2SO4) CONCENTRATION ON GERMINATION OF CEDRUS LIBANI SEEDS
Ersin Yücel,Kürşat Özkan, Semra Soydam – TURKEY *(Poster)* 651

AN INVESTIGATION ON COMPARISON OF ECOLOGICAL AND BIOLOGICAL PROPERTIES OF TWO ENDEMIC CENTAUREA SPECIES FOR TURKEY (CENTAUREA LYCIA AND CENTAUREA LUSCHANIANA)
Yavuz Bülent Köse, Ersin Yücel – TURKEY *(Poster)* 659

AN INVESTIGATION OF THE EFFECT OF PLANT DENSITY IN INTERCROPPING BETWEEN MAIZE AND BEAN ON YIELD AND COMPONENT OF YIELD IN EAST AZARBIJAN, IRAN.
Farhad Farahvash, Habib Amir- Halaji, Farhad Jafari – IRAN *(Poster)* 671

EVALUATION OF ALFALFA, CLOVER, AND SAINFOIN DIVERSITY IN EAST AZARBAIJAN, IRAN
R. Kanani, Mohammadian M. B. Khorshidi – IRAN *(Poster)* 675

THE POTENTIALS AND CHALLENGES FOR COMMERCIAL TREE PLANTING IN UGANDA: EXPERIENCES FROM NANSEGA FORESTS AND RESORTS
Florence Nangendo, James Seggane – UGANDA *(Poster)* 689

OBSERVATIONS ON THE URBAN FLORA OF ISTANBUL (TURKEY)
C. Yarcı, M. Serın, V. Altay, N. Şahın, E. Osma, P. Mutlu, B. Eskın - TURKEY (*Poster*).......... 695

DESERT VEGETATION OF THE MIL PART OF KURA-ARAKS LOWLAND
E. M. Gurbanov, K. A. Ibayeva – AZERBAIJAN *(Poster)* 749

CARBOHYDRATE METABOLISM IN PEPPER (CAPSICUM ANNUM L.) SEEDLINGS UNDER HIGH TEMPERATURE STRESS
Ahmet Ipek, Ece Turhan, Nezihe Koksal, Hatice Gulen, Atilla Eris – TURKEY *(Poster)* 753

RAPD-PCR ANALYSE OF HYPERACCUMULATOR PLANTS
Selcen Babaoğlu, Leyla Açık, Nezaket Adıgüzel, Şebnem Ellialtıoğlu – TURKEY *(Poster)* 761

VOLUME 3

MT-3: CULTURAL HERITAGE AND ENVIRONMENTAL FACTORS

THE VERNACULAR TARSUS HOUSES AS A SAMPLE FOR CULTURAL HERITAGE
Fehime Yeşim Gürani –TURKEY (*Oral*) 769

ASSESSMENT OF WOOD AS A BUILDING MATERIAL IN TURKEY IN TERMS OF ENVIRONMENTAL SUSTAINABILITY
Saadet Toker, Armağan Korkmaz, Hasan Ş. Haştemoğlu – TURKEY (*Oral*) 781

NEIGHBOURHOOD SUSTAINABILITY: A COMPARATIVE ANALYSIS IN THE NORTHERN AND SOUTHERN SECTORS OF NICOSIA
Derya Oktay, Can Kara – NORHERN CYPRUS (*Oral*) 789

VISUAL POLLUTION DUE TO FUNCTIONAL TRANSFORMATIONS AT EKINCILER STREET IN DIYARBAKIR, TURKEY
Sule Elhakan, Iclal Aluclu. Fuat Toprak – TURKEY (*Oral*) 823

AN ANALYSIS OF THE URBAN METAMORPHOSIS IN TARLABASI DISTRICT AND ITS IMPACTS ON THE CULTURAL FORMATION
Özlem Şenyiğit, N. Ferah Akıncı – TURKEY (*Oral*) 829

THE DETERIORATION REASONS AND REHABILITATION SUGGESTIONS OF DIYARBAKIR HISTORICAL HOUSES IN THE CONCEPT OF CULTURAL HERITAGE
F. Demet Aykal, Y. Berivan Ozbudak – TURKEY (*Oral*) 839

EFFECTS OF THE ENVIRONMENTAL FACTORS TO CULTURAL AND NATURAL HERITAGE OF PAMUKKALE
Ş. Gülin Beyhan, Mehmet Beyhan –TURKEY (*Oral*) 851

ECO-DESIGN APPROACH IN FURNITURE DESIGN
Tülay Özdemir – TURKEY (*Oral*) 861

A NEW APPROACH TO INTEGRATED APPLICATIONS IN CULTURAL HERITAGE DOCUMENTATION
Z. Duran, G. Toz - TURKEY (*Oral*) 871

AN ANATOLIAN ANCIENT CULTURAL HERITAGE, THE MIDAS MONUMENT: AN OVERVIEW
Mustafa Dursun Çaglar, Nazmi Oruç – TURKEY (*Oral*) 881

REHABILITATION OF HISTORICAL BUILDINGS OF ODUNPAZARI – ESKİŞEHİR – TURKEY
Burhan Sakallı, Hüsnü Kaptan, Aslı Tunçol, Ayşen Aksu, Saye Nihan Çabuk, Nazmi Oruç – TURKEY (*Oral*) 889

AN URBAN OPEN SPACE MODEL FOR MODERN TURKISH REPUBLIC: GAZI FOREST FARM IN ANKARA
A. Duygu Kaçar – TURKEY (*Oral*) 903

PRE-HISTORICAL LANDSCAPES AND CULTURAL HERITAGE OFFSHORE OF THE BALTIC SEA IN LITHUANIA
Vladas Žulkus - LITHUANIA (*Oral*) 911

THE EXAMINATION OF MADRASA BUILDINGS IN KONYA IN ENVIRONMENTAL, USAGE AND STRUCTURAL LEVEL
Esra Yaldiz, Bahtiyar Eroğlu, Süheyla Siramkaya Büyükşahin – TURKEY (*Oral*) 917

SECOND HOMES IN A COASTAL AREA-MAHMUTLAR SAMPLE
Elif Gündüz, Rahmi Erdem – TURKEY (*Oral*) 931

THE IMPORTANCE OF CULTURE TOURISM IN OWNING HISTORICAL CULTURE HERITAGE – KILISTRA SETTLEMENT (TURKEY) CASE
Ü.Gülsüm Ter, Dicle Aydin, Yusuf Ziya Ter – TURKEY (*Oral)* 941

IZNIK CITY WITH ITS HISTORICAL LANDSCAPE PROPERTIES
Murat E. Yazgan, Canan Cengiz – TURKEY (*Oral)* 955

ARCHAEOLOGICAL SITE PRESENTATION AS AN APPROPRIATE AND USEFUL MANAGEMENT TOOL: THE EXAMPLE OF LIMAN TEPE PRESERVATION AND SITE MANAGEMENT MODEL, IZMIR, TURKEY
Müge Bahçeci – TURKEY (*Oral)* 963

RELATIONSHIP BETWEEN URBAN REVIATLIZATION AND SUSTAINABILITY IN HISTORIC URBAN QUARTERS: TOWARDS A SUSTAINABLE URBAN REVITALIZATION APPROACH
Şebnem Önal Hoşkara, Beser Oktay Vehbi – NORHERN CYPRUS (*Oral)* 977

COMPARISON OF THE INTEGRATED AND NON-INTEGRATED PATTERNS IN A SPATIO-TEMPORAL DIMENSION IN THE CONTEXT OF AN ISLAND
Murat ŞAHIN, - TURKEY (Oral).. 987

ECONOMETRIC ANALYSIS OF WORLD HERITAGES' INFLUENCE ON TOURISM DEMANDS
Sukhong YOON, Maengsern KİM, Seunghoe CHOI- KOREA (Oral).. 997

THE PHRYGIAN ROCK-CUT ALTARS AND THEIR RESTORATION AND CONSERVATION PROPOSALS
Rahşan TAMSÜ, Yusuf POLAT- TURKEY (Oral).. 1005

AMATEUR ARCHAEOLOGY AND ARCHAEOLOGICAL PARK MODEL AT PEDASA: THE MAIN SITE OF THE LELEGIAN CIVILISATION, ON BODRUM PENINSULA
Adnan DiLER- TURKEY (Oral).. 1015

INTEGRATION OF HISTORICAL MONUMENTS INTO MODERN ENVIRONMENT AND LANDSCAPE IN GERMANY
Marko KIESSEL- TRNC (Oral).. 1021

THE INTERACTION DYNAMICS OF WATER AND THE ENVIRONMENT
Mohammad Esmaeil Asadi – IRAN (*Oral)* 1033

VOLUME 4

MT-4: ECONOMICS, DEVELOPMENT AND SUSTAINABILITY

BOTTOM - UP POLICIES AND RURAL DEVELOPMENT PEMBROKESHIRE LEADER+ EXPERIENCE
Antonio Prestia – ITALY (*Oral*) 1043

THE EFFECTS OF B AMENDED IRRIGATION WATERS ON COTTON YIELD AND B ACCUMULATION IN SOIL AND LEAF TISSUES
Sabri Sener, Fidan Akbas – TURKEY (*Oral*) 1057

AN APPROACH FOR ENABLING SUSTAINABLE ACCESS TO URBAN LAND AND LAND TENURE IN THE SOUTHERN AFRICAN COUNTRY OF NAMIBIA
Jane Gold – NAMIBIA (*Oral*) 1071

A QUALITATIVE APPROACH IN ENVIRONMENTAL VALUATION METHOD
Kamran Zendehdel, Wim De Keyser, Guido Van Huylenbroeck – BELGIUM (*Oral*) 1081

LANDSCAPE PLANNING AND MANAGEMENT STRATEGIES FOR ZIR VALLEY NEAR ANKARA IN TURKEY
Şükran Şahin , Ülgen Bekişoğlu– TURKEY (*Oral*) 1101

CULTURAL COLLISION AND PARTTERN RECONSTRUCTION OF NATIONAL FOREST PARK IN METROPOLIȘ A CASE STUDY IN ZIJIN MOUNTAIN, NANJING, CHINA
Li Ming-yang - CHINA (*Oral*) 1113

GEONOMICS: BOOTSTRAP DEVELOPMENT FOR A SUSTAINABLE PLANET
Jeffery J. Smith – USA (*Oral*) 1125

AN ANALYSIS OF RURAL DEVELOPMENT-NATURAL RESOURCE INTERACTION IN TURKEY
Ayten Erol, Yusuf Serengil – TURKEY (*Oral*) 1133

ECO-FRIENDLY AGRI-PRODUCTION FOR GLOBAL SURVIVAL AND SUSTAINABILITY
P. S. Shehrawat – INDIA (*Oral*) 1141

ECONOMICS, ENVIRONMENTAL PROTECTION AND SUSTAINABILITY
Halil Seyidoğlu – TURKEY (*Oral*) 1155

AN ASSESSMENT OF THE COMMERCIAL VIABILITY AND SUSTAINABLE DEVELOPMENT OF SELECTED NON-ALCOHOLIC INDIGENOUS BEVERAGES IN SOUTH AFRICA
Isaac Rampedi – SOUTH AFRICA (*Oral*) 1161

CROP PRODUCTION PLANNING THROUGH EFFICIENT USE OF NATURAL RESOURCES FOR SUSTAINABLE AGRICULTURE
DharmPal Malik – INDIA (*Oral*) 1179

STEERING TOWARDS A DYNAMIC EQUILIBRIUM OF DEVELOPMENT AND ENVIRONMENTAL SUSTAINABILITY: A DEVELOPING NATION'S PERSPECTIVE
P. K. Gogoi, D. K. Chakraborty – INDIA (*Oral*) 1195

LIFE CYCLE ASSESSMENT (LCA) METHOD IN THE BUILDING SECTOR
Arzuhan Burcu Gültekin, Gülser Çelebi – TURKEY (*Oral*) 1207

COMPARATIVE ANALYSIS OF IMF POLICIES FOR FINANCIAL CRISES IN TURKEY AND ARGENTINA
Nihâl Yıldırım-Mızrak , Mustafa Özer – TURKEY (*Oral*) 1219

ANALYSIS OF THE RELATIONSHIP BETWEEN ECONOMIC GROWTH AND ENVIRONMENT IN TRNC
Hüseyin Özdeşer – NORTHERN CYPRUS (*Oral*) 1243

ENVIRONMENTAL DIMENSIONS IN DEVELOPING NEWLY RECLAIMED DESERT LANDS
Salah Y. Awadalla – EGYPT (*Oral*) 1255

ENDANGERED NATIONAL PARK: MUNZUR - TURKEY
Özgür Yılmazer, Özlem Yılmazer, Servet Armac, İlyas Yılmazer, Yasemin Leventeli – TURKEY (*Oral*) 1275

URBAN AGRICULTURE: AN INSTRUMENT FOR SUSTAINABLE URBAN DEVELOPMENT IN THE METROPOLITAN CITY OF ISTANBUL
Ulas Akın – TURKEY (*Oral*) 1281

USER DEMANDS FOR SUSTAINABLE HOMESERVICES AN AUSTRIAN SURVEY
Thomas Madritsch – AUSTRIA (*Oral*) 1293

ECONOMIC DEVELOPMENT WITH FLEXIBLE EXCHANGE RATE REGIME: TURKISH EXPERIENCE
Ayhan Aytac, Fatma Cesur – TURKEY (*Oral*) 1303

ELECTRONIC WASTE – CURRENT STATUS AND MANAGEMENT PRACTICE
Suresh Chandra Saxena – INDIA (*Oral*) 1313

THE NATIONAL PARK OF KARABURUN-A POSSIBILITY TO PROTECT THE MARINE BIODIVERSITY, AND SUSTAINABLE DEVELOPMENT OF TRUISM IN ALBANIA
Liljana Elmazi, Evelina Bazini, Ada Kertusha – ALBANIA (*Oral*) 1323

DEPENDENCE OF GRAIN QUALITY ON FERTILIZATION, CROP ROTATION AND TILLAGE
Nadejda Tododrova,Svetla Bachvarova, Dafina Nikolova, Staika Stratieva – BULGARIA (*Oral*) 1331

HOW CAN WE COPE ENVIRONMENTAL SUSTAINABILITY WITH TOURISM-BASED ECONOMIC DEVELOPMENT?BEACH NOURISHMENT PROJECTS AS A WAY TO REHABILITATE OUR COASTS AND CONTRIBUTION TO TOURISM
Ozlem Unal, Kemal Birdir – ITALY, TURKEY (*Oral*) 1339

IN THE CULTURE-ENVIRONMENT RELATIONSHIP FRAMEWORK
Solmaz Karabaşa – TURKEY (*Oral*) 1357

A SUSTAINABLE WASTE WATER MANAGEMENT PROJECT: MEDAWARE
Filiz Dilek, İpek İmamoğlu, Gülerman Sürücü, Celal F Gökçay – TURKEY (*Oral*) 1365

CONSUMERS' ATTITUDES ABOUT ENVIRONMENTAL SENSIVITY
Cengiz Yilmaz , Tuncer Özdil , Beran Gülçiçek , İdil Altiparmakoğullari – TURKEY (*Oral*) 1379

THE ESTABLISHMENT OF RURAL PRODUCTIVE UNITS
Juan Guzmán, Martín Cervantes, Adrián Mendoza – MÉXICO (*Oral*) 1393

ANALYZING OF RELATIONSHIPS BETWEEN TRADE AND ENVIRONMENT: ECONOMIC AND SOCIAL LINKS
Nuray Terzi – TURKEY (*Oral*) 1399

A STUDY ON THE POTENTIALS OF BEYŞEHIR NATIONAL PARK WITHIN THE FRAMEWORK OF ENVIRONMENT-SENSITIVE TOURISM (ECOTOURISM) APPROACHES
Ü. Gülsüm Ter,Kadriye (Deniz) Topçu,Sedef Eryiğit – TURKEY (*Oral*) 1411

ENVIRONMENTAL IMPACT ASSESSMENT AND SUSTAINABLE TOURISM. THE CASE OF ALBANIA
Liljana Elmazi, Mirela Mersini – ALBANIA (*Oral*) 1427

PRE-TREATMENT OF INDUSTRIAL WASTEWATER: ISKI'S APPROACH IN TURKEY
Ahmet Samsunlu – TURKEY (*Oral*) 1437

OLIVE OIL AND ITS EXPANSION: SUSTAINING CULTURAL VALUES BY DESIGN
Ece Ariburun – TURKEY (*Oral)* 1449

ADMINISTRATIVE, MANAGEMENT AND ECONOMICAL EVALUATION OF MUNICIPAL SOLID WASTE COLLECTION SERVICES AND RECYCLING ACTIVITIES IN ISTANBUL METROPOLITAN
D. Karadag, S. Sakar, H. Bayhan – TURKEY (*Oral)* 1463

THE GREEN BUILDING INDUSTRY
Suat Gunhan – TURKEY (*Oral)* 1473

BLUEFIN TUNA (Thunnus thynnus L. 1758) FISHERY, FARMING AND MANAGEMENT IN THE MEDITERRANEAN SEA
Işık Oray, F. Saadet Karakulak – NORTHERN CYPRUS, TURKEY (*Oral)* 1481

COMMUNITY BASED ECO-TOURISM POTENTIALS AT THE DIPKARPAZ NATIONAL PARK AREA: OPPORTUNITIES AND THREATS
Dervis Yuksel – NORTHERN CYPRUS (*Oral)* 1491

ECOSAN AS A RECYCLING/RECOVERY/REUSE APPROACH AND A SUGGESTION FOR THE PROCESSING OF SEPARATELY COLLECTED URINE FOR AGRICULTURAL USE
Bilsen Beler Baykal – TURKEY (*Oral)* 1505

SUSTAINABLE CRITERIA IN MINERAL PROCESSING
M. Zeki Doğan, A.Ekrem Yüce, Caner Zanbak – TURKEY (*Oral)* 1515

ENVIRONMENTAL ETHICS IN RELATION TO MINING ACTIVITIES
M. Z. Doğan, Ali Güney – TURKEY (*Oral)* 1521

ORIENTATION OF THE TOURISM SECTOR TOWARD AN EMPHASIS ON ENVIRONMENTALISM AND ECO-FRIENDLY ISSUES
Frank Bates, Türkay Yildiz, Işık Özge Yumurtaci – TURKEY (*Oral)* 1527

TURKEY'S ENVIRONMENTAL POLICIES FOR AGRICULTURAL POLLUTION
H.Ece SALALI, Ela ATIŞ, Nurdan ERDOĞAN- TURKEY *(Oral*).. 1535

THE EFFECTS OF ECONOMIC GROWTH AND EDUCATION LEVEL ON AIR-WATER POLLUTION IN OECD COUNTRIES: A PANEL TIME SERIES ANALYSIS
Ercan Saridoğan, Sinan Sarisoy, M. Kemal Beşer – TURKEY (*Oral)* 1549

QUALITY APPROACH IN PURSUE OF SUSTAINABLE MOBILITY
Dalia Susniene, A. Valackiene – LITHUANIA (*Oral)* 1563

ACHIEVING GREEN PRODUCTION VIA INTEGRATING MANAGEMENT SYSTEMS
Maryam Salek Zamani, Ali Salek Zamani, Yagub Salek Zamani – IRAN (*Oral)* 1573

FOR INCREASING ENVIRONMENTAL SUSTAINABILITY ECO LABELLING AND IMPLEMENTATION IN TURKEY
Reha SAYDAN, Sima Nart- TURKEY *(Oral)*... 1575

ANALYSIS OF SUSTAINABILITY THEORIES
Sabri Azgun, Murat Taşdemir – TURKEY (*Oral)* 1589

TOWARDS ACHIEVING SUSTAINABILITY IN DEVELOPMENT: A CASE OF VARANASI CITY, INDIA
D. Mohan ,Saumya Sarkar – INDIA (*Oral)* 1597

SYSTEM PROBLEMS FOR REGION SUSTAINABLE DEVELOPMENT: THE INDICATORS AND INDICES BUILDING
M. Zgurovskiy, G. Statyukha – UKRAINE (*Oral)* 1609

ENVIRONMENTAL ENRICHMENT BY WATER
Vivek P. Kapadia, Mukesh B. Joshi – INDIA (*Oral*) 1617

RESERVES AND ECONOMICAL EVALUATION OF CONSTRUCTION MATERIALS IN THE LAND OF AZERBAIJAN REPUBLIC
Tevfik Ismailov, Ruhangiz Ismailova – TURKEY, AZERBAIJAN (*Poster*) 1633

EVALUATION OF THE YACHT SLIPWAY PLANTS IN TERMS OF ENVIRONMENTAL PROBLEMS AND SOLUTIONS: A CASE STUDY OF FETHIYE-TURKIYE
Remzi Karagüzel , Mahmut Mutlutürk, Raşit Altindağ, Rafet Kistir – TURKEY (*Poster*) 1641

ECOLOGICAL CONDITION OF THE ISSYK-KUL REGION
Tynybekov Azamat – KYRGYZ REPUBLIC (*Poster*) 1657

MONITORING URBAN GROWTH IN TURKEY: CURRENT TRENDS AND FUTURE PROJECTIONS FOR SUSTAINABLE URBAN PLANNING
Nükhet Günbeyaz, N. Gamze Turan – TURKEY (*Poster*) 1665

VOLUME 5

MT-5: ENERGY AND DEVELOPMENT: NEW AND RENEWABLE ENERGY

THE ASSESSMENT OF THE ENVIRONMENTAL BENEFIT OF FAST-GROWING ENERGY WILLOW CULTIVATED FOR RENEWABLE BIOMASS SUPPLYING
Aleh Rodzkin, Siarhei Pazniak, Cheslav Romanovsky – BELARUS (*Invited)* 1673

SEWAGE BIOGAS USED FOR ENERGY GENERATION
Suani Teixeira Coelho, Sílvia Maria Stortini González Velázquez, Orlando Cristiano Silva, Vanessa Pecora, Fernando Castro Abreu – BRASIL (*Oral)* 1685

SOUTH ASIA AND MANAGEMENT OF ENERGY SECURITY
Musarrat Jabeen – PAKISTAN (*Oral)* 1695

HYDROPOWER ENERGY SOURCE COMBINING WITH OTHER RENEWABLES, IN THE TERITORY OF KOSOVA
Zekirija Idrizi, Isak Idrizi, Farudin Hoxha, Kujtim Zena – MACEDONIA, ALBANIA, KOSOVA (*Oral)*.......... 1725

EVALUATION OF ENERGY EFFICIENCY IN APRICOT GARDENS OF WEST AZERBAIJAN PROVINCE /IRAN
Naser Akhondi, Abdollah Hasanzadeh Gurttapeh, Mohsen Roshdi, Asal Roohisalari, Abdollah Fatollah Zade – IRAN (*Oral)* 1737

DEVELOPMENT AND APPLICATION OF A NOVEL SORBENT PRODUCTION TECHNIQUE FOR DETERMINATION AND EMPLOYMENT OF THORIUM AS GREEN NUCLEAR ENERGY FUEL R.
Esra Demirdogen – TURKEY (*Oral)* 1747

THE FIELD TRIP ABOUT SOLAR ENERGY AND APPLICATIONS OF THE EFFECTS OF STUDENT’S ATTITUDE AND ACHIEVEMENT
H. S. Tortop, N. Ç. Bezir, N. Özek, M. Uzunkavak – TURKEY (*Oral)* 1767

BRAZILIAN BIOMASS GASIFICATION TECHNOLOGY FOR RURAL ELECTRIFICATION AT AMAZON STATE – GASEIBRAS PROJECT
Suani Teixeira Coelho, MSílvia Velázquez, Sandra M. Apolinario, Beatriz Lora – BRASIL (*Oral)* 1777

TRANSBORDER COOPERATION IN THE POWER GENERATION AMONG SOUTH ASIAN COUNTRIES: OPPORTUNITIES AND THREATS
Syed Muzammiluddin – INDIA (*Oral)* 1781

A NUCLEAR PLANTS DEATH AND BIRTH: ENERGY INFRASTRUCTURE COMMEMORATED INTO CULTURAL HERITAGE
Annelie Sjölander-Lindqvist, Petra Adolfsson – SWEDEN (*Oral*) 1793

WIND POWER PLANTS UPDATED SITUATION IN TURKEY AS RENEWABLE ENERGY
Levent Yılmaz – TURKEY (*Oral*) 1801

THE DESIGN OF SOLAR COOKER AND PRODUCE OF ITS PROTOTYPE
Ercan Köse, Gökhan Özdemir, Ali Keskin, Funda Kahraman – TURKEY (*Oral*) 1817

ENERGY SAVING BY USING HEAT RECOVERY DEVICES AT DIFFERENT CLIMATIC REGIONS IN TURKEY
Derya Burcu Ozkan, Handan Çubuk, Ozden Agra – TURKEY (*Oral*) 1821

ENERGY DISSIPATION AND HYDRAULIC JUMP CHARACTERISTICS IN THE FLOWS OVER THE STEPPED CHANNELS
Gökçen Bombar, M. Şükrü Güney – TURKEY (*Oral*) 1833

AN ALTERNATIVE POWER SOURCE: BIOFUEL AND ITS POSITION IN TURKEY
Hilmi Erdal, Gülistan Erdal, Kemal Esengün – TURKEY (*Oral*) 1849

THE POTENTIAL BIOGAS PRODUCTION FROM LIVESTOCK MANURES: A CASE STUDY FOR GAP REGION-SANLIURFA
Bulent Armagan, S. Batgı – TURKEY (*Oral*) 1859

ENVIRONMENTAL POTENTIALS IN IRAN FOR DEVELOPING THE RENEWABLE ENERGY RESOURCES
Hassan Zolfaghari – IRAN (*Oral*) 1869

ENVIRONMENTAL RENOVATION OF THE SOLAR HOUSE IN MIDDLE EAST TECHNICAL UNIVERSITY WITH COMPUTER BASED ANALYSIS AND DESIGN TECHNIQUES
Ömer Tuğrul Karagüzel – TURKEY (*Oral*) 1881

NO CHOICE BUT ENERGY TRANSITION
Andrew McKillop –USA (*Oral*) 1903

PEAK OIL AND PEAK GAS: RATIONAL ENERGY UTILISATION AND INTERNATIONAL ENERGY TRANSITION
Andrew Mckillop – USA (*Oral*) 1911

THE EVALUATION OF ENERGY BALANCE OF EGG-PLUM IN WEST AZERBAIJAN PROVINCE
Dabdollah Hassanzadeh Gorttapeh, Farmik Vali Mohamadi, Mahnaz Zahedmanesh, Parisa Nikzad,Hosin Ranji – IRAN (*Poster*) 1925

BIOMASS RESOURCES AND MAINLY USING AREAS IN TURKEY
İbrahim Bektaş, M. Hakkı Alma, Alaaddin Yüksel, Murat Ertaş – TURKEY (*Poster*) 1931

AN APPROACH BIOMASS FOR FUEL
Gülnur Mertoğlu-Elmas –TURKEY (*Poster*) 1941

ANALYSIS OF SOLAR RADIATION DATA INCIDENT HORIZANTAL AND TILTED SURFACE CASE STUDY FOR ISPARTA, TURKEY
N. Ç. Bezir, H. S.Tortop, N. Özek – TURKEY (*Poster*) 1947

MT-6: ENVIRONMENT AND HEALTH

ENERGY METABOLISM – AS A GENERAL PRINCIPLE – FOR MODELLING THE TRANSFER OF CARBON AND TRITIUM ACROSS ANIMALS
D. Galeriu, A. Melintescu, N. A. Beresford – ROMANIA , UK, USA (*Invited*) 1953

HEALTH EFFECTS FROM LOW LEVEL AND ENVIRONMENTAL EXPOSURE TO CHRYSOTILE
John A. Hoskins – UK (*Invited*) 1965

ENVIRONMENTAL HEALTH ASSESSMENT OF A PRIMARY SCHOOL IN ANKARA, TURKEY
S. A. Vaizoglu, F. Temel, C. E. Oguz, O. Sunger , N. O. Azizoglu, A. E. Akgun, C. Guler – TURKEY (*Invited*) 1975

PAIN KILLERS FROM CONUS SPECIES
Cem Hami, Laika Gokcekus - NORTHERN CYPRUS, UK (*Oral)* 1983

HEALTHCARE WASTE MANAGEMENT IN SAUDI ARABIA. A CASE STUDY
Khalid S. Al-shallash, Mohamed M. Shereif - SAUDI ARABIA (*Oral)* 1989

BIOPIRACY AND SENSITIVE ISSUES OF ENVIRONMENTAL ETHICS AND INDIGENOUS MECHANISM OF BIODIVERSITY CONSERVATION IN TRIBAL VILLAGES OF BASTAR: AN ANTHROPOLOGICAL APPRAISAL
Rabindra Nath Pati – INDIA (*Oral)* 1995

INVESTIGATION OF THE CONTAMINANTS IN DRINKING WATER DISTRIBUTION SYSTEM OF İZMİT
Ayla Arslan, Sibel Alioğlu – TURKEY (*Oral)* 2005

TRENDS AND CURRENT LEVELS OF ORGANOCHLORINE POLLUTANTS IN HUMANS AND ENVIRONMENT IN TURKEY
E. Durmaz, İ. Çok – TURKEY (*Oral)* 2015

FATTY ACID COMPONENTS AND ANTIMICROBIAL ACTIVITY OF
SEEDS OF ACANTHUS HIRSUTUS BOISS
Nazlı Böke, Levent Şik, N. Ülkü Karabay Yavaşoğlu, Süheyla Kirmizigül – TURKEY (*Oral)* 2029

MATERNAL CARE AMONG REPRODUCTIVE WOMEN IN SLUMS IN GREATER MUMBAI
Vijay M. Sarode – INDIA (*Oral)* 2037

THALASSEMIA IN NORTH CYPRUS RELATIONS WITH MALARIA AND THE RESULTS OF THALASSEMIA PREVENTATION PROGRAMME
Gülsen Bozkurt – NORTHERN CYPRUS (*Oral)* 2055

WATER POLLUTION EPIDEMIOLOGY, WATER HYGIENE AND PUBLIC HEALTH
Ö. Faruk Tekbaş – TURKEY (*Oral)* 2063

HEAVY METALS
Şennur Dabak – TURKEY (*Oral)* 2075

PRESERVATION OF THERMAL WATER RESOURCES AND SUSTAINABLE EXPLOITATION FOR THERAPEUTIC TOURISM
Suleyman Kocbas – TURKEY (*Oral)* 2085

MYCOTOXINS AS ENVIRONMENTAL CONTAMINANTS
F. Yesim Ekinci, Aytul Sofu, Sami Ozcelik –TURKEY (*Oral)* 2091

HOW VOLATILE ORGANIC COMPOUNDS EFFECT FREE RADICAL AND ANTIOXIDANT ENZYME ACTIVITES IN TEXTILE WORKERS
Sibel Bayil, Iclal Geyikli (Meram), Ahmet Celik, Hulya Cicek – TURKEY (*Oral)* 2099

A TURKISH EXAMPLE ON BREASTFEEDING CHARACTERISTICS OF 0-11 MONTHS OF AGE INFANTS
Fehminaz Temel, Dilek Aslan, Vinil Akbulut, Filiz Bulut, Sabri Raza , Güler Tepe – TURKEY (*Oral*) 2105

PUBLIC HEALTH IMPORTANCE OF RECREATION WATER
Zarema Obradović, I. Ćesir –Škoro, E. Čolaković, Edina Čolaković – BOSNIA AND HERZEGOVINA (*Oral*).................... 2115

HUMAN HEALTH AND THE ENVIRONMENT. CASE OF ALBANIA
Liljana Elmazi, Elsa Gega – ALBANIA (*Oral*) 2123

ANTIOXIDANT VITAMINS (VITAMIN E AND C) IN ACTIVE AND PASSIVE MALE NIGERIAN CIGARETTE SMOKERS
O. M. Akinosun, O. G. Arinola, O. O. Oyetayo – NIGERIA (*Oral*) 2133

MICRONUCLEUS INDUCTION AND ALTERATIONS ON BODY WEIGHT IN THE MICE EXPOSED TO LEAD AND MERCURY HEAVY METAL IONS
Kültiğin Çavuşoğlu, Emine Yalçın, Meltem Maraş – TURKEY (*Oral*) 2139

IN VITRO ORAL BIOAVAILABILITY TESTING IN HUMAN HEALTH RISK ASSESSMENT OF METAL CONTAMINATED SOILS: A SHORT REVIEW
Gerald J. Zagury – CANADA (*Oral*) 2149

NOISE HAZARD AND HEARING IMPAIRMENT IN AN URBAN COMMUNITY IN IBADAN, SOUTHWEST NIGERIA
Folashade O. Omokhodion – NIGERIA (*Oral*) 2157

ECONONOMIC VALUE OF IZMIR CULTURE PARK
Nurdan Erdogan, H. Ece Salali, Ela Atiş, Bülent Miran – TURKEY (*Oral*) 2163

DETERMINATION OF EXPOSURE LEVELS TO UV AND THE KNOWLEDGE OF THE PEOPLE ABOUT PREVENTIVE MEASURES IN TURKISH REPUBLIC OF NORTHERN CYPRUS
Fehminaz Temel, Funda Sevencan, Songül Vaizoğlu,Didem Evci, Faruk Tekbaş, Çağatay Güler – TURKEY (*Oral*) 2173

ASSESSING THE OCCUPATIONAL ENVIRONMENT OF ANESTHESIOLOGY DOCTORS FROM COGNITIVE ERGONOMICS PERSPECTIVE
Sarp Uner, Ayca Telatar, Tahsin Gokhan Telatar, Alev Yucel – TURKEY (*Oral*) 2187

SPATIAL DISTRIBUTION OF WELLS AND THE OCCURRENCE OF CHOLERA IN OUALA: THE CASE OF SOME NEIGHBOURHOODS IN THE CITY OF DOUALA CAMEROON
Epule Terence Epule – CAMEROON (*Oral*) 2195

A STUDY ON THE KNOWLEDGE, OPINION AND BEHAVIOURS ABOUT CRIMEAN-CONGO HAEMORRHAGIC FEVER AMONG HEALTH CENTER ATTENDANTS
Fehminaz Temel, Hakan Altıntaş , Nesrin Çilingiroğlu – TURKEY (*Oral*) 2205

ATMOSPHERIC POLLUTERS RELEASED FROM INDUSTRIAL PLANTS
FACTORS OF RISK PERTAINING TO CANCER
Biserka Dimiskovska, Katerina Biseva – MACEDONIA (*Oral*) 2213

INFLUENCE OF HIGH ENVIRONMENTAL TEMPERATURE ON THE LEVEL OF SOME HORMONES IN RATS
T. Gjyladin (Isai), S. Dinevska, B. Miova, M. Ismaili, A. Abazi – MACEDONIA (*Oral*) 2225

HEALTH STATUS OF PRE-SCHOOL CHILDREN LIVING IN UST-KAMENOGORSK BIOGEOCHEMICAL PROVINCE
N. Khussainova, A. Savinkov, L. V. Lim, S. A. Utelbayeva, G. M. Kulniyazova, V. V. Kozhanov, G. A. Urazova, A. L. Salpynova – KAZAKHSTAN (*Oral*) 2233

BACILLUS SUBTILIS MZ-7 WITH ANTAGONISTIC ACTIVITY AGAINST NOSOCOMIAL CLINICAL ISOLATES
Muaaz Mutaz Al-Ajlani, Shahida Hasnain – PAKISTAN (*Oral*) 2243

MEDICAL WASTE SURVEY IN A UNIVERSITY HOSPITAL: DO INTERN DOCTORS AND EMERGENCY NURSES KNOW AND PAY ATTENTION TO SEGREGATION OF WASTES?
Nur Aksakal, Evin Aras, Mustafa N. İlhan, Sefer Aycan – TURKEY (*Oral*) 2257

ULTRAVIOLET AND SKIN CANCER
Tamer Irfan Kaya – TURKEY (*Oral*) 2265

EFFECTS OF LOCAL CURRENTS ON THE DISTRIBUTION OF FECAL POLLUTION IN THE SOUTH –EASTERN BLACK SEA
Nuket Sıvrı, Sinan Guneysu, Ercan Kose, Coskun Eruz – TURKEY (*Oral*) 2275

ENVIRONMENT AND ALLERGIC SKIN DISEASES
Nilgün Bilen – TURKEY (*Oral*) 2281

WASTE MINIMISATION AT THE HEALTHCARE INSTITUTIONS AND THE PRESENT STATUS AND PROPOSALS FOR ISTANBUL
Tamer Atabarut – TURKEY (*Oral*) 2287

ENVIRONMENT AND HEALTH [PROBLEM OF FLUORIDE IN RAJASTHAN VILLAGE]
Sumana V. Pandey – INDIA (*Oral*) 2295

ENVIRONMENTAL EPIDEMIOLOGY
Banu Cakir – TURKEY (*Oral*) 2301

BRONCHIAL ASTHMA AND THE ENVIRONMENT
Ahmet Uğur Demir – TURKEY (*Oral*) 2305

CHLORINATION LEVEL OF WATER AND PREVALENCE OF VIRAL HEPATITIS IN FLOOD AFFECTED AREAS OF VADODARA CITY
Mohsin Shaikh, V. S. Mazumdar, R. K. Baxi – INDIA (*Poster*) 2307

THE EFFECTS OF SELENIUM ON RAINBOW TROUT SPLEEN TREATED WITH HEAVY METALS
Zeliha Selamoglu Talas, Ibrahim Orun, Ilknur Ozdemir, Kenan Erdogan – TURKEY (*Poster*) 2311

ANTIBACTERIAL AND ANTIFUNGAL ACTIVITY IN CLADOPHORA GLOMERATA L. KÜTZ. (CHLOROPHYTA) EXTRACTS
Semra İlhan, Filiz Savaroğlu, Ferdağ Çolak – TURKEY (*Poster*) 2321

ROLE OF PLANT ENDEMICS IN THE ENVIRONMENT & HEALTH-A CASE STUDY ON TEUCRIUM MONTBRETII
Gülcan Özkan, R. Süleyman Göktürk, Orhan Ünal, Sezgin Çelik – TURKEY (*Poster*) 2327

ANTIOXIDANT ACTIVITIES OF THE EXTRACTS OF SOME STACHYS L. (LAMIACEAE) TAXA
Nilgün Öztürk, Onur Koyuncu, İsmühan Potoğlu Erkara – TURKEY (*Poster*) 2333

NOISE AND CHILDREN: OUTDOOR SOUND LEVELS IN PRIMARY SCHOOLS
Ersin Uskun, Tufan Nayir, Hakan Turkoğlu, Selçuk Kılınç, Ahmet Nesimi Kisioglu,
Mustafa Ozturk – TURKEY........ 2343

GLOBAL HEALTH PROBLEM : AVIAN INFLUENZA A (H5N1)
Tamer Sanlidag, Elcin Akduman, Sinem Akcali – TURKEY (*Poster*) 2353

NATIONAL ACADEMY OF SCIENCES OF AZERBAIJAN INSTITUTE OF GEOGRAPHY
Afig Malıkov – AZERBAIJAN (*Poster*)........ 2359

A MUSHROOM POISONING IN ISPARTA, TURKEY
Mustafa Işıloğlu, Hayrünisa Baş, Hakan Allı, Mehmet İşler, Altuğ Şenol – TURKEY 2365

VOLUME 6

MT-7: ENVIRONMENTAL AWARENESS, EDUCATION, AND LIFELONG LEARNING

ENVIRONMENTAL AWARENESS, EDUCATION AND LIFE-LONG LEARNING BANGLADESH
M Shamsher Ali – BANGLADESH (*Invited)* 2369

SEEKING ENVIRONMENTAL AWARENESS IN POSTMODERN FICTIONS
Serpil Opperman – TURKEY (*Invited)* 2375

ENVIRONMENTAL EDUCATION IN BOSNIA AND HERZEGOVINA STATUS, VISIONS AND NEEDS
Azra Jaganjac , Sanda Midzic-Kurtagic, Paul Ravn Jepsen, Zalkida Hadzibegovic –
DENMARK, BOSNIA AND HERZEGOVINA (*Oral)* 2387

VOCATIONAL EDUCATION AND SUSTAINABLE DEVELOPMENT: EXPLORING THE CONNECTIONS
Alberto Arenas – USA (*Oral)* 2395

ENVIRONMENTAL AWARNESS, EDUCATION AND LIFE LEARNING
Devrim. Y. Besim – NORTHERN CYPRUS (*Oral)* 2417

UNIVERSITY STUDENTS' VIEWS ABOUT A COURSE ON THE SUSTAINABLE DEVELOPMENT: RESULTS OF A NEED ANALYSIS STUDY
Mehmet Erdoğan, Gaye Tuncer – TURKEY (*Oral)* 2421

USING OUTDOOR THEATRE FOR ENVIRONMENTAL AWARENESS, EDUCATION AND LIFELONG LEARNING AT THE MOUNT CAMEROON ECO-REGION, CAMEROON
Edwin Njeba Nganji – CAMEROON (*Oral)* 2435

A PROPOSAL FOR AN ENVIRONMENTAL EDUCATION MODEL AIMING AT SUSTAINABLE DEVELOPMENT
Oğuz Özdemir, Muammer Tuna – TURKEY (*Oral)* 2441

UNITED NATIONS DECADE OF EDUCATION FOR SUSTAINABLE DEVELOPMENT (2005-2014): THE INITIATIVES OVERSEEN BY THE ITALIAN NATIONAL COMMISSION
Anna Re – ITALY (*Oral)* 2451

IMBIBING ENVIRONMENTAL AWARENESS IN SOCIETIES
Beyza Şat Güngör – TURKEY (*Oral)* 2461

F. NIETZSCHE AND MARTIN HEIDEGGER: BUILDING UP AN ECOPHILOSOPHICAL OUTLOOK
Ayten Sururi – NORTHERN CYPRUS (*Oral)* 2471

ECOLOGISTS' TRAINING IN FUEL ENERGY AND CHEMISTRY TECHNOLOGY SPHERE IN AZERBAIJAN STATE OIL ACADEMY
Qarayev Siyavush Farkhad, Akhmedov Zaur Musa – AZERBAIJAN (*Oral)* 2479

PERCEPTION OF ECOLOGICAL RISKS AS AN ESSENTIAL ASPECT OF ECOLOGICAL CONSCIOUSNESS
Smolova Lidia – RUSSIA (*Oral)* 2485

AGENTS OF SUSTAINABILITY AND ISSUES IN IMPLEMENTATION OF SUSTAINABILITY PROJECTS
Nerkis Kural – TURKEY (*Oral)* 2497

STUDENTS' USAGE LEVEL OF ENVIRONMENTAL ATTITUDES AND USAGE LEVEL OF ENVIRONMENTAL COGNITIVE KNOWLEDGE IN FIFTH GRADE OF THE TURKISH BASIC SCHOOLS
Tuğrul Ural, Eren Sarıkaya – TURKEY (*Oral)* 2505

THE EFFECTIVENESS OF ENVIRONMENTAL EDUCATION ON ENVIRONMENTALLY- SENSITIVE BEHAVIORS
Gamze Yücel Işıldar, Feriha Yıldırım – TURKEY (*Oral*) 2517

A STUDY ON THE UTILIZATION OF THE TECHNOLOGICAL MATERIALS USED IN SCIENCE CLASSES BY TEACHERS IN ELEMENTARY SCHOOLS
Mahmut Sarı – TURKEY (*Oral*) 2527

THE RELATIONSHIP BETWEEN THE PLACES WHERE PEOPLE LİVE AND THEIR QUALITY OF LIVING IN TRNC
Hakan Atamtürk – NORTHERN CYPRUS (*Oral*) 2533

THE EVALUATION OF ENVIRONMENTAL PERCEPTIONS OF THE STUDENTS AND TEACHERS OF A SECONDARY SCHOOL IN ANKARA
F. Sevencan , F. Temel, G. Boztas, S. Vaizoğlu – TURKEY (*Oral*) 2539

EDUCATION FOR SUSTAINABLE DEVELOPMENT: TRANSFORMING LEARNING INTO REAL LIFE ACTIONS: EXPERIMENTING ACTION-BASED LEARNING MODEL (ALM) AT ELEMENTARY SCHOOL LEVEL IN THE CONTEXT OF PAKISTAN
Qamar Shahid Siddiqui – PAKISTAN (*Oral*) 2543

CHILDREN'S CURIOSITY ON ENVIRONMENTAL ISSUES: TURKISH CASE
Mehmet Erdoğan, Murat Aydemir – TURKEY (*Oral*) 2549

PROMOTION OF NURSERY SCHOOL TEACHER AND JUNIOR GRADE TEACHER EDUCATION FOR ENVIRONMENT AND SUSTAINABLE DEVELOPMENT IN CROATIA
Vinka Uzelac, Aleksandra Pejčić, Dunja Andic – CROATIA.. 2559

LIFELONG LEARNING AS NEW PARADIGM OF EDUCATION FOR ENVIRONMENT AND SUSTAINABLE DEVELOPMENT WITHIN THE CONTEXT OF PROFESSIONAL IMPROVEMENT OF TEACHERS ORIENTATED TOWARDS DIRECT RESEARCH OF EDUCATIONAL PRACTICE
Lidija Vujičić – CROATIA (*Oral*) 2569

STANDPOINTS OF PARENTS AND EDUCATORS TOWARDS TASKS OF ENVIRONMENTAL EDUCATION IN KINDERGARTEN
Jurka Lepicnik Vodopıvec - *SLOVENIA* (*Oral*)... 2575

ECOLOGICAL EDUCATION IN INTERRELATION WITH EDUCATION FOR SUSTAINABLE DEVELOPMENT
Gagik Torosyan – ARMENIA (*Oral*) 2585

A COMPARATIVE STUDY OF TEACHER'S ATTITUDES TOWARDS ENVIRONMENTAL ISSUES
Cem Birol, Zafer Bekiroğullari, Ceren Paralik – NORTHERN CYPRUS (*Oral*) 2591

EVALUATION OF THE ENVIRONMENT PROTECTION EDUCATION PROJECTS IN THE SPECIALLY PROTECTED AREAS
Naim Uzun, Funda Varnacı – TURKEY (*Poster*) 2603

CHILDREN EDUCATION: FOUNDATION FOR GREEN FUTURE
Maryam Salek Zamani, Ali Salek Zamani, Yagub Salek Zamani – IRAN (*Poster*) 2613

MT-8: ENVIRONMENTAL KNOWLEDGE AND INFORMATION SYSTEMS

SURVEY OF NATURAL RESOURCES IN THE BASIN OF KUFRINJA VALLEY AND INVESTMENT BY USING TECHNIQUE OF REMOTE SENSING
Aiad Ashor Altaay, Ali Abdual Zeahrah Alwaily, Mohammad Yousif al Hity – IRAQ (*Oral)* 2615

AUTOMATED VERSUS MANUAL LINEAMENT ANALYSIS
Gulcan Sarp, Vedat Toprak – TURKEY (*Oral)* 2631

EFFECTS OF TELECOMMUTING ON SUSTAINABLE URBAN DEVELOPMENT AND ENVIRONMENT
Filiz Alkan Meşhur – TURKEY (*Oral)* 2647

HISTORICAL DEVELOPMENT OF THE MERIC RIVER DELTA: FROM 16TH CENTURY TO PRESENT
Cankut Ormeci, Semih Ekercin – TURKEY (*Oral)* 2657

MULTITEMPORAL CHANGE DETECTION AT THE SALT LAKE IN TURKEY USING REAL-TIME SPOT IMAGERY AND IN-SITU SPECTRAL MEASUREMENTS
Cankut Ormeci, Semih Ekercin – TURKEY (*Oral)* 2667

AN INTELLIGENT SYSTEM FOR INTEGRATED SOLID WASTE MANAGEMENT
Latifah Abd Manaf – MALAYSIA (*Oral)* 2675

GIS BASED RISK QUALITY OBSERVATION ANALYSIS AT GEDIZ BASIN IN IZMIR METROPOLITAN MUNICIPALITY BOUNDARY
Vildan Gündoğdu, Münevver Elele, Gözde Akgün – TURKEY (*Oral)* 2687

REHABILITATION OF ASBESTOS MINING WASTE: A REHABILITATION PRIORITISATION INDEX (RPI) FOR SOUTH AFRICA
L. van Rensburg, S. Claassens, J.J. Bezuidenhout, P.J. Jansen van Rensburg – SOUTH AFRICA (*Oral)* 2701

A CASE STUDY ON OPTIMAL LAND USE OF SELCUK (IZMIR) AND ITS ARROUND
Emine Zaimoglu, Umit Erdem – TURKEY (*Oral)* 2711

DEFINING LAND COVER TYPE OF EDREMIT REGION IN TURKEY BY USING OPTICAL AND RADAR FUSED IMAGES
Y. Kurucu, F. Balik Sanli, M.T. Esetlili – TURKEY (*Oral)* 2727

SOIL CLASSIFICATION STUDY USING GEOMORPHOLOGIC BASED METHOD CASE STUDY: ZIDASHT REGION, IRAN
Mohsen Maleki, Marzieh Mosayebi – IRAN (*Oral)* 2739

A NATIONAL MONITORING SYSTEM FOR RANGE ASSESSMENT IN IRAN
H. Arzani, M. Frahpour, M. Azimi, H. Mirdavodi, M.Borhani, J. Abdollahi – IRAN (*Oral)* 2747

AIRBORNE HYPERSPECTRAL IMAGING SYSTEM FOR MANAGEMENT AND CONSERVATION OF MOUNTAIN FOREST PARK IN KELANTAN, MALAYSIA
Kamaruzaman Jusoff, Dahlan Taha – MALAYSIA (*Oral)* 2761

STUDY OF ENVIRONMENTAL DEGRADATION AROUND THE JAJRUD RIVER USING GEOGRAPHICAL INFORMATION SYSTEM AND REMOTE SENSING
Ammar Rafiei Emam – IRAN (*Oral)* 2769

PROPOSED STRATEGY FOR ESTABLISHING A TURKISH ENVIRONMENTAL INFORMATION EXCHANGE NETWORK
Mehmet Karaoğlan , Mustafa Aydin, Özlem Esengin – TURKEY (*Oral)* 2775

A DECISION SUPPORT SYSTEM FOR WATER RESOURCES MANAGEMENT
D. Ouazar, M. Touji, M.D. Hasnaoui – MOROCCO (*Oral)* 2785

ENVIRONMENTAL INSITE: AN ENVIRONMENTAL INFORMATION SYSTEM USED FOR ASSESSING GROUNDWATER QUALITY IN MERSIN
Zeynel Demirel, Zafer Özer, Olcay Gülçiçek, Aylin Kaya – TURKEY (*Poster*) 2793

MT-9: ENVIRONMENTAL LAW AND ETHICS

THE EUROPEAN HUMAN RIGHTS COURT AND ENVIRONMENTAL PROTECTION
Nükhet Yilmaz Turgut – TURKEY (*Invited*) 2807

ENVIRONMENTAL LAW AND FOREST LEGISLATION IN IRAN
S. Mohsen Hosseini, Moslem Akbarinia – IRAN (*Invited*) 2823

LIABILITY OF THE POLLUTANT: CRIMINAL & CIVIL
Emel Badur, Burcu Ertem – TURKEY (*Oral)* 2833

ENVIRONMENTAL RIGHT IN TURKISH CONSTITUTIONAL LAW
Funda Çetindağ, İlker Kılıç – TURKEY (*Oral)* 2845

WHY DO WE CARE? ETHICS AND HONESTY ABOUT ENVIRONMENTAL ISSUES
Sevda Caliskan – TURKEY (*Oral)* 2853

EVALUATION OF RECENT AMENDMENTS IN ENVIRONMENT LAW
Huriye Kubilay, Meltem Kutlu Gürsel, Muhlis Öğütçü – TURKEY (*Oral)* 2863

SUSTAINABLE DEVELOPMENT AND ENVIRONMENTAL JUSTICE
Mahir Fisunoglu, Berna Balcı İzgi – TURKEY (*Oral)* 2869

ENVIRONMENTAL LAW AND ETHICS
Ghorban Elmi – IRAN (*Oral)* 2879

ASSESSING ENVIRONMENTAL IMPACT ASSESSMENT AN INDIAN CRITIQUE
Nawneet Vibhaw – INDIA (*Oral)* 2889

MT-10: ENVIRONMENTAL ORGANIZATIONS: ROLES, PROBLEMS AND PROSPECTS

HOW THE ENVIRONMENTAL PROFESSIONALS IN TURKEY PERCEIVE THE "ENVIRONMENT" AND ACT?
Gamze Yücel Işıldar – TURKEY (*Oral)* 2895

THE ROLE OF NON GOVERNMENTAL ORGANIZATIONS IN REALIZATION OF SUSTAINABLE DEVELOPMENT: TURKISH CASE
Elif Karakurt Tosun, Canturk Caner – TURKEY (*Oral)* 2907

ENVIRONMENTAL ESTABLISHMENTS AND ORGANIZATION
Aylin Çinçinoğlu Salici, Nurgül Konakli, Onur Boyacigil, Faruk Altunkasa – TURKEY (*Oral)* 2917

VOLUME 7

MT-11: ENVIRONMENTAL SCIENCE AND TECHNOLOGY

ALTERNATIVE PATH ON SEWERAGE SYSTEM; CONDOMINIAL METHOD AND ITS APPLICATION
Umut Türker, Majed Hamad Abu Zahrah, Hüseyin Gökcekuş – NORTHERN CYPRUS *(Oral)* 2923

SALINITY-ALKALINITY & POLLUTION PROBLEMS IN THE GEDIZ BASIN-TURKIYE
Munir Ozturk, Serdal Sakçalı, Hakan Bahadır, Güven Görk, Müslüm Beyazgül – TURKEY *(Invited)* 2935

AMBIENT AIR PATTICULATE DRY DEPOSITION POLLUTANTS (METALLIC ELEMENTS, IONIC SPECIES) STUDY IN TAIWAN
Guor-Cheng Fang – TAIWAN *(Invited)* 2943

SOLID WASTE MANAGEMENT IN THE DEVELOPING COUNTRIES: A CASE STUDY IN TURKEY
Günay Kocasoy – TURKEY *(Invited)* 2971

MANAGEMENT OF HAZARDOUS ROAD DERIVED RESPIRABLE PARTICULATES USING MAGNETIC PROPERTIES OF TREE LEAVES.
K. Prajapati, B.D. Tripathi – INDIA *(Oral)* 2983

RAPID MEASURMENT OF APPLE VINEGAR'S ADDED SODIUM METABISULFITE BY A NEW ULTRASONIC METHOD
Gökhan Savaroğlu, Filiz Savaroğlu – TURKEY *(Oral)* 2989

RECLAMATION OF SODIC SOILS THROUGH VERMITECHNOLOGY
Abdullah Adil Ansari – TURKEY *(Oral)* 3003

USING OF THE LIGNOSULFONATES: FERTILIZERS
Ali Rıza Demirkıran – TURKEY *(Oral)* 3013

MODELING THE AEROBIC BIO-OXIDATION STAGE OF AN INDUSTRIAL WASTEWATER TREATMENT PLANT USING ANFIS AS A SOFTWARE SENSOR
G. Civelekoglu, A. Perendeci, N.O. Yigit, M. Kitis – TURKEY *(Oral)* 3019

REMOVAL OF COBALT ION FROM AQUEOUS SOLUTIONS BY LIGNOSELLULOSICS MODIFIED WITH PAN
Mustafa Karaboyaci, Fethiye Gode, Aziz Şencan, Mustafa Cengiz – TURKEY *(Oral)* 3027

A STUDY ON APPLICATION OF DIFFERENT DISOLVED OXYGEN (DO) VARIATIONS IN SEQUENCING BATCH REACTOR
Engin Gürtekin, Nusret Şekerdağ – TURKEY *(Oral)* 3037

MICROALGAE REMOVAL FROM SYNTHETIC WASTEWATER BY TILAPIA (OREOCHROMIS NILOTICUS AND OREOCHROMIS AUREUS)
Ahmet Yüceer, Olcayto Keskinkan – TURKEY *(Oral)* 3043

BIOREMEDIATON OF CD(II)-CONTAMINATED KAOLINE BY RHAMNOLIPID BIOSURFACTANT
Yeliz Aşçı, Macid Nurbaş, Yeşim Sağ Açıkel – TURKEY *(Oral)* 3051

PROPOSAL FOR A SOLID WASTE MANAGMENT SCHEME FOR THE TURKISH REPUBLIC OF NORTHERN CYPRUS
Selnur Uçaroğlu, Mustafa YILDIRIM, İpek Yilmaz, Orhan Küçükgül, Bülent Topkaya – NORTHERN CYPRUS *(Oral)* 3059

A STUDY ON RECOVERY AND RECYCKLING OF USEFUL MATERIAL IN LEATHER TANNING INDUSTRY
Hafiz Moghira Badar, Ahmad Khan, Fatima Batool – PAKISTAN *(Oral)* 3069

COMPARISON OF THE METALS CONCENTRATIONS IN ATLANTIC HORSE MACKEREL, TRACHURUS TRACHURUS, FROM COASTAL WATERS OF TURKEY
Aysun Türkmen, Yalçın Tepe, Mustafa Türkmen, Alpaslan Ateş, Kutalmış Gökkuş – TURKEY 3081

EFFECT OF TOTAL AMMONIA NITROGEN CONCENTRATION AND pH ON GROWTH RATES OF LEMNA MINOR
Yalçın Tepe, Mustafa Türkmen, Yalçın Töre, Elif Kuzu – TURKEY *(Oral)* 3089

SEQUENTIAL (ANAEROBIC- AEROBIC) TREATMENT OF CHEESE WHEY
Cansu Filik İşçen, Semra İlhan – TURKEY *(Oral)* 3097

DECADES OF TIN MINING IN JOS PLATEAU NIGERIA AND A LEGACY OF IMPOVERISHED AGRICULTURAL LAND AND HIGH RADIOACTIVE ELEMENTS: AN OVERVIEW OF INFRASTUCTRAL NEGLIGENCE
N.N. Jibiri – NIGERIA *(Oral)* 3105

PARTICULATE MATTER AND PAH POLLUTION IN ON INDUSTRIAL TOWN: DILOVASI CASE
Aytuğ Sivaslıgil, Pınar Kuş – TURKEY *(Oral)* 3119

AN INTEGRATED PREVENTIVE PRODUCTION PLANNING PROGRAM WITH WASTE MINIMIZATION
Sedef Elker, Sibel Uludag-Demirer – TURKEY *(Oral)* 3127

LEVELS OF HEAVY METALS IN WATER AND FISH (CARASOBARBUS LUTEUS HECKEL, 1843) WERE SAMPLED FROM GÖLBAŞI LAKE, HATAY, TURKEY.
Ayşe Bahar Yılmaz, Mustafa Doğan – TURKEY *(Oral)* 3139

IMPACTS OF SOLUTION PH ON ARSENIC REMOVAL BY NANOFILTRATION AND TIGHT-ULTRAFILTRATION MEMBRANES
Evrim Celik, Jaeweon Cho, Zhang Yang, Eunkyung Lee, Sungyun Lee, Mehmet Kitis – TURKEY, KOREA, KOREA, KOREA, TURKEY *(Oral)* 3149

NONDESTRUCTIVE TEST TO TACK POLLUTANT TRANSPORT INTO LANDFILL LINERS
A. Bezzar, F. Ghomari, H. Q. Wang – ALGERIE, FRANCE *(Oral)* 3157

INVESTIGATION OF BIOACCUMULATION OF COPPER AND NICKEL IONS BY RHIZOPUS DELEMAR
Ünsal Açıkel, Tuğba Alp – TURKEY *(Oral)* 3169

COMPARISON OF BIOACCUMULATION AND BIOSORPTION OF COPPER IONS BY CANDIDA LIPOLYTICA
Ünsal Açıkel, Tuğba Alp – TURKEY *(Oral)* 3177

ENVIRONMENTAL IMPACTS OF FLY ASHES FROM THERMAL POWER STATION
S.A. Kadioğlu, A. Balci, A. Demirak, E. Tilkan – TURKEY *(Oral)* 3187

PLANTS, BRYOPHYTES, EPIPHYTIC MICROORGANISMS AND FUNGI AS BIOINDICATORS OF AIR POLLUTION
Marilena Onete, Mihaela Pauca-Comanescu, Ioana Gomoiu, Sorin Stefanuț, Daniela Șincu – ROMANIA *(Oral)*...................3197

IMPORTANCE OF RAPID MIXING TIME ON SLUDGE DEWATERING PROPERTIES
S. Sam, M.A. Yukselen – TURKEY *(Oral)* 3213

TOLUENE INHIBITION OF AN ANAEROBIC REACTOR SLUDGE IN TERMS OF ACTIVITY AND COMPOSITION OF ACETOCLASTIC METHANOGENS
O.Ince,M.Kolukirik, Z.Çetecioglu, O.Eyice, N. Ayman Oz, Ozgul Inceoglu, B.Ince – TURKEY *(Oral)*................................ 3227

CLEAN DYEING TECHNOLOGY WITH BASIC NATURAL DYE ON COTTON FABRICS USING ULTRASONIC TECHNIQUE
M.M Kamel, H.F. Mansour, H. M. Mashaly, A.A.Haroun – EGYPT *(Oral)* 3237

ADDRESSING SYNERGIES BETWEEN CHEMICAL SAFETY AND SUSTAINABLE PRODUCTION AND USE OF CHEMICALS
Sulejma Čehić – SLOVENIA *(Oral)* 3251

ACUTE TOXICITY OF MERCURIC CHLORIDE ON RAINBOW TROUTS AND CHUBS
Bülent Verep, E. Sibel Beşli, İlhan Altinok, Cengiz Mutlu – TURKEY *(Oral)* 3267

REMOVAL OF COLOUR FROM INDUSTRIAL WASTEWATER
D. Mohan, S. Sarkar, K. Ankur – INDIA *(Oral)* 3279

APPLICABILITY OF PHOTOCATALYTIC OXIDATION PROCESS TO EFFLUENT OF THE COMBINED WASTEWATER TREATMENT PLANT
Ayla Arslan – TURKEY *(Oral)* 3291

TRACE ELEMENT CONCENTRATIONS OF LICHENS NEAR SEYITOMER COAL-FIRED POWER PLANT
Filiz Gür, Günseli Yaprak – TURKEY *(Oral)* 3301

REMOVAL OF TOXIC COPPER AND MANGANESE IONS FROM LEFKE-GEMIKONAĞI DAM WATER
Selahattin Gökmen, Nilay Taşer – TURKEY, NORTHERN CYPRUS *(Oral)* 3313

DEVELOPMENT AND ENVIRONMENTAL POLLUTION IN TURKEY AND IN KOCAELİ
Savaş Ayberk – TURKEY *(Oral)* 3319

ZOOPLANKTON COMPOSITION AND WATER QUALITY OF LAKE GOLBASI (HATAY-TURKEY)
Yalçın Tepe, Ahmet Bozkurt – TURKEY *(Oral)* 3325

THE SUSTAINABILITY OF WASTE DISPOSAL: POLLUTION OF UNDERGROUND WATER BY LEACHATES FROM OLD BURDENS (DUMPSITE)
Sokefun Olusola Bolarinwa – NIGERIA*(Oral)* 3343
.

NOISE AS AN INFLUENTIAL ENVIRONMENTAL PROBLEM.CASE STUDY: LEVELS OF DISTURBANCE BY ROAD TRAFFIC NOISE IN THE CITY OF NIGDE.
Lale Guremen, Cahit Tagi Celik – TURKEY *(Poster)* 3353

RECOVERY OF ZINC FROM QUARTZ BY RHAMNOLIPID BIOSURFACTANT
Yeliz Aşçı, Macid Nurbaş, Yeşim Sağ Açıkel – TURKEY *(Poster)* 3359

DRAINAGE GEOCHEMISTRY AND ENVIRONMENTAL IMPACT OF THE WHITTLE COALFIELD AREA, NORTHERN UK
Leyla Kalender – TURKEY *(Poster)* 3365

PROTECTION OF MARBLE USING BIODEGRADABLE POLYMERS
Yılmaz Ocak, Aysun Çakan Sofuoğlu, Funda Tıhmınlıoğlu, Başak İpekoğlu, Hasan Böke – TURKEY *(Poster)* 3393

SOLID WASTE MANAGEMENT AT THE SOUTH-EASTERN BLACK SEA COASTLINE
Egemen Aras, Mehmet Berkun – TURKEY *(Poster)* 3401

UTILIZATION OF THE RESIDUAL BRINES OF WATER DEMINERALIZERS
N.A.Salimova, F.M.Sultanova, L.V.Huseynova – AZERBAIJAN *(Poster)* 3411

BIODEGRADATION OF AZO DYES
Jonstrup Maria, Blánques Paqui, Guieysse Benoit – SWEDEN *(Poster)* 3415

PLANT SPECIES OF CMC MINING WASTE AREA AND HEAVY METAL ACCUMULATION
Gülriz Bayçu – TURKEY *(Poster)* 3419

GALVANIC WASTE WATER TREATMENT WITH CHELATING MACROPOROUS COPOLYMER AT STATIC AND DYNAMIC CONDITIONS
Aleksandra Nastasović, Antonije Onjia, Zvjezdana Sandić, Ljiljana Malović, Sladjana Kljajević, Dragana Đorđević, Dragica Jakovljević – SERBIA *(Poster)* 3423

THEORETICAL SUBSTANITATION OF PROCESS OF RECTIFICATION OF OIL-POLLUTED SOIL.
Hasanov G. S, Abdullaev F. Z, Latifov F.I. – AZERBAIJAN *(Poster)* 3433

THE USE OF PURIFICATION SLUDGE OF PAPER INDUSTRY IN AGRICULTURE
Gümüs Funda Gökçe – TURKEY *(Poster)* 3443

DETERMINATION OF SEA POLLUTION IN ALIAGA BAY, IZMIR, TURKEY:7-ETHOXYRESORUFIN O-DEETHYLASE (EROD) INDUCTION IN LEAPING MULLET (LIZA SALIENS).
O. K. Ulutaş, A. Şen, B. Tütüncü, İ. Çok – TURKEY *(Poster)* 3459

EXAMINATION OF SOME PARAMETERS FOR ECOLOGICAL GROWTH OF MAIZE IN PELIC VERTISOL
I.Stoimenova, St. Alexieva, S. Stratirva, E. Djonova, A.Taleva, N. Kaloyanova – BULGARIA *(Poster)* 3465

DECOLORIZATION OF TEXTILE DYES BY A FILAMENTED FUNGUS ASPERGILLUS ORYZAE
Hatice Ataçağ Erkurt, Mustafa Özyurt, Ayla Özer – TURKEY *(Poster)* 3471

ADSORPTION OF CHROMIUM (VI) BY WOOL
Nilgün Balkaya, Nilden Bektas – TURKEY *(Poster)* 3481

REMOVAL OF LEAD FROM AQUEOUS SOLUTIONS BY PHOSPHOGYPSUM TREATED WITH LIME
Nilgün Balkaya, Hasan Cesur – TURKEY *(Poster)* 3495

DECOLORIZATION OF DRIMARENE BLUE K2-RL BY FUNALİA TROGII ATCC 200800 CULTURE FILTRATE IMMOBILIZED IN ALGINATE BEADS
Emrah A. Erkurt, Mehmet A. Mazmanci, Hatice A. Erkurt, Ali Unyayar – TURKEY *(Poster)* 3509

ZETA POTENTIAL: A NEW WATER TREATMENT AND THE ALUMINUM INDUSTRY
Luiz Antonio Ferrari, Romeu Rovai Filho – BRAZIL *(Poster)* 3517

SIMULATION OF AN ACTIVATED SLUDGE TREATMENT SYSTEM USING ASM AND ANFIS MODELS
G. Civelekoglu, N.O. Yigit, O. Cinar, M. Kitis – TURKEY *(Poster)* 3523

TOXICITY ASSESSMENT OF METHYL TERT-BUTYL ETHER, TERT-BUTYL ALCOHOL AND FORMALDEHYDE USING REDUCED INHIBITION CONSTANTS
W. Cho, K. S. Cho, H. W. Ryu – SOUTH KOREA *(Poster)* 3533

A GRAPHICAL APPLICATION IN TREATMENT OF RESIDENTAL WASTEWATER BY THE ACTIVATED SLUDGE PROCESS
S. Serkan Nas, Adem Bayram – TURKEY *(Poster)* 3541

INVESTIGATION OF RADON RISK IN WELL WATER
Akkurt, H.A. Yalim, H. Akyıldırım, A. Akkurt, F.B. Ozdemir, R. Unal, A. Sandikcioglu – TURKEY *(Poster)* 3551

THE EFFECT OF SOLAR - COSMIC RAYS ON THE BACKGROUND RADIATION
I. Akkurt, N.Ç.Bezir, B. Mavi, H. Akyıldırım, C.Yalçın, F. Kulalı – TURKEY *(Poster)* 3555

SEASONAL AND SPATIAL DISTRIBUTIONS OF THE METALS IN THE WATER, SEDIMENT AND AFRICAN CATFISH, CLARIAS GARIEPINUS, FROM THE RIVER ASI (ORONTES) IN SOUTHERN EAST MEDITERRANEAN AREA OF TURKEY
Mustafa Türkmen, Evren Çalışkan – TURKEY.......... 3559

GEOSYNTHETIC MATERIALS USED IN WASTE CONTAINMENT SYSTEMS
Pelin Aklik – TURKEY *(Poster)* 3577

RADIONUCLIDE EMISSION FROM THE SEYİTÖMER COAL-FIRED POWER PLANT AND THE POPULATION EXPOSURE TO EXTERNAL RADIATION IN ITS VICINITY
Filiz Gür, Günseli Yaprak – TURKEY *(Poster)* 3585

BIOMONITORING OF TRACE ELEMENTS OF ZINK AND MANGANESE POLLUTION BY THE BARK OF TURKISH RED PINE (PINUS BRUTIA) IN WESTERN ANATOLIA
Y. Dogan, N. Durkan, S. Baslar, H.Aydin – TURKEY *(Poster)* 3595

INDUSTRIAL SOLID WASTE MANAGEMENT IN TURKEY
Başak Mesci, Osman Nuri Ergun – TURKEY *(Poster)* 3601

MT-12:GLOBAL WARMING: HOW MUCH OF A THREAT?

DEVELOPING COUNTRIES AND THE CHALLENGE OF CLIMATE CHANGE
Ishfaq Ahmad – PAKISTAN *(Invited)* 3607

GLOBAL WARMING THREAT ON WATER RESOURCES AND ENVIRONMENT
Zekai Şen – TURKEY *(Invited)* 3623

TRENDS AND VARIATIONS OF AIR TEMPERATURE AND PRECIPITATION SERIES IN NORTHERN CYPRUS
Murat Türkeş, Faize Sariş – TURKEY *(Oral)* 3657

CONTROL OF GHG EMISSIONS RESULTING FROM THE TRANSPORT SECTOR IN TURKEY
Cem Soruşbay, Metin Ergeneman, M. Aydın Pekin – TURKEY *(Oral)* 3669

REGIONAL CLIMATE CHANGE AND ITS IMPACTS FOR TURKEY
Mehmet Karaca, Ozan M. Göktürk, Omer Lutfi Sen, Barış Onol, Tayfun Kındap, Nüzhet Dalfes – TURKEY *(Oral)* 3679

GLOBAL WARMING AND CLIMATIC CHANGES IN PAKISTAN
Abdul Razzaq Ghumman, Muhammad Ali Shamim, Raza Ali – PAKISTAN *(Oral)* 3687

WHO PAYS THE BILL? – THE IMPACT OF CLIMATE CHANGE ON REAL ESTATE MARKETS
Sven Bienert Mrics – GERMANY *(Oral)* 3707

SIGNAL AND TREND ANALYSIS OF TEMPERATURE SERIES: A TURKISH CASE
Mete Tayanç, Murat Doğruel, Ulaş İm, Mehmet Karaca – TURKEY *(Oral)* 3723

INTERNATIONAL CLIMATE CHANGE POLICIES AND TURKEY
Deniz Babuş, Muzaffer Yücel – TURKEY *(Oral)* 3735

EVALUATIONS ON FOREST RESOURCES MANAGEMENT OF NORTHERN CYPRUS AND NEW PLANNING APPROACH IN ACCORDANCE WITH SUSTAINABILITY AND CLIMATE CHANGE RISK
Said Dağdaş, Rüstem Kırış – TURKEY *(Oral)* 3747

GLOBAL WARMING: HOW FAR A PROBLEM
Somlata Sharma – INDIA *(Oral)* 3759

MODELING METHANE EMISSION FROM ÇANAKKALE OPEN DUMPSITE AND ITS EFFECT ON GLOBAL WARMING: A LANDGEM USE APPROACH
Edip Avşar, Hasan Göksel Özdilek – TURKEY *(Oral)* 3767

INTEGRATED APPROACH IN SEARCHING SUSTAINABLE DEVELOPMENT OPPORTUNITIES
Giuseppe Fumarola, Aniello Russo Spena – ITALY *(Oral)* 3777

VOLUME 8

MT 13 -GREEN FACTOR IN POLITICS

ANOTHER FALSE DAWN? TOWARDS A NON-LEGALLY BINDING INSTRUMENT ON FORESTS - CONTEMPORARY ISSUES AND POLITICAL UNCERTAINTIES
David Humphreys – UK *(Oral)* 3785

GREEN POLITICS AND SOCIAL SUPPORT FOR ENVIRONMENTALISM IN TURKEY
Baran Dural – TURKEY *(Oral)* 3797

THE GREENS IN TURKISH POLITICS TRANSFORMATION FROM AN NGO TO A POLITICAL PARTY
Ceren Uysal Oğuz – TURKEY *(Oral)* 3813

USING THE SLEUTH URBAN GROWTH MODEL TO SIMULATE THE IMPACTS OF FUTURE POLICY SCENARIOS ON URBAN LAND USE IN THE HOUSTON-GALVESTON-BRAZORIA CMSA
Hakan Oguz – TURKEY *(Oral)* 3819

MT-14: INTEGRATED WATER RESOURCES MANAGEMENT

ANALYSIS OF RESEARCH AND DEVELOPMENT OF SOIL FERTILITY AND WATER MANAGEMENT TECHNOLOGIES IN MALAWI- A REVIEW
D. M. S. Kadyampakeni, V. H. Kabambe – MALAWI *(Oral)* 3847

IMPACTS OF LAND-USE CHANGE ON THE WATER QUALITY OF THE MAIN SOURCE OF PIPE BORNE WATER FOR KUMASI, GHANA (A CASE STUDY OF THE BAREKESE RESERVOIR CATCHMENT AREA)
Tyhra Carolyn Kumasi, K. Obiri-Danso, J. B. Ephraim – GHANA *(Oral)* 3863

MULTIPLE PURPOSE FOREST RESOURCES MANAGEMENT: THE WATER PERSPECTIVE
Yusuf Serengil, Kenan Ok – TURKEY *(Oral)* 3875

A NEW APPROACH TOWARDS FLOOD CONCERNED SPATIAL PLANNING
Mariele Evers, Kai-Uwe Krause, Stefan Tressl – GERMANY *(Oral)* 3887

DECISION SUPPORT SYSTEMS FOR INTEGRATED WATER RESOURCES MANAGEMENT REQUIREMENTS FOR A COMPREHENSIVE APPROACH
Mariele Evers – GERMANY *(Oral)* 3899

CONSERVING WETLANDS BY WATERSHED MANAGEMENT, SAMPLE OF LAKE BEYSEHİR (KONYA)
Fadim Yavuz Özdemir, Elif Gündüz – TURKEY *(Oral)* 3915

TRADITIONAL WATER MANAGEMENT; AN INSPIRATION FOR SUSTAINABLE IRRIGATED AGRICULTURE IN CENTRAL IRAN
Majid Labbaf Khaneiki – IRAN *(Oral)* 3929

INTEGRATING ECONOMICS IN TO INVASIVE AQUATIC PLANTS (IAP) MANAGEMENT IN SRI LANKA: ALIEN AQUATIC PLANTS: IS AN ECONOMIC PROBLEM?
Sujith Ratnayake, Leel Randeni, Champika Kariyawasam – SRI LANKA *(Oral)* 3939

PARTICIPATORY APPROACH TO SUSTAINABLE WATER RESOURCE MANAGEMENT IN A WATERLOGGED AREA
Firdaus Fatima Rizvi – INDIA *(Oral)* 3951

THE EFFECT OF MINING WORKS ON WATER COLLECTION BASIN: ÇATALAN EXAMPLE
Mesut Anıl, Ahmet Yüceer, Zülküf Kaya, Bayram Ali Mert, Mehmet Türkmenoğlu – TURKEY *(Oral)* 3961

A SURVEY OF RELATIONSHIP BETWEEN EVAPORATION AND WIND SPEED OF EĞIRDIR LAKE BY USING CLUSTERING TECHNIQUES
Veysel Güldal, Hakan Tongal – TURKEY *(Oral)* 3981

A MANAGEMENT MODEL FOR WATER QUALITY CONTROL USING A GENETIC ALGORITHM
Egemen Aras, Vedat Togan, Mehmet Berkun – TURKEY *(Oral)* 3991

OBSERVATIONS ON SUSTAINABLE WATER RESOURCE MANAGEMENT IN TURKEY: THE NEED FOR A COLLABORATIVE APPROACH
Ömer Eker, Sultan Bekiroğlu – TURKEY *(Oral)* 4001

REVISION AND MODIFICATION OF WATER QUALITY MONITORING STUDIES IN TURKEY
M. Karaman, D. Guler, A. K. Onur, F. Baltacı, S. Tahmiscioğlu – TURKEY *(Oral)* 4007

RIVER BASIN ORIENTED URBAN WASTEWATER TREATMENT IN TURKEY
Arslan Alaton, G. Iskender, P. Ongan Torunoglu, M. Gurel, S. Ovez, A. Tanik, D. Orhon – TURKEY *(Oral)* 4015

GENERAL PLANNING APPROACH TO THE LAND USE AT THE RIVER BASIN IN THE CASE: ALTINAPA BASIN IN THE MIDDLE OF ANATOLIA
Çiğdem Çiftçi, Havva Alkan Bala – TURKEY *(Oral)* 4027

NEW TECHNOLOGY TO MEASURE THE WATER LEVEL AND THE SEA STATE
Christoph J. Blasi – GERMANY *(Oral)* 4037

ECOLOGICAL CONTROL OF A CONDITION OF WATER BODIES IN LARGE CITY
N. Ignatyeva, O. Susareva, D. Kuznetsov, O. Pavlova – RUSSIA *(Oral)* 4047

INVESTIGATION OF PUMPING EFFECTS ON GROUNDWATER IN TORBALI
A. O. Aksoy, T. Scheytt, M. S. Guney – TURKEY, GERMANY *(Oral)* 4059

TONLE SAP ECOSYSTEM FISH SPECIES BIOLOGICAL GROUPS AND HYDRO-ECOLOGICAL INDEX
Nguyen Thi Hai Yen, Kengo Sunada, Satoru Oishi, Kou Ikejima –JAPAN, THAILAND *(Oral)* 4067

WATER RESOURCE AND THEIR PROTECTION IN SLOVAK REPUBLIC
Jozef Kriš, Martin Faško, Ivona Škultétyová – SLOVAK REPUBLIC *(Oral)* 4081

SITNICA RIVER FLOOD PROTECTION
Zekirija Idrizi, Kujtim Zena, Violeta Hoxha, Isak Idrizi – MACEDONIA *(Oral)* 4093

MODELING GROUNDWATER FLOW IN A RAW MATERIAL SITE OF A CEMENT FACTORY, KOCAELI-DARICA, TURKEY
Yeliz Isıklı, Nurkan Karahanoglu – TURKEY *(Oral)* 4105

SUSTAINABLE USE OF WATER RESOURCES AND RURAL DEVELOPMENT IN DROUGHT AFFECTED AREAS
Giovanni Quaranta, Rosanna Salvia – ITALY *(Oral)* 4109

MULTI DISCIPLINARY MODELING, IN STRATIGRAPHY AND GROUNDWATER STRATIGRAPHY OF THE JORDAN RIVER BASIN
Yaakov Anker, Akiva Flexer, Haim Shulman, Eliahu Rosenthal – ISRAEL *(Oral)*.................................... 4121

INDIGENOUS WATER MANAGEMENT SYSTEMS IN ARID AREAS OF SOUTH AFRICA: THE CASE OF THE BATSWANA PEOPLE IN THE NORTH WEST PROVINCE (SOUTH AFRICA)
Hassan O. Kaya – SOUTH AFRICA *(Oral)* 4133

ROOF TOP RAIN WATER HARVESTING IN INDUSTRIAL SECTOR
Apurba Bhattacharyya – INDIA *(Oral)* 4143

WET MEADOW MANAGEMENT IN ZAMANTI RIVER CROSSING OF BTC CRUDE OIL PIPELINE PROJECT
Şükran Şahin, Ekrem Kurum, Arturo Sousa Martin –TURKEY, SPAIN *(Oral)* ... 4155

ECOLOGICAL-BASED WATER RESOURCE PLANNING AND MANAGEMENT
Henning Schroll – DENMARK *(Oral)* ... 4169

ASSESSMENT OF USLE NOMOGRAPH FOR ESTIMATING ERODIBILITY OF CALCAREOUS SOILS FROM NORTHWESTERN IRAN
A. R. Vaezi, H. A. Bahrami, S. H. R. Sadeghi, M. H. Mahdian – IRAN *(Oral)* ... 4183

THE SYSTEMS APPROACH TO DESIGN OF OPTIMAL WATER USAGE AND WASTEWATER TREATMENT NETWORKS
M. Zgurovsky, G. Statyukha, O. Kvitka, A. Shakhnovsky, I. Dzhygyrey – INDIA *(oral)* ... 4199

MANAGEMENT OF WATER RESOURCES AND SUSTAINABLE REGIONAL DEVELOPMENT
Majid Yasouri – IRAN *(Oral)* ... 4207

ANCIENT ECO-TECHNOLOGY OF QANATS FOR ENGINEERING A SUSTAINABLE WATER SUPPLY IN THE MEDITERRANEAN ISLAND OF CYPRUS
Huseyin Gokcekus, Theodore A. Endreny – NORHERN CYPRUS, USA *(Oral)* ... 4219

URGENT ARMENIAN NATIONAL PROBLEM - LAKE SEVAN
Gagik Torosyan, Mikayel Harutyunyan, Yeva Torosyan – ARMENIA *(Oral)* ... 4237

THE SIMULATION GEOLOGICAL FOR WATER SHORTAGE FROM JIFARA PLAIN BASIN NORTHWEST OF LIBYA
Fathi Elosta – LIBYA *(Oral)* ... 4243

EVALUATION OF BORON IN DRINKING WATER IN SOME VILLAGES OF SEYDISUYU WATERSHED (ESKISEHIR) OF TURKEY
Demet Uygan, Oner Cetin – TURKEY *(Oral)* ... 4255

STOCHASTIC INTEGRATED WATER RESOURCES MANAGEMENT MODELS
Nasreddine Saadouli, Habib Saadouli – KUWAIT, TUNISIA *(Oral)* ... 4263

FORECAST OF WATER DEMAND USING ARTIFICIAL NEURAL NETWORK: A CASE STUDY IN ISPARTA
Gökhan Yılmaz, M. Erol Keskin, E. Dilek Taylan – TURKEY *(Poster)* ... 4279

WATER RESOURCES MANAGEMENT IN ARID REGIONS OF IRAN
A. Salajegheh, A. R. Keshtkar, H. Keshtkar – IRAN *(Poster)* ... 4287

GLOBAL AND REGIONAL FRESHWATER AVAILABILITY AND FUTURE DEMAND
Naser Ghavzan Jafari – IRAN *(Poster)* ... 4291

KARST WATER AT NACKARUD, MAZANDRAN, IRAN
Jafar Naji – IRAN *(Poster)* ... 4301

ARIDITY PROBLEM IN CYPRUS
Zeki Koday – TURKEY *(Poster)* ... 4307

PROTECTION OF WATER SOURCES AND AQUATIC LIVING FROM THE DAMAGES OF AGRICULTURAL CHEMICALS
Muhammed Atamanalp, Nilgun Ozdemir – TURKEY *(Poster)* ... 4317

EXAMPLES OF THE SUSTAINABLE ARCHITECTURE IN BOSNIA AND HERZEGOVINA
Ahmet Hadrović, Haris Bradic – BOSNIA AND HERZEGOVINA *(Poster)* ... 4325

AN INTERFACE BETWEEN METROPOLITAN AREA AND PERI URBAN EDGE
Havva Alkan Bala, Çiğdem Çiftçi – TURKEY *(Poster)* ... 4333

EVALUATION OF ACOUSTICS FOR MEASURING SUSPENDED SEDIMENTS IN RIVERS
Ramazan Meral – TURKEY *(Poster)* 4343

ASSESSING GROUNDWATER VULNERABILITY: CASE STUDY FOR KARST AQUIFERS
Mustafa Yildirim, İpek Yilmaz, Bülent Topkaya – TURKEY *(Poster)* 4349

CHARACTERISTICS OF SPRING WATER IN THE MID-BLACK SEA REGION
Feza Geyikçi – TURKEY *(Poster)* 4361

VOLUME 9

MT-15: INTERNATIONAL RELATIONS AND ENVIRONMENTAL ISSUES

IMPACT OF GLOBALIZATION ON POLLUTION AND RESOURCE DEPLETION: THE CASE OF NIGERIA
Mete Feridun, Folorunso Sunday Ayadi, Jean Balouga – NORTHERN CYPRUS, NIGERIA (*Oral)* 4367

ENVIRONMENTAL SCARCITY AND INTRASTATE CONFLICTS: THE CASE OF NEPAL
Fiona J.Y. Rotberg – SWEDEN (*Oral)* 4387

AS AN INTERNATIONAL ACTOR OF ENVIRONMENTAL REGIME INFLUENCES OF EU'S ENVIRONMENTAL POLICIES ON TURKISH ENVIRONMENTAL POLICIES
Uğur Yildirim, Sevim Budak, Zehra Gül – TURKEY (*Oral)* 4399

AN EVALUATION OF CIVIL ACTION ON ENVIRONMENT IN THE LIGHT OF INTERNATIONAL DOCUMENTS: CASES FROM TURKEY AND EUROPE
Aysu Kes, R. Erdem Erkul – TURKEY (*Oral)* 4417

INTERNATIONAL CONFLICT MANAGEMENT STRATEGIES IN WATER STRESSED REGIONS: A CASE STUDY OF BALOCHISTAN POST 9/11
Musarrat Jabeen – PAKISTAN (*Oral)* 4425

UNDP-ACT – BUILDING ENVIRONMENTAL BRIDGES IN CYPRUS
Nicolas Jarraud – USA (*Oral)* 4443

INTERNATIONAL EFFORTS DIRECTED TOWARDS BLACK SEA ENVIRONMENTAL ISSUES
Selma Yel, Gökhan Kayadurmuş – TURKEY (*Oral)* 4453

RE-ITERATION OF THE MIDDLE EAST PEACE PIPELINE PROJECT
Osman N. Ozdemir – TURKEY (*Oral)* 4463

A SURVEY ON UNDERSTANDING OF SOCIAL RESPONSIBILITY IN TURKISH SMALL AND MEDIUM SIZED INDUSTRIAL ENTERPRISES
Güngör Turan – TURKEY (*Oral)* 4469

IMPACT OF DECOMISSIONING OF NUCLEAR FACILITIES ON AFRICAN COUNTRIES
Babagana Abubakar – NIGERIA (*Oral)* 4477

INTERNATIONAL RELATIONS AND ENVIRONMENTAL ISSUES
Sourav Kumar Keshri, Amit Kulkarni – INDIA (*Oral)* 4481

ENVIRONMENTAL ASPECTS OF THE EUROPEAN UNION NEIGHBOURHOOD POLICY FOR UKRAINE
Mykola Shestavin, Maryna Yepik – UKRAINE (*Oral)* 4491

IR THEORY AND THE ENVIRONMENT: PARADIGMS OF ISOLATION AND CONVERGENGE
Vakur Sümer, Ayşegül Kibaroğlu, İlhan Sağsen – TURKEY (*Oral)* 4507

UNSUSTAINABILITY: THE CHALLENGE CONFRONTING "MIDDLE EASTERNERS"
Aharon Klieman – ISRAEL (*Oral*) 4517

MT-16: LITERATURE AND ENVIRONMENTAL AWARENESS

SUSTAINABLE COMMUNITIES: PRESCRIPTIONS AND ILLUSIONS
Nader Yehia, Mohamed Azab – BAHRAIN (*Oral)* 4527

ECOLOGICAL ROMANTCISM IN BRITISH LITERATURE
Nurdan Atamturk – TURKEY (*Oral)* 4551

TONGUES IN TREES: SHAKESPEARE AND THE ENVIRONMENT
Himmet Umunç – TURKEY (*Oral)* 4557

ENVIRONMENT EFFECTS ON THE ARCHIVE PAPERS
Öznur Özden – TURKEY (*Oral)* 4567

READER RESPONSE THEORY AND ENVIRONMENTAL AWARENESS
Alev Baysal – TURKEY (*Oral)* 4575

ENVIRONMENTALISM VS. COLONIALISM
Fatma Kalpaklı – TURKEY (*Oral)* 4581

MT-17: NATURAL AND MAN-MADE DISASTERS: EMERGING LINK AND CHALLENGES

EFFECTS OF THE LANDSLIDES ON THE ENVIRONMENT: SOME TYPICAL LANDSLIDE EXAMPLES FROM TURKEY
Aziz Ertunç – TURKEY (*Invited)* 4587

APPLICATION OF SHEET CRACK THEORY IN ANALYZING THE MECHANICS OF MOUZHUDONG LANDSLIDE
Fu He-lin, Zhou Ning, Luo Qiang, Guo Jian-feng – CHINA (*Oral)* 4597

PARTICIPATION AS AN ELEMENT OF SUSTAINABILITY I.N POST-DISASTER SETTLEMENTS
Berna Baradan – TURKEY (*Oral)* 4605

SPATIAL ANALYSIS OF EARTHQUAKE EPICENTERS IN; NORTH-WEST OF ANKARA
Gulcan Sarp, S.Duzgun, V.Toprak – TURKEY (*Oral)* 4619

A MANMADE DISASTER ALONG THE BLACK SEA COST: TURKEY
Ilyas Yılmazer, Özgür Yılmazer, Özlem Yılmazer, Coşkun Bulut, Levent Akduman – TURKEY (*Oral)* 4635

FLOOD HAZARD ZONING USING MATHEMATICAL MODEL AND GIS (A CASE STUDY JAJROOD RIVER TEHRAN PROVINCE)
H.Abghari, M.Mohseni Saravi, M.Mahdavi, H.Ahmadi – IRAN (*Oral)* 4647

AN ENVIROMENTAL AND ARCHITECTURAL APPROACH FOR USING EXTERNAL STRENGTHENING METHOD ON REINFORCED CONCERETE BUILDINGS IN TURKEY
M.Yaşar Kaltakcı, M.Hakan Arslan, U.S.Yılmaz, H.Derya Arslan – TURKEY (*Oral)* 4655

SOIL SUSTAINABLE – AS A FUNCTION OF ITS ECOLOGICAL AND TECHNICAL WAY OF USE
Husnija Resulović, Esad Bukalo – BOSNIA AND HERZEGOVINA (*Oral)* 4665

PROBLEM NATURAL AND MAN-MADE DISASTERS ON REGIONAL AND GLOBAL SCALES
Gregory Koff, Irina Chesnokova –RUSSIA (*Oral)* 4673

THE RISK-SOCIETY; “THE EFFECTS OF NATURAL AND MAN-MADE DISASTERS ON URBAN PEOPLE AND URBAN SOCIETY”, THE EXPERIENCE OF THE 1999 MARMARA EARTHQUAKE
İsmail Gündüz – TURKEY (*Oral*) 4677

SOLID WASTE MANAGEMENT AFTER OCTOBER 2005 EARTHQUAKE IN PAKISTAN
Azhar Ali – PAKISTAN (*Oral*) 4689

NATURAL OR MANMADE DISASTER? THE CASE OF FLOODS IN MUMBAI CITY
Janki Andharia –INDIA (*Oral*) 4695

THE THREAT OF THE OIL POLLUTION INCIDENT OCCURRED IN LEBANON TO THE NORTHERN CYPRUS COASTS AND THE IMPORTANCE OF OPERATIONAL SATELLITE MONITORING SYSTEM
Filiz Sunar, Ayda Akkartal, Barış Göral, Z. Damla Uça Avci –TURKEY (*Oral*) 4709

A STUDY ON THE AFTERSHOCK SEQUENCES OF EARTHQUAKES OCCURRED IN TURKEY
Serkan Öztürk, Yusuf Bayrak – TURKEY (*Oral*) 4719

LANDSLIDES: AN ENVIRONMENTAL DISASTER IN NORTHERN IRANIAN FOREST ECOSYSTEM
Seyed Hamidreza Sadeghi – IRAN (*Oral*) 4727

MAN’S ATTITUDE TOWARD THE WORLD AND ITS ROLE IN ENVIRONMENTAL PROTECTION
Qorban Elmi – IRAN (*Oral*) 4735

MT-18: PESTICIDES IN THE ENVIRONMENT AND FOOD COMMODITIES

THE EFFECTS OF SOME PESTICIDES ON VERTICILLIUM LECANII (ZIMMERMAN) VIÉGAS
Sebahat K. Ozman-Sullivan, Heval Ocal, Melih Micik – TURKEY (*Oral*) 4741

ENVIRONMENTAL GOVERNANCE FOR SUSTAINABLE AGRICULTURE WITH SPECIAL REFERANCE TO PUBLIC HEALTH: A CRITICAL REVIEW
Anjum Suhail, Muhammad Arshad– PAKISTAN (*Oral*) 4753

MONITORING OF CHLORINATED HYDROCARBON POLLUTION OF ENVIRONMENT AND ANIMALS IN ALBANIA
J. Abeshi, L. Dhaskali, B. Bizhga, L. Tafaj, E. Dimco – ALBANIA (*Oral*) 4769

MAIN ASPECTS OF RAW MILKS’ QUALITY ORIGINALITY AND SAFETY IN ALBANIA
Laura Shabani, Tania Floqi – ALBANIA (*Oral*) 4783

THE PESTICIDES SORPTION FROM WATER SOLUTION BY ARMENIAN NATURAL ZEOLITES
G.Torosyan, S.Harutyunyan, V.Davtyan, A.Mikaelyan, D.Hovhannisyan – REPUBLIC OF ARMENIA (*Oral*) 4791

HISTOLOGICAL AND BIOCHEMICAL EFFECTS OF INSECTICIDES MALATHION AND ENDOSULFAN ON RAT TESTIS
Nazan Deniz Koç, Figen Esin Kayhan, Gazi Contuk, Nüzhet Cenk Sesal – TURKEY (*Poster*) 4797

A BEVERAGE HAVING BENEFICIAL SUBSTANCES ON HUMAN HEALTH: WINE
Nilgün Göktürk Baydar, Gülcan Özkan – TURKEY (*Poster*) 4801

MT-19: THE ROLE OF MEDIA : PROBLEMS AND CHALLENGES

A CONTENT STUDY ON ENVIRONMENTAL JOURNALISM WITH SPECIAL REFERENCE TO PRINT MEDIA
Swathi Karamcheti – INDIA *(Oral)* 4809

A RESEARCH ON EVALUATING THE NEWSPAPER PHOTOGRAPHS FROM THE POINT OF ENVIRONMENTAL CONSCIENCENESS
E. Gülbuğ Erol – TURKEY *(Oral)* 4845

ENVIRONMENTAL EDUCATION VIA TV
Nedim Gürses, Cosgül Yüksel– TURKEY *(Oral)* 4859

THE REFLECTION OF CULTURAL HERITAGE INTO THE CHARMING ENVIRONMENTAL OF MEDIA VIA ADVERTISEMENT FILMS
Incilay Yurdakul – TURKEY *(Oral)* 4867

NIGERIAN MEDIA AS EARLY WARNING SIGNS IN ENVIRONMENTAL RISK REPORTING
Ebenezer Adebisi Olawuyi – NIGERIA *(Oral)* 4885

ROLE OF MEDIA IN CONSERVING THE CULTURAL HERITAGE
Eti Akyüz Levi – TURKEY *(Oral)* 4899

VOLUME 10

MT-20: SEAS, ECOLOGICAL BALANCE, AND SUSTAINABLE ENVIRONMENT

PROTECTED ECOLOGICAL AND FISHING ZONE IN THE REPUBLIC OF CROATIA AND ENVIRONMENTAL PROTECTION
Mira Lulić, Nives Mazur – CROATIA (*Oral)* 4915

ECO-FRIENDLY PRAWN CULTURE WITH POKKALLI PADDY –TRADITIONAL PRACTICE FOR SUSTAINABLE COASTAL RESOURCE MANAGEMENT.
Joseph S. Paimpillil – INDIA (*Oral)* 4927

SHORT TIME SERIES OF PHYTOPLANKTON, NUTRIENT AND CHOLOROPHYLL-A IN WINTER PERIOD IN THE DARDANELLES (ÇANAKKALE STRAIT, TURKEY)
Muhammet Türkoğlu, Yeşim Büyükateş, Cenk Öner – TURKEY (*Oral)* 4935

EVALUATION OF THE BLACK SEA DIVIDED COASTAL HIGHWAY PROJECT WITH AN ENVIRONMENTAL VIEW
Ferit Yakar, Fazıl Çelik – TURKEY (*Oral)* 4955

SENSITIVITY OF TURKISH PRECIPITATION TO SST VARIABILITY IN THE SURROUNDING SEAS
Deniz Bozkurt, Ömer L. Şen – TURKEY (*Oral)* 4965

CONSERVATION OF SEA TURTLE ON A NESTING BEACH IN SAN JUAN DE LOS PLANES, BAJA CALIFORNIA SUR MEXICO
Juan Guzmán, Karen Oceguera – MÉXICO (*Oral)* 4975

MONITORING MARINE RECREATINAL WATER QUALITY IN ANTALYA BAY AND INTERANNUALY CHANGES OF MICROBIAL INDICATORS
Gönül Tugrul-Icemer, Ceren Keles, Hüseyin Karaca – TURKEY (*Oral)* 4987

FUTURE BERTH REQUIREMENTS FOR SUSTAINABILITY OF IZMIR CONTAINER PORT SERVICES
Adem Eren, Umit Gokkus – TURKEY (*Oral)* 4995

SOLID WASTE MANAGEMENT AFTER OCTOBER 2005 EARTHQUAKE IN PAKISTAN
Azhar Ali – PAKISTAN (*Oral)* 5009

OCEAN POLLUTION AS A RESULT OF OFFSHORE AND ONSHORE PETROLEUM ACTIVITIES IN THE AFRICAN GULF OF GUINEA REGION
Babagana Abubakar – NIGERIA (*Oral*) 5015

COASTAL ZONE MANAGEMENT AND VULNERABILITY STUDY OF A SMALL ISLAND STATE - MAURITIUS
Roshan T. Ramessur – REPUBLIC OF MAURITIUS (*Oral*) 5021

MODIFIED SHAPE PARAMETER FOR REPRESENTING EQUILIBRIUM BEACH PROFILES
Umut Türker, M. Sedat Kabdaşlı – NORTHERN CYPRUS, TURKEY (*Oral*) 5037

MEDITERRANEAN ENDEMIC DECAPOD CRUSTACEANS IN THE TURKISH SEAS
A.Suat Ateş, Tuncer Katağan, Ahmet Kocataş – TURKEY (*Poster*) 5051

FEEDING ACTIVITY OF THE HOLLOWSNOUT GRENADIER, CAELORINCHUS CAELORHINCUS (RISSO, 1810) IN THE AEGEAN SEA
Halit Filiz, Tuncay M. Sever, Bahar Bayhan, Ertan Taskavak,Gökçen Bilge – TURKEY (*Poster*) 5055

INVESTIGATION OF MICROBIOLOGICAL POLLUTION OF SEA WATER IN MERSIN
Mustafa Özyurt , Ece Ümmü Deveci, Ahmet Acar, Hakan Aygün, Bahar Tank , İrfan Sayan, Veysi Özel – TURKEY (*Poster*) 5063

COASTAL ZONE MANAGEMENT
Sibel Aslan, Nusret Şekerdağ – TURKEY (*Poster*) 5075

CONTAINER FORECASTING TO MACRO AND MICRO PROJECTION FOR FUTURE DEVELOPMENT AT PORT OF IZMIR
Umit Gökkuş, Emine Budak – TURKEY (*Poster*) 5083

FUTURE STORAGE AREA REQUIREMENTS FOR SUSTAINABILITY OF IZMIR CONTAINER PORT
Dogan Canivar, Umit Gökkuş, Adem Eren – TURKEY (*Poster*) 5095

PRELIMINARY STUDY ON THE NORTH-AEGEAN CONTAINER PORT DEVELOPMENT
Umit Gökkuş, Adem Eren, Berra Gultekin Sinir – TURKEY (*Poster*) 5105

MT-21: SOCIAL AND PSYCHOLOGICAL DIMENSIONS OF ENVIRONMENTAL ISSUES

HUMAN RESOURCE DEVELOPMENT STRATEGY FOR OIL SECTOR IN LIBYA
Bouazzi, Nagia, Hussein Lahmar, S.P.Bindra – LIBYA *(Oral)* 5117

PUBLIC ENVIRONMENTAL ATTITUDES IN TURKEY
Muammer Tuna – TURKEY *(Oral)* 5133

SUSTAINABLE BIODIVERSITY CONSERVATION IN THE NIGER DELTA: A PRACTICAL APPROACH TO CONSERVATION SITE SELECTION
P. O. Phil-Eze, I. C. Okoro – NIGERIA *(Oral)* 5155

RELIGIOUS AND SECULARIST VIEWS OF THE ENVIRONMENT: GOD, HUMANITY AND NATURE IN SOCIOLOGICAL PERSPECTIVE
M. Ali Kirman – TURKEY *(Oral)* 5165

RELIGIONS AND ENVIRONMENT: THE PRACTICE OF MORAL APPROACH TO NATURE IN TURKISH CULTURAL HISTORY
H. Ezber Bodur – TURKEY *(Oral)* 5179

A RAPIDLY RISING TREND: DESIGNING FOR ‘HEALTHY’ HEALTHCARE BUILDINGS
Aslı Sungur Ergenoglu, Ayfer Aytug – TURKEY *(Oral)* 5189

ASSESSMENT OF BEHAVIOUR AND ATTITUTES OF RURAL PEOPLE TOWARDS ENVIRONMENTAL ISSUES: A CASE OF TURKEY
Hasan Akca, Kemal Esengun,Metin Can – TURKEY *(Oral)* 5197

RANGELANDS OF BALOCHISTAN IN GLOBAL PERSPECTIVE OF CLIMATE CHANGE AND INTERNATIONAL INSTITUTIONS: SINCE 1990.
Jabeen Musarrat – PAKISTAN *(Oral)* 5209

AN INVESTIGATION ON OUTDOOR NOISE LEVELS IN THE TUZLA SHIPYARDS REGION IN ISTANBUL
Ömer Apaydin, M. Talha Gönüllü, Yaşar Avşar – TURKEY *(Oral)* 5225

DETERMINANTS OF AGRICULTURAL INTENSIFICATION IN SOUTHWEST NIGERIA
A. S. Oyekale – NIGERIA *(Oral)* 5233

DEVELOPMENT AND POVERTY
Emel Yıldız, Ebru Z. Boyacıoğlu – TURKEY *(Oral)* 5247

ALLEVIATION OF RISKS AND VULNERABILITY FACING ISOLATED COMMUNITIES THROUGH CONSERVATION AND MANAGEMENT OF BIO-DIVERSITY: THE LOWER KUISEB RIVER BASIN, NAMIBIA
Josephine Phillip Msangi – NAMIBIA *(Oral)* 5257

THE RELATIONSHIP BETWEEN ENVIRONMENTAL CONCERN AND SOCIO-ECONOMIC STRUCTURE
Beyza Üstün, Beyza Ağcıoğlu, Zafer Yenal, Nilsun İnce, Serap Yaman, Serkan Yılmaz, İdil Alkaya, Çağrı Gökdemir – TURKEY *(Oral)* 5269

IMPACT OF NATURAL FACTORS ON THE PSYCHO-SOCIAL RELATIONSHIPS
Myqereme Rusi, Hana Rusi – Saliu – MACEDONIA *(Oral)*... 5281

LIGHT POLLUTION
Martin Morgan Taylor – UK *(Oral)* 5291

THE IMPORTANCE OF PHYSICAL ENVIROMENT IN A CHILD GROWING
H. Derya Kol Arslan – TURKEY *(Oral)* 5301

THE ENVIRONMENTAL JUSTICE APPROACH AS BASIS FOR POLITICAL SOCIO-ENVIRONMENTAL CHANGE IN IMPLEMENTING SUSTAINABILITY STRATEGIC POLICY
Carmit Lubanov – ISRAEL *(Oral)*.. 5309

COMMUNICATION AND EDUCATIONAL APPROACHES AND STRATEGIES FOR FOREST MANAGEMENT: A NIGERIAN PERSPECTIVE
E.O. Soola – NIGERIA *(Oral)* 5317

ENVIRONMENTAL SECURITY: ECOLOGY OR INTERNATIONAL RELATIONS?
Mayor John Willimas, Obasohan Queen – NIGERIA *(Oral)* 5327

ELDERLY ROLES IN THE ENVIRONMENTAL DESIGN OF REST HOMES
Demet Aykal, Derya Cakir Aydın – TURKEY *(Oral)* 5343

RESTRICTIONS IN DAILY LIVING ACTIVITIES AND SOCIAL ISOLATION STATUS OF ELDERLY LIVING IN ANKARA PROVINCE GULSEREN DISTRICT
Derya Çamur, Songül Acar Vaizoğlu, Ramazan Akmeşe, Bahri Aydin, Aytan Hakan, Fikret Özgür, İlyas Tenlik, Çağatay Güler – TURKEY *(Oral)* 5357

ENVIRONMENTAL RISK PERCEPTION AMONG KEÇİÖREN MUNICIPALITY WORKERS
T. Gökhan Telatar, Dilek Dehmen, S. Gonca Deprem, Gülşah Eldoğan, Duygu Erdoğan, M. Nur Eroğlu, Bahar Güçiz Doğan – TURKEY *(Oral)* 5365

PHYSICAL FITNESS IN RURAL CHILDREN COMPARED WITH URBAN CHILDREN IN NORTH CYPRUS
Cevdet Tınazcı, Nazım Burgul, Tuğra İnceer – NORTHERN CYPRUS *(Oral)* 5371

PRINCIPLES OF ISLAM IN SOLVING ENVIRONMENTAL PROBLEMS
Davut Aydüz, Hüseyin Akyüzoğlu – TURKEY *(Oral)* 5381

IMPORTANCE OF TREE IN ISLAM
Davut Aydüz, Hüseyin Akyüzoğlu – TURKEY *(Oral)* 5391

THE BUBBLES OR THE BOILING POT?
AN ECOSYSTEMIC APPROACH TO CULTURE, ENVIRONMENT AND QUALITY OF LIFE
André Francisco Pilon – BRAZIL *(Oral)* 5399

INDIVIDUAL AND MIXED INFLUENCE OF HEAVY METALS (COPPER AND CADMIUM) AND DETERGENT (LAS) ON ALGAE SCENEDESMUS OBLIQUUS
M. Gholami, S.M.R Fatemi., M. Falahi, A. Esmaili, A. Machinchiyan– IRAN *(Oral)* 5421

MEASURING THE RESIDENTS' PERCEPTIONS TOWARDS COMMUNITY APPROACH TO TOURISM PLANNING: THE CASE OF FAMAGUSTA IN NORTH CYPRUS
Hale Özgit, Nesrin Menemenci, Aytaç Yıldırım – NORTHERN CYPRUS *(Oral)* 5429

THE IMPORTANCE OF ENVIRONMENTAL MASTER PLANS:
A SOCIOLOGICAL APPROACH
Suavi Tuncay, A.Bülent Göksel, Carol Yürür, H. Ece Salalı – TURKEY *(Oral)* 5453

PREDICTING URBAN GROWTH IN HOUSTON-GALVESTON-BRAZORIA CONSOLIDATED METROPOLITAN STATISTICAL AREA (HOUSTON CMSA)
Hakan Oguz – TURKEY *(Oral)* 5469

ESTABLISHING HEAVEN UPON EARTH: THE GREAT RESPONSIBILITY OF RELIGIOUS LEADERS AND MOVEMENTS
Maryam Salek Zamani, Ali Salek Zamani, Yaghoub Salek Zamani – AZARBAIJAN *(Poster)* 5495

PROCEEDINGS

Edited by Prof.Dr. Hüseyin Gökçekuş

Papers & Posters

VOLUME 7

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ALTERNATIVE PATH ON SEWERAGE SYSTEM; CONDOMINIAL METHOD AND ITS APPLICATION

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Simplified sewerage is an off-site sanitation technology that removes all wastewater from the household environment. Conceptually it is same as conventional sewerage, but conscious efforts made to eliminate unnecessarily conservative design features and to match design standards to the local situation. Most of the new technologies are developed and designed to deal with health and environmental concerns. Mainly, the third world countries usually face with wastewater collection and treating problems. The reason is generally linked with unplanned urban development. In this study, the fundamental of theory of simplified sewer design is discussed by the help of readily available computer program called; “Pc-based simplified sewer design”. The theory is used to analyze the effect of the sewer diameters and gradients for alternative solutions. It is proved that considerable savings in the length and diameter of pipes for water and sewerage and savings in the volume of soil excavation as a result of shallower trenches are maintained with the theory. The theories also speeds up the design calculation and design configurations approaching to a result at a short time interval.

1.INTRODUCTION

As research into the characteristics of wastewater has become more extensive, and as the potential health and environmental effects have become more comprehensive, the body of scientific knowledge has expanded significantly (Metcalf and Eddy, 2003). Wastewater collecting and treating problems usually arises when they are directed to near by rivers, or via the pits into the groundwater. The search for pilot solution is generally preferred due to the lack of financial help. The concerns on environmental issues finally motivate the experts to minimize the cost of wastewater network system. This is achieved by simplified sewerage which was achieved by researchers from Brazil and Pakistan (de Andrade Neto, 1985; Azevedo Netto, 1992 and Sinnatamby, et al., 1986). The reason is clearly due to the financial problems in their countries. As it is mentioned in Mara, (1999) it is now abundantly clear that simplified sewerage is generally the sanitation technology of first choice in high-density low-income urban and semi-urban areas. The advantage of the simplified sewerage sanitation technology is that a small diameter pipe at shallow depths reduces the cost over the conventional sewerage systems. It is also proved that the technology possesses high service levels and suitable for high density communities. However, even the cost is less than the conventional methods it still remains as a problem for low income communities. The comparison between the simplified and conventional method is given is the following figure;

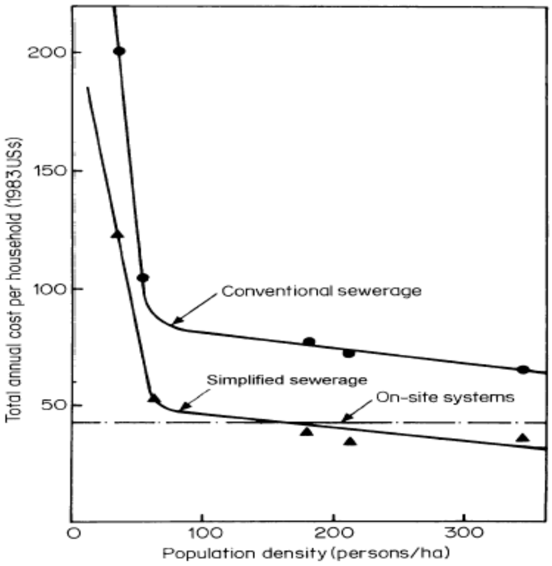

Figure 1 Costs of conventional and simplified sewerage, and on-site sanitation in Natal in northeast Brazil in 1983.

The simplified sewerage is an off-site sanitation technology that removes all wastewater from the household environment. Conceptually, it is the same as conventional sewerage, but with conscious efforts made to eliminate unnecessarily conservative design features and to match design standards to the local situation. In this study, the fundamental theory of simplified sewer design is discussed by the help of readily available computer program called, “Pc-based simplified sewer design”. It is used to analyze the effect of the sewer diameters and gradients for different cases, and finally, a case study is carried over to apply the simplified sewerage techniques for semi-urban Taskinkoy region.

2. HYDRAULIC DESIGN CHARACTERISTICS OF SIMPLIFIED SEWERAGE

It is necessary to estimate the daily peak flow capacity available in order to be able to design a suitable sewerage network system. This can be achieved by use of the following equation:

$$q = k_1 k_2 pw / 86400 \tag{1}$$

Where q is daily peak flow rate, l/s; k_1 and k_2 are peak factor and return factor respectively; p stands for the population served by length of sewer under consideration and w is the average water consumption, l/capita/day. 86400 is the number of seconds in a day. Peak factor is the ratio between the daily peak flow and average daily flow. A suitable design value for peak flow for simplified sewerage is 1.8. Return factor, however, is the ratio between rate of wastewater flow and water consumption. Usually the ratio is 0.85. The design equation is subject to a minimum value which is limited by 1.5 l/s. This minimum flow is not justifiable in theory but, as it is approximately equal to the peak flow resulting from flushing a WC, it gives sensible results in practice, and it is the value recommended in sewer design codes (ABNT, 1986; Sinnatamby et al, 1986).

The flow in simplified sewers is always following a hydraulic flow, resembling the open channel flow – that is to say, there is always some free space above the flow of wastewater in the sewer. The hydraulic design of simplified sewers requires knowledge of the area of flow and the hydraulic radius. Both these parameters vary with the depth of flow. The dimensionless ratio d/D is termed as proportional depth of flow. In simplified sewerage the usual limits for d/D are as follows:

$$0.2 < \frac{d}{D} < 0.8 \qquad (2)$$

The lower limit ensures that there is sufficient velocity of flow to prevent solids deposition in the initial part of the design period, and the upper limit provides for sufficient ventilation at the end of the design period.

2.1 The limitations and factors in design process

Simplified sewerage should only be considered where a reliable water supply is or can be made available on or near each plot so that total water use is at least 60 liters per person per day. If this basic criterion cannot be met, other options should be evaluated. Sewers, preceded by settlement tanks and carrying ‘settled’ wastewater might be considered when water use is lower, perhaps down to 30 liters per person per day. Settled sewerage (also called small-bore, or solids-free, sewerage) is described by Otis and Mara (1985) and Mara (1996).

Other factors to be considered are population density, the arrangements for effluent disposal and the preferences of the local people; for evaluating on-site sanitations options the plot size, the infiltration capacity of the soil and the potential for groundwater pollution should also be considered (Franceys *et al*., 1992; Cotton and Saywell, 1998; and GHK Research and Training, 2000). Simplified sewerage became cheaper than on-site systems at a population density of around 160 people per hectare. Simplified sewerage is more likely to be viable where an existing collector sewer with spare capacity is available reasonably close at hand. The existing sewer represents a sunk cost and the cost of simplified sewerage is therefore reduced.

In theory, the cost of sewered sanitation can be reduced by treating wastewater locally, thus removing the need for expensive trunk mains. In practice, lack of both land and the skills necessary to operate local treatment facilities may prevent the adoption of this option.

2.2 Description of input parameters

Return factor defines the percentage of total water consumption that will be discharged to the sewer. It is often assumed to be 80% or 85%, although there are indications that lower return factors may be appropriate in some areas. The wastewater flow from an area will be equal to the water consumption in the area multiplied by the return factor. Peak wastewater flow factor is required to allow for the fact that the wastewater flow varies through the day, reaching a peak when people get up in the morning and falling to almost nothing during the night. The peak *foul* flow in any sewer can be taken as the average flow in that sewer multiplied by the peak factor. Peak factors tend to decrease as the population contributing to the flow increases. However, even for a population of a few hundred, the peak factor is unlikely to exceed 2.

If somehow, the sewer system is laid below the groundwater table. Infiltration is commonly estimated on the basis that it is a set percentage of the average per-capita wastewater flow. A theoretically more accurate approach will be to assume an infiltration rate per unit length of sewer. The first method is simpler. Furthermore the accuracy of available information will normally be insufficient to justify the adoption of the second approach. However, laying sewers below the groundwater table should be avoided wherever possible. Sewers can be designed as separate, partially combined or combined. Separate sewers carry only wastewater; partially combined sewers are designed to carry some storm water in addition to wastewater, while combined sewers are designed to carry the full wastewater and stormwater flows. Combined sewerage has several disadvantages. In all but the driest climates, the size of sewer required to carry the full stormwater run-off is likely to be much larger than that required for the wastewater flow. Combined sewerage thus requires a high level of investment, which is not utilized except in wet weather. Combined sewers also have the disadvantage that stormwater run-off often carries a high concentration of grit and other suspended solids and this can lead to higher rates of silting. Sewers have therefore to be laid at greater gradients than would be required if they carried only wastewater. For these reasons, simplified sewer systems should not be designed as combined but also it would appear to be unrealistic to design simplified sewerage systems to be completely separate. Where surface water drainage is a major problem, greater attention to the alternatives will have to be paid at the design stage; for more detailed information on planning for stormwater drainage, reference should be made to Kolsky (1998).

Minimum cover distances over a sewer is also important; to provide protection against imposed loads, particularly vehicle loads; to allow an adequate fall on house connections, and; to reduce the possibility of cross-contamination of water mains by making sure that, wherever possible, sewers are located below water mains.

The minimum cover criteria adopted will depend on local factors, in particular on the pipe material used (Sinnatamby, 1986). It is also necessary to specify a minimum sewer diameter because sewers transport wastewater which contains gross solids. There is no theoretical reason, why the minimum sewer diameter should not be 100mm. However, statutory authorities tend to be conservative on this point: for example, the minimum acceptable sewer diameter in Cairo, Egypt, is 180 mm; while that in Pakistan is 230 mm. Conventional sewer calculations assume steady-state conditions.

3. SIMPLIFIED SEWER APPLICATION; TASKINKOY CASE

The case study about the simplify sewer method is applied to the Taskinkoy region, which is one of the most populated area of capital Lefkosa. Initially, the number of houses, the location of houses and streets are figured out by the help of maps, in 1/2500 scale. Those maps are digililized by the help of software Arcmap. Since the population at the region is not uniform, it is preferred to use the number of houses as the design criteria. This non uniformity is due to the fluctuations in student residence at the region. In Figure 2 detailed surface elevations which are given in 0.5m intervals are plotted. The number of houses available at the region is 180, and the total distance under the consideration is 1360 m.

All the necessary information taken from the Arcmap software is an input value for the program "PC-based simplified sewer design program" so that the analyses carried out efficiently. The length of sewer; number of houses and the ground levels of the junction points are all determined.

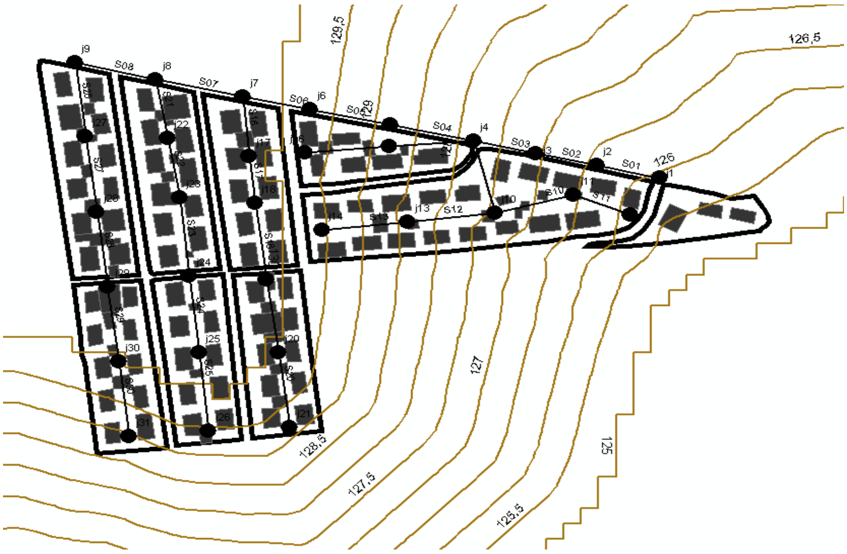

Figure 2 surface elevations which are given in 0.5m intervals.

The method of application is carried for two different network design named design I and design II. In one of these design studies (Fig 3), it is preferred to collect the network system at the center of the region and make sub connections through the backyards of the houses. By this way, it's tried to shorten the length of the individual connections to the main sewer. The approximate distances between each junction is around 30-50 meters.

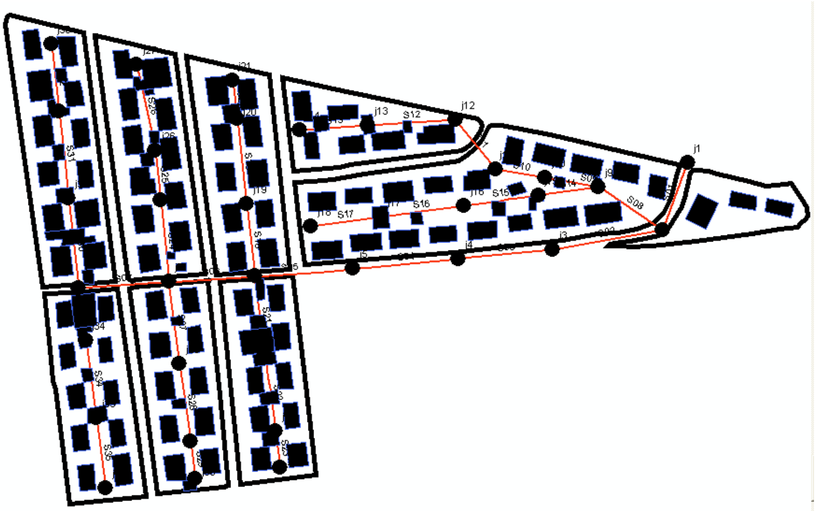

Figure 3 sewer network designs at Taskinkoy, titled, design I.

In Figure 4 the network system is arranged to discharge the out flows through the main road, which is at the Northern part of the region. However the disadvantage of this design system is that the backyard connection takes long distances. The data input for design I and design II is given as an order of junction names, lengths between each junction, the number of houses connected to the each junction interval, the ground level elevations of each junction.

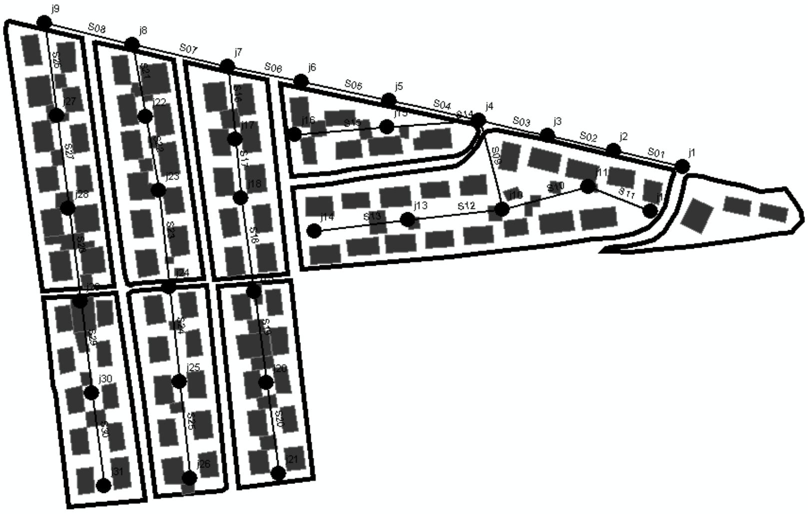

Figure 4 Alternative sewer network design at Taskinkoy, titled, design II.

4. DISCUSSION AND RESULTS

The software also needs some other input data in order to accurately facilitate the analysis. These information are, initial water use per capita; final water use per capita; initial mean number of people per house; final mean number of people per house; minimum self-cleaning velocity; G-Manning's n; minimum sewer cover; return factor; peak flow factor; minimum flow; minimum diameter. These values are attained as given as follows, in order to compare design I and design II. Initial water use per person: 50(liters/day); Final water use per person: 120 (liters/day); Initial mean number of people house: 5; Final mean number of people per house: 5; Minimum self-cleansing velocity: 0.50 (m/s); G-Manning's n: 0.0130 Minimum sewer cover: 0.40 (m); Return factor: 85 (%); Peak flow factor: 1.80; Minimum flow: 1.50 (liters/s); Minimum diameter: 100 (mm).

After the first trial it is observed that all the required restrictions are maintained. Especially the d/D ratio is checked and it is confirmed that d/D is between 0.2 and 0.8 for all the sewer connections. The same check is done for both designs I and designs II. Some other controls are carried for only design I. For example, minimum diameter restriction is released and checked whether the network system will work or not. After the application of the analyses the result show that even for smaller diameter pipes, the sewerage can easily carried in the network. However, the pipe diameters that are proposed by the program are not logic. The result shows that it is necessary to use the pipe diameter which is available at the market. This means that the minimum diameter of the network should be 100mm.

The next step is to check if the diameter of 150mm is suitable or not. On this purpose the minimum diameter of the pipes are set to 150mm. The model is run and the results are analyzed. According to the results it is observed that the first check which is the d/D ratio is not satisfied

The main discussion between the two sewer network designs, design I and design II, is to understand which one of them is economic. Since the total length of pipe line is approximately same, only difference between the two designs is the volume of excavation. Therefore the total volume of excavation in both designs are calculated where the trench width of the excavation is 0.8 meters. For design I, the total surface area to be excavated is measured to be 943.2 square meters whereas the total volume is estimated to be 754.6 cubic meters. For design II, the total surface area to be excavated is measured to be 1772.3 square meters whereas the total volume is estimated to be 1417.8 cubic meters. According to the results it is observed that the excavation volume of design I is less than design II by 87.89%.

This result mentions that shorter backyard network system will support the economic way of sewer design. The main reason of such result is because of the slope of the sewer network. Since the slope is nearly same for all the connections, the shorter distances will need less excavation, resulting in economic solutions.

It is also important to observe how the changes in variables affect the sewerage analysis. For such results, it is proposed to check the proportionality effect of the variables affecting the sewerage analysis. The analyses show that:

- Water consumption is inversely proportional with number of houses.
- The slope of the sewers is directly proportional with velocity of flow.
- The roughness of the pipes is inversely proportional with velocity of flow.
- The roughness of the pipes is inversely proportional with number of houses connected to the sewer.

First of all, it is studied to check the changes of water consumption with respect to number of houses connected to sewer. In Figure 5 the pipe diameter is 100mm where in Figure 6 it is 150mm. The result depicted that for the constant water consumption, any increment for the pipe diameter from 100mm to 150mm will increase the number of houses quadruple.

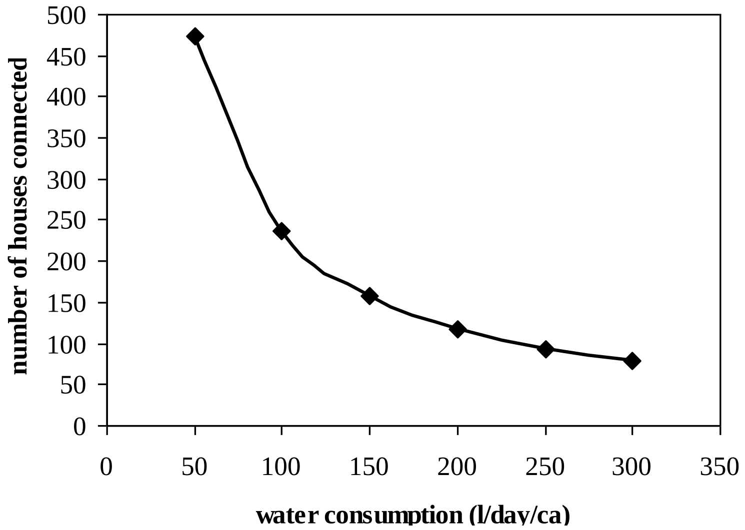

Figure 5 The change of number of houses connected to sewer with respect to water consumption, for a sewer diameter of 100mm.

The changes in slope and its effects on velocity of flow are studies under constant diameter of 100mm and constant roughness (Figure 7). It is observed that as the slope increase the change in velocity also increases. The changes in roughness coefficient and its effects on velocity of flow are studied under constant diameter of 100mm and constant slope (Figure 8). It is observed that as the roughness increase the change in velocity decrease.

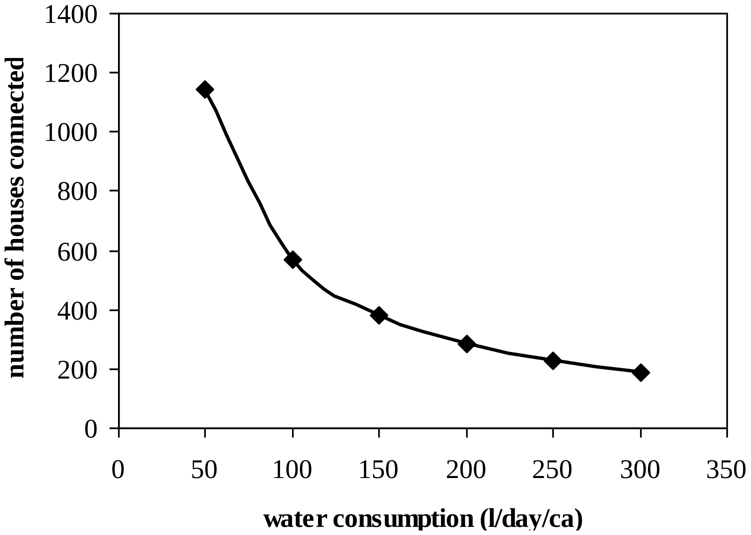

Figure 6 The change of number of houses connected to sewer with respect to water consumption, for a sewer diameter of 150mm.

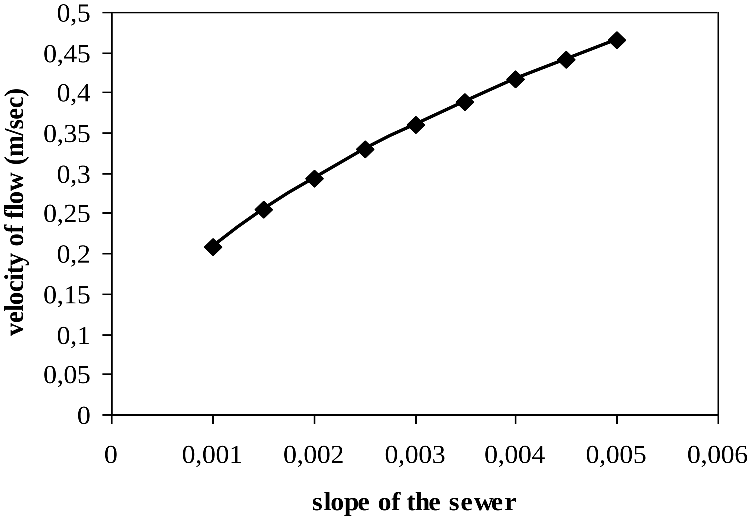

Figure 7 Roughness coefficient and the diameter are constant 100mm, change in velocity of flow when the slope is changing.

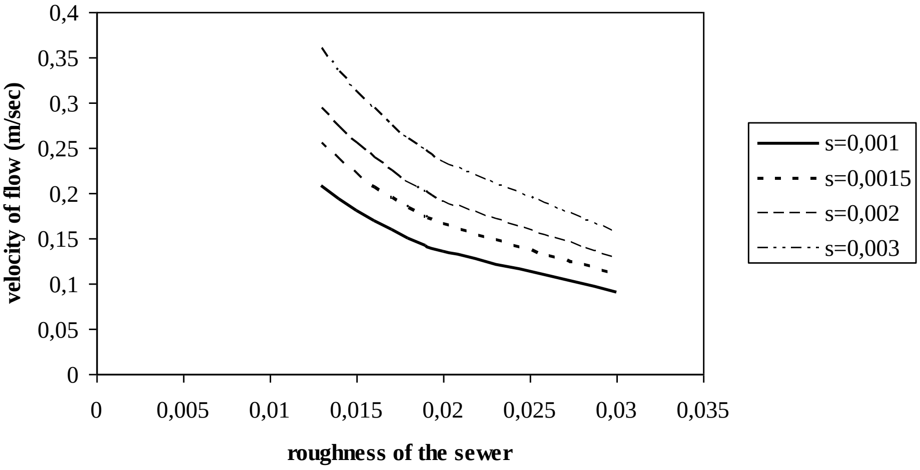

Figure 8 Slope and the diameter are constant 100mm, change in velocity of flow when the roughness is changing.

A feasible result for roughness versus number of houses is maintained when the roughness is in between 0.013 and 0.02 (Figure 9 and Figure 10). Even for different pipe diameters it is observed that if roughness shows any deficiency from the limit of 0.013 and 0.02, the number of houses changes defiantly.

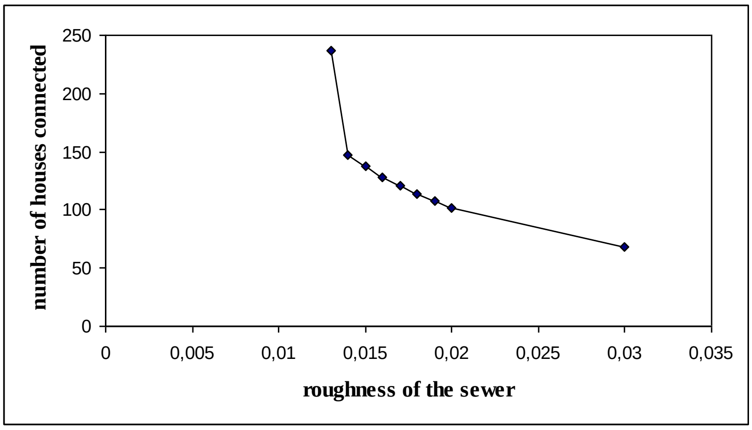

Figure 9 The change of number of houses connected to sewer with respect to roughness of the sewer, for a sewer diameter of 100mm.

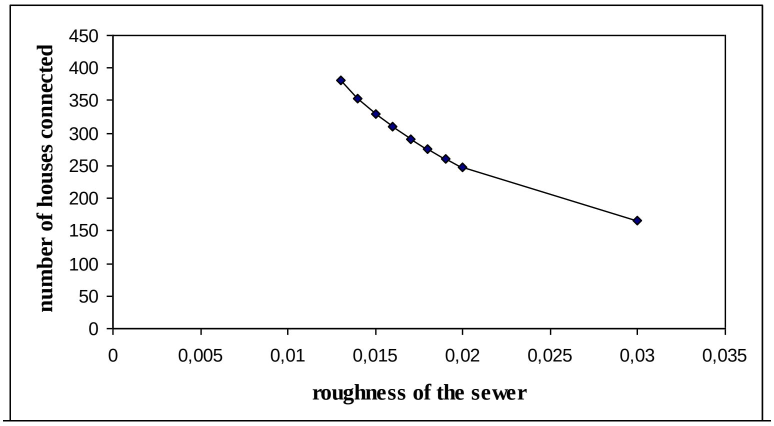

Figure 10 The change of number of houses connected to sewer with respect to roughness of the sewer, for a sewer diameter of 150mm.

5. CONCLUSION

The study has investigated the theory of the hydraulic design of simplified sewerage systems. In addition, the standards associated with the condominial designs and PC-based simplified sewer design program led to savings in the length and diameter of pipes for water and sewerage and savings in the volume of soil excavation as a result of shallower trenches. A simplified sewerage system is much more important because less pipeline is needed and the design requires a narrower diameter pipeline. Another advantage is that, pipes can be buried at shallower depths because there is no need to protect them from the weight of passing vehicles.

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SALINITY-ALKALINITY & POLLUTION PROBLEMS IN THE GEDIZ BASIN-TURKIYE

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Nearly 80 thousand ha. of the soils in Gediz basin show different kinds of salinity and alkalinity problems. Soils in the lower parts of the basin are of rendzina type with a clay dominated texture, $CaCO_3$ varying between 10-64 % and pH is 7.6-7.8, whereas in the upper parts soils are reddish-chestnut colored, calcareous in nature with a pH varying between 7.5-8.3, and boron content lies around 0.5 ppm. The number of industrial areas is increasing and industrial effluents entering the Gediz River lead to pollution of its waters. The values of lead, chromium and cadmium on seasonal basis are higher than allowed values. Water analysis shows that pH varies between 6.55 to 8.30 and EC between 46-3823 (µS/cm). The anthropogenic salinization due to over irrigation and pollution of waters vis-a-vis the water scarcity due to competition for water among various uses; mainly irrigation versus the domestic and fast growing industrial demand; are becoming a significant problem and posing a great threat equally for the soils and waters. An attempt has been made here to enlighten the situation in this context and suggestions put forth to overcome these problems.

Keywords: *Pollution, Salinity & Alkalinity, Gediz Basin.*

1.Introduction

An anthropogenic salinization is growing rapidly in the Gediz basin (Fig.1) and crop production under these conditions becomes less sustainable each year, mainly due to quality and quantity of irrigation water used, method of irrigation, climate and precipitation regime (Ayyıldız, 1983). The average annual surface water potential is 1.95 billion m^3 which is 1.1 % of the annual surface water potential (186.05 km^3) of Turkey. Water use in the basin is limited to a total of approximately 550 million m^3/year i.e.,some 450 mm of irrigation water for the growing season. Demirköprü Dam provides 650 million m^3 per year. Gediz basin with 18.000 km^2 drainage area out of a total area of 42.621 km^2 experiences droughts from time to time thus several large scale and over hundred small scale irrigation schemes are running in the basin (Geçgel et al., 2000). The major large scale irrigation associations and the area commanded by these are Sarıgöl (1,927 ha), Bağ (4,486 ha), Alaşehir Üzüm (6,930 ha), Salihli Right Bank (9,101 ha), Salihli Left Bank (9,237 ha), Ahmetli (3,275 ha), Gökkaya (997 ha), Turgutlu (12,102 ha), Sarıkız (13,702 ha), Mesir (13,679 ha), Gediz (10,962 ha), Menemen Right Bank (6,365 ha), and Menemen Left Bank (16,500 ha).The total area commanded by these associations lies around 109,263 ha.These mainly include vineyards and cotton cultivation areas. The basin includes 2.3 % (1.722.000 ha) of the total area of Turkey, 1/3 of which comprises soil classes I-IV (Tuncay,1986;Alpaslan and Atış,1995).

The wrong use of cultivated lands, wrong irrigation practices are leading to erosion, high levels of bases and cemented layers in the soils of the basin (Altınbaş et al., 1994; Taysun and Uysal, 1995; Öztürk et al. 1994). The industrial establishments are polluting Gediz river waters which ultimately reach İzmir Bay (Gündoğdu et al.,2007). As such, in this investigation an attempt has been made to evaluate the salinity-alkalinity problems, boron content and pollution due to heavy metals in the basin.

2.Material and Methods

This study was undertaken during the years 1998-2002.The representative soil samples (0-50 cm depth) were collected from different sites at the enterance and exit locations of the cities and industrial centres. The physico-chemical parameters were determined following the methods given by Soil Survey Staff (1951), Richards (1954) and Tüzüner (1990). The water samples from 10 sites (3 samples from each site) alongside the Gediz river were collected during May and June. These sites too were selected at the enterance and exit locations of the cities and industrial centres. The temperature was measured by thermometer, pH by pH meter, and electrical conductivity by conductivity bridge (APHA,1992). Pb, Cr and Cd in the waters of the river were determined on seasonal basis from 5 sites using the methods outlined in detail in Aksoy and Öztürk (1997).

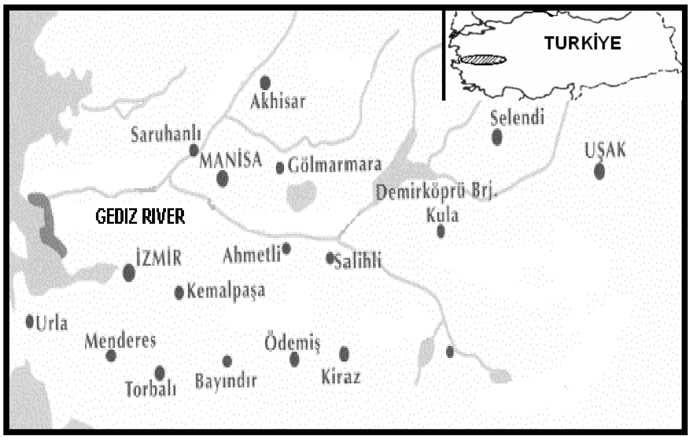

Figure 1. Location of the study area (Gediz basin) in Turkiye.

3.Results and Discussion

3.1. Salinity and Alkalinity Problems

Biological degradation is the reduction in the quantity of organic matter and living organisms in particular plant cover decomposition, whereas chemical degradation includes salinity, alkalinity, or acidity. A high concentration of salts in the soil gives rise to saline or alkaline soils. This is often the result of irrigation without adequate drainage (Armitage, 1985). About 900 million ha. of land are presently affected by excessive salts in the world (Zonn and Orlovsky 1986). The accumulation of the soluble salts of Na ions (salinization) produces soil degradation over the entire profile, resulting in such harmful effects as: changes in compactness, porosity and permeability, organic matter content, soil pH, plant cover characteristics, soil-plant-water balance.The man-made share of these salinity problems arises principally from rasing of the water table through continuous passage of large amounts of H_2O through unsuitable canals, thus converting large productive areas from a renewable resource to a non-renewable one. According to recent estimates, over 220 mill. ha. of land are irrigated worldwide. Approximately 25 to 40% of that land is affected by salinization (Yensen, 1988).

Our survey studies and reports published by Tuncay (1986) and Eroglu (1994) reveal that in the productive valley of Manisa,Turgutlu and Salihli alone, nearly 40 thousand ha of soils show salinity-alkalinity problems due to bad drainage out of a total area of about 80 thousand hactares. The rendzina, brown forest, chestnut coloured soils are commonly found on calcareous neojen areas, whereas red mediterranean soils occupy calcareous rocks and marble. The andesite, gneiss and dasit are found on the basalt, and brown soils on non-calcareous parent material. The noncalcareous brown forest soils cover quartz and regosol occurs on crystalline schists.The soils towards the coastal part of Gediz basin are of rendzina type with a clayey-loam or clayey texture, $CaCO_3$ varying between 10-64 %, pH 7.6-7.8, organic matter 0.05-1.5%. In the upper parts of the basin soils are mainly reddish-chestnut coloured, calcareous in nature showing sandy-clayey-loam or clayey-loam texture, with 1-45 % $CaCO_3$, pH 7.5 (neutral)- 8.3 (strongly alkaline), organic matter between 0.35-1.00 %, boron 0.50 ppm, boron content lies around 0.5 ppm, SAR between 5-15%, Cl 1. 25 meq/l, SO_4 2.05 meq/l and Na 1.20 meq/l. The problematic soils (saline-alkaline, arid, stony) cover 900.000 ha out of which the area of saline-alkaline soils in different States is around 350.000 ha (Fig. 2). Approximately 80.000 ha embody the plains out of which slightly saline-alkaline, weakly saline, saline and saline-alkaline soils cover nearly 8, 20, 21 and 31 thousand ha respectively.

3.2. Water Pollution

The basic character of pollution is its cumulative nature and it knows no boundries.It is a well known fact that sewage systems in Gediz basin are resulting in nitrate pollution in the Gediz river (Ökmen, 2005). The urban dwellers from İzmir (40 km), Manisa (204 km), Kütahya (50 km) and Uşak (92 km) pollute the Gediz river jointly. The maximum impact is visible around Uşak due to the textile and lerather industries. The polluted waters coming from here reach demir kopru dam resulting in pollution of its waters. Although not fully confirmed there are some reports of cancer incidence from the area. The river on its way to the Izmir bay is said to bring a mean annual load of 1983 kg of nickle, 790 gm of zinc, 148 kg of mercury and 55 grams of cadmium.The boron content of the waters is very high and the river is suffering from heavy metal pollution due to different types of effluents (Ökmen, 2005).

Studies on the heavy metal pollution have been undertaken by Altinbaş et al. (1994), Bakaç and Kumru (2001) and Kayar and Çelik (2003). In our studies the water analysis showed that pH varies between 6.55 (neutral) to 8.30 (strongly alkaline) and EC between 46 - 3823 (µS/cm). In general most of the water samples belong to the third quality saline waters, some are of second quality with a medium degree of salinity and a few can be included in the fourth and fifth quality waters with a high degree of salinity (Fig. 3). During the present investigation we found that highest Pb concentration (600 µg/l) was recorded in Manisa and lowest (75 µg/l) around delta zone, whereas Cr was highest (70 µg/l) in Menemen area and lowest (13 µg/l) in Salihli, Cd highest (70 µg/l) in Menemen and lowest (2 µg/l) in the delta zone. The values of Pb, Cr and Cd were highest in winter, spring and summer respectively (Fig. 4). The allowed concentrations of these elements are 20 (Pb), 50 (Cr) and 5 (Cd) µg / l. Our values indicate that the waters of Gediz river are suffering from a pollution of heavy metals. An analysis of the representative soil samples from the lower, central and upper parts of the basin revealed that the values lie around 2.0, 40.0 and 20.0 ppm (Pb), 250, 900 and 500 ppm (Cr) and 1.0, 2.0 and 1.5 ppm (Cd) respectively. The allowed concentrations being 100, 3 and 100 ppm respectively of Pb, Cd and Cr, confirming the fact that the basin is suffering from heavy metal pollution. These findings are in conformity with those of Altınbaş et al. (1994) as well as Bakaç and Kumru (2001). The reason is industrial effluents.

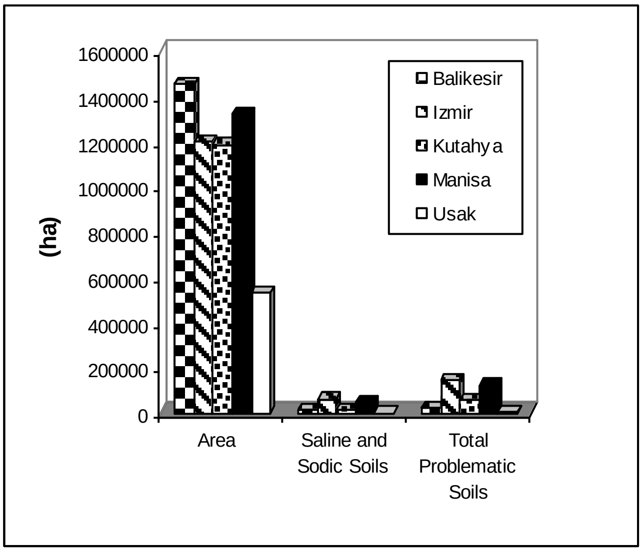

Fig. 2. Area of soils facing salinity-alkalinity problems in the Gediz Basin.

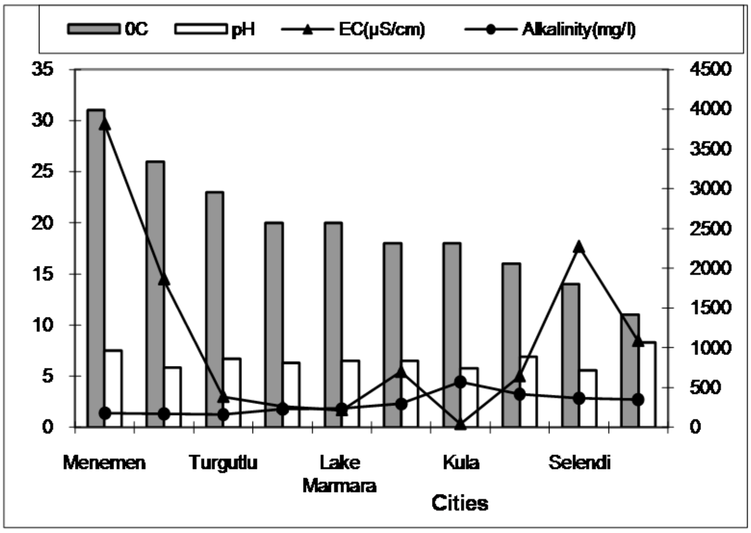

Fig.3. Average values of some physical parameters of water samples from Gediz basin.

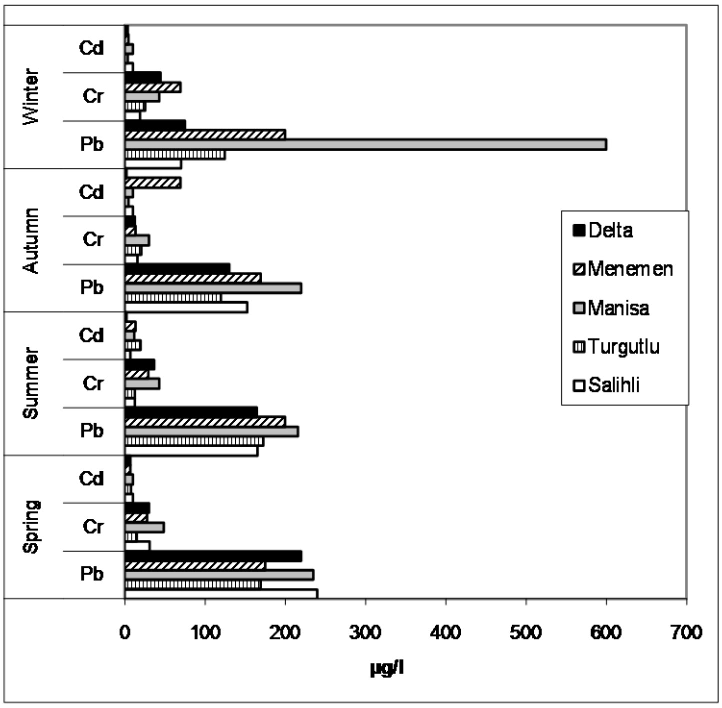

Fig. 4. Seasonal distribution of some heavy metals in the waters of Gediz river

4.Conclusion

The basin experiences droughts and floods from time to time which predispose the land to risks of salinisation, alkalisation and accelerated rates of soil erosion. Overuse of Gediz river has resulted in the rise of water table, water-logging, salinization over a large area in the basin and eco-disaster of the wetlands around the deltaic zone. Poor natural draining capacity, flooding, low efficiency of drainage system promotes the rise of the level of mineral composition of water and secondary salting of soil. Secondary salinization (human caused) is growing rapidly and crop production under these conditions becomes less sustainable each year. Drought and salinity can have a far greater effect on food security in this area. Not only the quantity, but the source of water has been changing. For example,until 1980 deep wells were almost unknown in the basin.

In the Gediz River Basin the demands on the functions of the water resources system vis-a-vis their uses are increasing at an alarming rate due to demographic outburst, industrialisation and fast economic growth. Conflicts are likely to arise regarding allocation on an equal basis. One of the reasons is bad water management due to strong interaction between the basin and the neighbouring states. The latter are consuming a large part of the groundwater resources of the basin without feeding it back. Not only the quantity, but the source of water has been changing, e.g., deep wells almost unknown until 1980 are now very common in the area. A total area of 110.000 ha is used mainly for the production of grapes, tobacco and cotton (Eroğlu, 1994). However, water scarcity is becoming a significant problem basically due to competition for water among various uses, mainly irrigation versus the domestic and fast growing industrial demand. This trend is offset by salinization problems today. Two major reasons for this are quality of irrigation waters. The basin experiences droughts and floods from time to time which predispose the land to risks of salinization, alkalisation, erosion and these will have a far greater effect on the agricultural productivity in this area. In the areas showing high salinity-alkalinity values in the upper layers 8 tons per da of gypsum should be applied for reclamation purposes as proposed by Eroğlu (1994) too. A cheaper technology could be, use of salinity tolerant plant taxa like *Salicornia europaea, Arthrocnemum fruticosum*, *Halocnemum strobilaceum* and *Halimione portulacoides* which can be used as fodder plants as well (Güvensen et al., 2006). The number of industrial areas in the basin is also increasing. The values of Pb, Cr and Cd on seasonal basis were observed to be higher than allowed values. This is originating from industrial effluents entering the Gediz river. There is an urgent need for establishment of treatment plants for these industrial effluents. The plant renovation systems could be used to bring down the costs in the villages around the basin (Öztürk et al., 2006). There is an immediate and great need for a sustainable water resources management programme. This can be done by improving water use efficiency in agriculture and industry. An encouragement towards the reuse of wastewater will prove highly beneficial.

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AMBIENT AIR PARTICULATE DRY DEPOSITION POLLUTANTS (METALLIC ELEMENTS, IONIC SPECIES) STUDY IN TAIWAN

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In recent years, since the great efforts made by Taiwan government towards the reduction of O_3 and PM_{10} concentrations by controlling the emission rates of local pollutants sources, the frequency of exceeded PSI has gradually decreased to the value of 4.9% in 1999 (Taiwan EPA, 2000).Urban populations are exposed to metals in suspended particles and these are often well above natural background levels owing to anthropogenic processes. The purpose of this study summarized the atmospheric mass, metallic elements and ionic species monitoring in Taiwan. The average downward dry deposition fluxes (averaged 26.22μg/m^2 s) were also about two times as that of upward dry deposition fluxes (averaged 12.11μg/m^2 s) in the nighttime period in central Taiwan. The study showed that the average dry deposition velocity for mass, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, and Ca^{2+} were 9, 3.8, 0.3, 0.25, 0.46, 0.18, 0.51 and 2.28 (cm sec^{-1}) in central Taiwan, respectively. The results also indicated that the average ratios of fine to coarse particulates were 2.66 during the sampling periods at Taichung Harbor sampling site. Compared with the previous study, the average ratios of fine to coarse particulates were 2.04 and 2.24 at suburban and farm sampling sites near central Taiwan, respectively. Furthermore, three major soluble inorganic species concentrations (sulfate + nitrate + ammonium) accounted for 60% ~ 80% out of $PM_{2.5}$ and $PM_{2.5-10}$ mass concentrations at any sampling sites in central Taiwan. In addition, the ionic species $SO_4{}^{2-}$ is more associated with ambient gaseous SO_2, the higher levels of SO_4^{2-} are likely due to increased coal (Taichung Thermal Power Plant) consumption during the sampling time. The results indicated that the concentration of ionic species SO_4^{2-} increased as the averaged TSP concentration increased at any sampling sites near central Taiwan. Besides, high PM_{10} concentration of metallic elements Pb, Cu, Mn, Cr and Ni concentrations obtained in PM_{10} was higher than any other Asia countries.

1. Water-soluble species of dry deposition at Taichung Harbor

The characterization for water-soluble species of dry deposition flux, total suspended particulate (TSP), fine particle (particle matter with aerodynamical diameter < 2.5 μm, $PM_{2.5}$), coarse particle (particle matter with aerodynamical diameter 2.5-10 μm, $PM_{2.5-10}$), and dry deposition velocity were studied at Taichung Harbor sampling sites of central Taiwan during February–August of 2004. The average downward dry deposition flux, TSP, PM10 concentrations obtained in Taichung harbor were about 0.51, 0.3, and 3.4 times as those values obtained by traffic sampling site in central Taiwan. And average dry deposition velocity for mass, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, and Ca^{2+} were 9, 3.8, 0.3, 0.25, 0.46, 0.18, 0.51 and 2.28(cm sec^{-1}), respectively at harbor sampling site. In general, average particle mass dry deposition velocity about 1.8 times as those values obtained by traffic sampling site. Chemical analysis, also indicated that three major soluble inorganic species concentrations (sulfate + nitrate + ammonium) accounted for 59.8% and 80.6% of the $PM_{2.5}$ and $PM_{2.5-10}$ mass concentrations, respectively at Taichung harbor sampling site.

The average ratios of fine to coarse particulates are listed in Table 1-1. The average ratios of fine and coarse particulates were 2.66 during the sampling periods. Compared with the previous study, the average ratios of fine to coarse particulates were 2.04 and 2.24 at suburban and farm sampling sites, respectively (Fang et al., 2000; 2003). The average ratios of fine to coarse particulates obtained in this study were slightly higher compared with the above studies. In addition, Taichung harbor sampling site is located in the region with high wind speed. Thus, soil re-suspended in ambient air may explain the high concentrations of $PM_{2.5}$ and PM10 at the Taichung harbor sampling site.

Table 1-2 summarizes the average and standard deviation of the ionic species concentrations for downward dry deposition flux and TSP concentration at Taichung harbor sampling site. The average downward dry deposition flux for Cl^-, NO_3^-, SO_4^2,Na^+ ,NH_4^+, Mg^{2+}, and Ca^{2+} were 5.25±1.54, 4.15±2.54, 5.73±3.28, 1.93±0.67, 1.64±0.82, 2.36±1.21,and 14.65±7.25 (□g m^{-2} sec^{-1}), and the average TSP concentration for Cl^-, NO_3^-, SO_4^2, Na^+, NH_4^+, Mg^{2+}, and Ca^{2+} were 1.38±0.45, 8.67±3.25, 26.32±12.73, 4.23±1.88, 10.67±4.52, 4.75±2.08,and 6.54±3.73 (□ g m^{-3}), respectively at the harbor sampling site.

$NH_4{}^+$, $NO_3{}^-$ and $SO_4{}^{2-}$ showed higher harbor sampling site concentrations in spring (February-May), and lower in summer (June-August). The results indicated that the $SO_4{}^{2-}$ is more associated with ambient gaseous SO_2, the higher levels of SO_4^{2-} in spring are likely due to increased coal (Taichung Thermal Power Plant) consumption during the sampling time. The same seasonal variation of NO_3^- was also observed in Qingdao (China), which was attributed to gas-to-particle conversion depending on the ambient temperature (Huet al., 2002). One possible cause for this phenomenon is that ammonium nitrate volatilized at higher air temperature and thus made the shift in the ratios. The phenomena have also been reported by other researchers (e.g. Huet al., 2002). Our research presented here also indicated that the NH_4^+ has the lowest concentration among four seasons. The possible reason this result is because of the high pH values 8.4 obtained in TSP around this sampling region. This result was consistent with the result obtained by Xiao and Lin (2004). The lower values of $NH_4{}^+$ in summer might be closely associated with the higher pH values of TSP (Xiao and Liu, 2004). In addition, Ca^{2+} and Mg^{2+} did not show the same seasonal variations as those of $NH_4{}^+$, NO_3^- and $SO_4{}^{2-}$, indicating that they are of same emissions sources. Statistical analysis each season of average TSP concentration for the Mg^{2+} at the harbor sampling sites yielded a T statistic of 1.18, which is greater than $t_{\alpha/2,15}=2.151$, suggesting that the sample population means are equal. By the same token, statistical analysis each season of average TSP concentration for the Ca^{2+} at the harbor sampling sites also yielded a T statistic of 0.03, which is greater than $t_{\alpha/2,15}= 2.151$, suggesting that the sample population means are equal. Because Ca^{2+} and Mg^{2+} are the typical crustal elements, the largest contributor might be the air-slake of the earth's surface, which is mainly dependent on air temperature and rainfalls around this region.

Fig. 1-2 shows the average downward dry deposition velocity of mass, anions (Cl^-, NO_3^-, and SO_4^{2-}), and cations (Na^+, NH_4^+, Mg^{2+}, and Ca^{2+}) at the Taichung harbor and traffic site. Among the ions studied, the average downward dry deposition velocity for Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, and Ca^{2+} were 3.8, 0.3, 0.25, 0.46, 0.18, 0.51 and 2.28(cm sec^{-1}), respectively at the harbor sampling site. However, Wu et al. (2004) indicated average downward dry deposition velocity for Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, and Ca^{2+} were 4.13, 1.46, 0.12, 0.36, 0.18, 0.45 and 2.09(cm sec^{-1}), respectively at the traffic sampling site. The average downward dry deposition velocity for mass obtained in Taichung harbor were about 1.8 times those values obtained of the traffic sampling site. Among the ions, the deposition velocity of these three major soluble inorganic species (sulfate, nitrate, and ammonium) obtained in Taichung harbor were about 2.08, 0.21, and 1 times those values obtained at traffic sampling site. The average downward dry deposition velocity of both sea salt particle components (sodium and chloride) and soil particle contents (sodium and chloride) obtained in Taichung harbor were about 0.92 and 1.23 times as those values obtained at traffic sampling site.

2. Seasonal DDF and TSP of particulate soluble ions

The characterization for water-soluble species of total suspended particulate (TSP), dry deposition flux, and dry deposition velocity (V_d) were studied at Taichung Harbor (TH) and Wuchi traffic sampling sites at offshore sampling site near Taiwan Strait of central Taiwan during March 2004 to January 2005. The average concentrations of TSP and dry deposition flux at the TH sampling site were higher than at the WT sampling site during the sampling period. The samples collected were analyzed by a Ion Chromatography (DIONEX-100) for the ionic species (Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Na^+, Ca^{2+}, and Mg^{2+}) analysis. The dominant ionic species for TSP are SO_4^{2-}, NO_3^-, and NH_4^+ of the total mass of the inorganic ions at both sampling sites. In addition, the results indicated that the NH_4^+, NO_3^- and SO_4^{2-} showed higher concentrations in winter and lower in summer for both TH and Wuchi sampling sites. Statistical methods such as correlation coefficient and principal component analysis were also used to identify the possible pollutant source.

The seasonal variation for water-soluble ionic components in the dry deposition flux (DDF) was showed in Fig. 2-1. There is a clear seasonal pattern within March 2004 to January 2005 (spring (March– May), summer (June–August), autumn (September–November) and winter (December–January)) for both two sampling sites. It was observed that deposition fluxes at two sampling sites were maximum in winter followed by spring, autumn and summer for all soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Mg^{2+}, Ca^{2+} ,and Na^+), except for NH_4^+. The summer/winter flux ratios for Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Mg^{2+}, Ca^{2+} ,and Na^+ were 0.8, 0.3, 0.7, 1.3, 0.8, 0.8, and 0.6, respectively at TH. In addition, the summer/winter flux ratios for Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Mg^{2+}, Ca^{2+} ,and Na^+ were 0.7, 0.8, 0.8, 1.4, 0.9, 0.7, and 0.5, respectively, at Wuchi. In general, the particulate NH_4^+, mainly from neutralizing NH_3 with H_2SO_4 or HNO_3, was distributed in the fine mode and was not a predominant species in dry deposition pollutants. Though the flux of NH_4^+ was higher in summer than in winter, the absolute differences in NH_4^+deposition fluxes among four seasons were indistinct as compared with the other soluble ions in this study. Seasonal variation in TSP concentration for major soluble ions at TH and Wuchi was showed in Fig. 2-2. There is a clear seasonal pattern within March 2004 to January 2005 at TH and Wuchi. The results indicated that the NH_4^+, NO_3^- and SO_4^{2-} showed higher concentrations in winter, and lower in summer for both TH and Wuchi sampling sites.

Deposition velocity is used as a measure of mass transfer into the canopy (Hosker and Lindberg, 1982) and is calculated by dividing the deposition flux of major ions by their respective atmospheric concentrations. The deposition velocities of seasonal variation for Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Mg^{2+}, Ca^{2+} and Na^+ were displayed at TH and Wuchi sampling sites during March 2004 to January 2005 (Fig. 2-3. A (anions) and B (cations)). The annual average Vd of Cl^-, NO_3^-, and SO_4^{2-} were 1.8 ± 0.3, 0.2 ± 0.1, and 0.2 ± 0.0 cm sec^{-1} at TH and 1.7 ± 0.4, 0.3 ± 0.2, and 0.2 ± 0.1 cm sec^{-1} at Wuchi. In addition, the annual average Vd of NH_4^+, Na^+,Ca^{2+}, and Mg^{2+} were 0.1 ± 0.0, 1.8 ± 0.5, 2.5 ± 0.6 and 1.1 ± 0.3 cm sec^{-1} at TH and 0.2 ± 0.1, 1.7 ± 0.5, 2.1 ± 0.4 and 1.0 ± 0.3 cm sec^{-1} at Wuchi.

3. Review of atmospheric Metallic Elements

Metallic element transfer through the atmosphere is a significant part of the biogeochemical cycle of these elements. Natural and anthropogenic were two processes which can increase heavy metal concentrations in the atmosphere. Atmospheric particulates, especially secondary anthropogenic fine particles ($PM_{2.5}$), have been influence human health. Generally speaking, the total daily mortality increases by approximately 1% for every 10 μgm^{-3} increase in PM_{10} concentration (Lippmann, 1998). This is why the PM_{10} and $PM_{2.5}$ measurements are included in the US ambient air quality standards (US-EPA, 1987 for PM10; 1996 for PM2.5) (Querol et al., 2001).

In recent years, since the great efforts made by Taiwan government towards the reduction of O_3 and PM_{10} concentrations by controlling the emission rates of local pollutants sources, the frequency of exceeded PSI has gradually decreased to the value of 4.9% in 1999 (Taiwan EPA, 2000).

Urban populations are exposed to metals in suspended particles and these are often well above natural background levels owing to anthropogenic processes (Espinosa et al., 2002). This results in elevated metal concentrations that can pose an important risk to human health

Understanding emissions from traffic includes identification of the sources, which is also crucial for designing control measures. Road traffic involves numerous potential sources of metals, combustion products from fuel and oil, wear products from tires, brake linings, bearings, coach and road construction materials, and re-suspension of soil and road dust.

The different sample collection devices, pretreatment and analysis methods were discussed in this study. The purpose of this study arranges the atmospheric metallic elements investigations in Asia regions. The data obtained here can also help to understand the sources, concentration, phase distribution and health impact of atmospheric metallic elements in Asia countries.

Ambient suspended particulate ($PM_{2.5}$, $PM_{2.5–10}$, TSP) was collected from June 1998 to February 2001 in Taichung, central Taiwan. In addition, the related metallic species (Fe, Zn, Pb, Ni) were analyzed in this study. The results showed that the concentrations of particulate mass are higher in the traffic site (CCRT) than the other sampling sites in this study. The results of diurnal variation at THUC sampling site are also discussed in this study. Therefore, ambient suspended particulate monitoring in Taichung, central Taiwan will be continuing in our following study to provide more information for the government to formulate environmental strategy. (Fang et al., 2002)

Table 3-1 indicated bulk metal element samples of suspended particulates and metallic elements collected in different areas around Asia. Ambient suspended particulate concentrations were measured at Tzu Yun Yen temple in this study. This is representative of incense burning and semi-open sampling sites. The Universal-sampler collected fine and coarse particle material was used to measure suspended particulate concentrations, and sampling periods were from 16/08/2001 to 2/1/2002 at Tzu Yun Yen temple. In addition, metallic element concentrations, compositions of $PM_{2.5}$ and $PM_{2.5–10}$ for incense burning at Tzu Yun Yen temple were also analyzed in this study. The $PM_{2.5}/PM_{10}$ ratios ranged between 31% and 87% and averaged 70±11% during incense the burning period, respectively. Fine particulates ($PM_{2.5}$) are the main portion of PM_{10} at Tzu Yun Yen temple in this study. From the point of view of PM_{10}, these data reflect that the elements Fe, Zn, and Cr were the major elements distributed at Tzu Yun Yen temple in this study. (Fang et al., 2003)

Downward, upward dry deposition fluxes and total suspended particulate of particulate heavy metals (Fe, Pb, Zn, Cu, Mg and Mn) were measured in daytime and nighttime period in Sha-Lu, a small city in the central Taiwan during summer period of 2003. The results showed that the total suspended particulate concentrations of particulate mass in the daytime period (averaged 996.2μg/m3) were higher than in nighttime period (averaged 560.7μg/m3). Furthermore, the average downward dry deposition fluxes (averaged 26.22μg/m2 s) were also about two times as that of upward dry deposition fluxes (averaged 12.11μg/m2 s) in the nighttime period. In addition, the average downward dry deposition fluxes are greater than the upward dry deposition fluxes for all the heavy metals in either daytime or nighttime period. The proposed reasons are that the wind speed and concentration difference for daytime and nighttime period lead to these results at the traffic sampling site of central Taiwan. (Fang et al., 2004)

The concentrations of atmospheric PM_{10} on days with episodes of pollution were examined at four different sampling sites (CC, DL, LY, and HK) in southern Taiwan. These different sampling sites CC, DL, LY and HK were typical of inland urban, inland industrial, coastal industrial and coastal urban, respectively. The variations in PM_{10} concentrations at LY and HK exceeded those at CC and DL, perhaps because both LY and HK are close to the seashore and are influenced by wind over the sea or land. The results of this paper are preliminary, pending more extensive research, because data obtained herein are limited. (Chen et al., 2003)

Table 3-1 indicated bulk metal element samples of suspended particulates and metallic elements collected in different areas around Asia. In general, Fe is the most abundant element in various studies. The highest TSP concentrations of Fe (ranged from 165,500-265,500 ngm^{-3}, Kumar et al., 2001) were found at Mumbai and Gandhinagar traffic junction sampling sites, which were about 100 times the concentrations found by Taichung, Taiwan (Fang et al., 2004). Concentrations of element Fe (averaged 1,421ngm^{-3}, Lau et al., 2001) found at Hong-Kong sampling site in China were similar to this result. Average TSP concentrations of element Fe at urban sampling site was 2904 ngm^{-3} (Hien et al., 2001), which was about 4.3~4.6 times as that of Sapporo and Tokyo, Japan (Var et al., 2000). As for fine particulate ($PM_{2.5}$) and coarse particulate ($PM_{2.5-10}$) concentration, the lowest average Fe concentrations were founded by Bukit Tinggi, Indonesia (2.6 ngm^{-3} and 14.8 ngm^{-3}, Maenhaut et al., 2002) at the tropical jungle sampling site. The element Fe concentration in fine particulate ($PM_{2.5}$) obtained in Taichung, Taiwan study (Fang et al., 2002) were about 120 times as the Fe concentration obtained in Indonesia (Maenhaut et al., 2002) at rural sampling site. In urban sampling site, the element Fe concentration in fine particulate ($PM_{2.5}$) were 190 ngm^{-3}, 743 ngm^{-3}, 900 ngm^{-3} and 1222 ngm^{-3} (PM_2) as that of China (Ho et al., 2003), Korea (Kim et al., 2003), China (Ye et al., 2003) and Vietnam (Hien et al., 2001), respectively. The element Fe concentration in coarse particulate ($PM_{2.5-10}$) obtained in Taichung, Taiwan study (Fang et al., 2002) were about 28 times as the Fe concentration obtained in Indonesia(Maenhaut et al., 2002). The highest $PM_{2.5-10}$ concentration (averaged 1,615ngm^{-3}) of Fe was found at Korea (Kim et al., 2003).

The averaged TSP concentration of element Zn obtained in traffic junction from Taichung, Taiwan (Fang et al., 2004) was averaged 1060 ngm^{-3}, which is higher than any other different areas around Asia. The metallic element concentrations of Zn obtained in urban sampling site were Vietnam (203ngm^{-3}, Hien et al., 2001) and Tokyo, Japan (299ngm^{-3}, Var et al., 2000). The highest PM_2 and PM_{2-10} concentrations in urban region were Ho Chi Minh, Vietnam (326ngm^{-3} and 245ngm^{-3}, Hien et al., 2001). The average Zn concentration of fine and coarse particulate was about 0.71 ngm^{-3} and 0.83 ngm^{-3} (Maenhaut et al., 2002), which was the lowest concentration among the Asia countries. The element Zn concentration in fine particulate ($PM_{2.5}$) obtained in Taichung, Taiwan study (Fang et al., 2002) was about 28 times as the Zn concentration obtained in Indonesia(Maenhaut et al., 2002). The element Zn concentration in coarse particulate ($PM_{2.5-10}$) obtained in Taichung, Taiwan study (Fang et al., 2002) were about 5.6, 0.13 and 0.1 times as the Zn concentration obtained in Indonesia (Maenhaut et al., 2002), Taiwan (Fang et al., 2003) and Korea(Kim et al., 2003), respectively of different regions.

The higher TSP concentrations of Pb were also measured in Mumbai, India (ranged 820–1060 ngm^{-3}, Kumar et al., 2001) and Taejon, Korea (260 ngm^{-3}, Kim et al., 2002) in Asia region. And the average concentrations of Pb are 180ngm^{-3} in Taichung, Taiwan (Fang et al., 2004). These values were about 0.2 times lower than Mumbai, India (ranged 820–1060 ngm^{-3}, Kumar et al., 2001) sampling site. The highest fine particulate and PM_{10} concentrations of Pb was in Hong-Kong, China (Ho et al.,2003) at the industrial, traffic and urban regions around Asia. In addition, Indonesia was founded to have the lowest Pb concentration in $PM_{2.5}$ and $PM_{2.5-10}$ (1.22 ngm^{-3} and 0.3 ngm^{-3}, Maenhaut et al., 2002) for all Asia countries. The element Pb concentration in TSP obtained in Taichung, Taiwan (Fang et al., 2004) study were about 0.17, 1.23, 1.44 and 2.28 times as the Pb concentration obtained in Sakinaka, India(Kumar et al., 2001), Ho Chi Minh, Vietnam(Hien et al., 2001), Tokyo, Japan(Var et al., 2000) and Hong Kong, China(Lau and Luk., 2001), respectively.

As for element Cu, the highest TSP concentrations were collected in Mumbai, India (ranged 370–1550 ngm^{-3}, Kumar et al., 2001) and the second highest values were obtained in Taichung, Taiwan (ranged 230–240 ngm^{-3}, Fang et al., 2004). The average Cu concentration of fine particulate was about 26780ngm^{-3} (Ho et al., 2003), which was the highest concentration among the Asia countries. And the average Cu concentration was about 0.14 ngm^{-3} (Maenhaut et al., 2002), which was the lowest concentration among the Asia countries, $PM_{2.5-10}$ also reflected that element Cu concentrations obtained in Indonesia was ranked lowest. The element Cu concentration in TSP obtained in Taichung, Taiwan study (Fang et al., 2004) were about 0.65, 2.73 and 7.94 times as the Cu concentration obtained in Sakinaka, India(Kumar et al., 2001), Hong Kong, China(Lau and Luk., 2001) and Tokyo, Japan (Var et al., 2000), respectively.

The highest TSP concentrations of element Mn were obtained in Mumbai, India (ranged 850–1,470ngm^{-3}, Kumar et al., 2001). It was also founded that the average TSP concentrations in Taichung, Taiwan (Fang et al., 2004) were about 2.7 times as those of Tokyo, Japan (ranged 16.8-40.1ngm^{-3} , Var et al., 2000) sampling site but much lower than Mumbai sampling site (Kumar et al., 2001). As for fine particulate ($PM_{2.5}$) concentrations, the average Mn concentration was about 0.121ngm^{-3} (Maenhaut et al., 2002). Coarse particulate ($PM_{2.5\text{-}10}$) concentration was 0.57ngm^{-3} (Maenhaut et al., 2002). Indonesia was founded have the lowest Mn concentration of $PM_{2.5}$ and $PM_{2.5\text{-}10}$ in all Asia countries. However, the highest $PM_{2.5}$ concentrations of Mn were 19720ngm^{-3}, 9960ngm^{-3} and 9410ngm^{-3} in industrial, traffic and urban regions, respectively. (Hong-Kong, China (Ho et al., 2003)). The element Mn concentration in TSP obtained in Taichung, Taiwan study (Fang et al., 2004) were about 0.13, 1.66 and 6.55 times as the Mn concentration obtained in Sakinaka, India (Kumar et al., 2001), Taejon, Korea (Kim et al., 2002) and Sapporo, Japan (Var et al., 2000), respectively.

The TSP concentrations of Cr were measured in Sapporo and Tokyo, Japan (2.61ngm^{-3} and 6.09ngm^{-3}, Var et al., 2000) and Taejon, Korea (31.8ngm^{-3}, Kim et al., 2002). As for fine particulate ($PM_{2.5}$) and coarse particulate ($PM_{2.5\text{-}10}$) concentrations, the highest $PM_{2.5}$ concentrations were 2430ngm^{-3}, 4190ngm^{-3} and 4510ngm^{-3} in Hong-Kong, China (Ho et al., 2003) at different sampling sites, and the highest $PM_{2.5\text{-}10}$ concentrations was 147ngm^{-3} in Taichung temple, central Taiwan (Fang et al., 2003). The study related to Cr research in Asia country was seldom.

The TSP concentrations of Ni were measured in Sapporo and Tokyo, Japan (3.81 ngm^{-3} and 5.63 ngm^{-3}, Var et al., 2000). Highest fine particulate ($PM_{2.5}$) and coarse particulate ($PM_{2.5\text{-}10}$) were obtained in Hong-Kong, China (ranged from 5,340-6,330ngm^{-3}) and Taichung temple (73 ngm^{-3}, Fang et al., 2003). The element Ni in urban region is 19.6ngm^{-3} (fine particulate) and 29.2ngm^{-3} (coarse particulate), respectively. It was also founded that the average fine and coarse particulate concentrations in Taichung, Taiwan (Fang et al., 2002) were about 2.8 and 2.5 times as those of Korea (Kim et al., 2003) sampling site.

Average PM_{10} concentration of metallic elements Pb, Cu, Mn, Cr and Ni was obtained highest concentrations than any other Asia countries in Hong-Kong, China (Ho et al., 2003). However, PM_{10} was obtained higher concentration in Kaohsiung industrial, Taiwan (Chen et al., 2003).

In addition, the Table 3-1 summarizes the atmospheric studies at different sites around the Taichung and Kaoshiung. The average concentrations discussions of those PM10, metallic elements and ionic species were as follows;
Other study (Chen et al., 2004) presents the average PM10 concentrations were 260 □ gm^{-3} during the ADS (Asian dust storm) period in southern Taiwan. And the average PM10 particulates concentrations were 260 □ gm^{-3}. The results founded that the average PM10 concentrations during during the ADS period were approximately about 2.3 and 3.3 times the non-ADS particle concentrations (i.e., 113 □ gm^{-3} in 2000 and 79.5 □ gm^{-3}) at sampling site. Results also show that the percentages of PM2.5/PM10 were approximately in the ranges from 60% to 70% before and after the ADS periods, but this ratio decreased to smaller than 45% during the ADS periods, because the coarse particulate concentrations (PM2.5–10) increased in southern Taiwan. And the average particulation related metallic species concentrations (Mass, Fe, Zn, Pb, Mn, Cr and Cu) were analyzed in this study. The results

showed that the average concentrations of particulate mass concentration averaged (766 μg m^{-3}) are higher in the traffic site (CCRT) than the Kaoshiung sampling sites in this study. The average concentration of element Fe in Taichung is 1685 μg m^{-3} which in low than Kaoshiung sampling sites. The averaged concentration of element Pb obtained in traffic junction from Taichung, Taiwan (Fang et al., 2005) was averaged 180 μg m^{-3}, which is higher than other different sampling sites inland urban and indusial around Kaoshiung. However, the average metallic element such as concentration of Pb in Taichung was lower than coastal urban and indusial, Kaoshiung. In addition, the average element average concentration of Zn (960 μg m^{-3}) observed in Taichung is higher than that any sampling sites in Kaoshiung. Besides, the average concentration of Manganese displayed same concentration distribution trend. For ionic species Ca^{2+}, the result indicated that the major mode occurred in coarse size in the range from 3.2 to 5.6 μm in southern Taiwan during the ADS periods.

4. Correlation coefficient and principal component analysis of TSP

4.1 Correlation coefficient

Aerosol samples for total suspended particulate matter were collected by two PS-1 samplers from October 2002 to April 2003 at Tunghai University and Taichung Industrial Park in central Taiwan. The average concentrations of TSP at the industrial sampling site were higher than at the suburban sampling site during the sampling period. The samples collected were analyzed by a flame atomic absorption spectrophotometer for the elemental analysis. Statistical methods such as correlation coefficient and principal component analysis were also used to identify the possible pollutant source.

As show in Table 4-1, high correlation coefficients of Fe and Zn were observed at the TIP (R = 0.72) and THU (R = 0.71) sampling sites, respectively. This finding indicated that pollutants at the TIP and THU sampling sites originated from the same source. At the THU sampling site, moderate correlation coefficients with Fe, Zn and Pb were observed; indicating traffic emission was the major source for these metallic elements. Moderate correlation coefficients were also observed with Fe, Zn and Mn, which indicate that emission from soil/resuspended (Fang *et al.*, 2003) and was a possible contributor at the THU sampling site. At the TIP sampling site, high correlation coefficients were also obtained for the metallic elements Fe and Zn indicating that same source was the major one at TIP. In addition, moderate correlation coefficients were also obtained between Cu and Mn at the TIP sampling site. These results indicated that these metallic elements originated from the same pollutant source. Our finding is consistent with the results obtained in previous study (Kumar *et al.*, 2001). As for other meteorological parameters such as atmospheric temperature, wind speed, relative humidity, and atmospheric pressure, lower correlations between meteorological parameters and metallic elements were observed in this study.

4.2 Principal component analysis

Source groupings were determined using principal component analysis (PCA) with Varimax rotation and retention of principal components having eigenvalues > 1 (SPSS 8.0) of the complete farm sampling site data set of metal concentrations in Taichung, central Taiwan. The principal component analysis performed on TSP data is shown in Table 4-2. The PCA results showed that two and three factors explain the main part of the data variance, therefore one element for each factor has been chosen as a tracer. At the TIP sampling site, factor 1 explained 42.7 % of the total variance of the data and had high loading for Zn (0.899) and Cu (0.880), which were identified as industrial/traffic emission sources. More than eight hundred factories, located in the TIP area, possessed large traffic volume especially during work time; this was the main reason for the above mentioned results. Factor 2 is relative to soil dust and/or resuspended source with high loading of Fe (0.903) and Mn (0.764). At the THU sampling site, 49.0 % of the total variance of the data was observed in factor 1. Higher loading of Fe (0.901), Zn (0.785), Pb (0.770), and Mn (0.705) were contributed by traffic emission and the soil source. Taijunggang Road near THU contains heavy traffic flow, so it was responsible for this result. The effect of soil dust in the THU sampling site was also significant. Factor 2 had high loading of Mg (0.940); this phenomenon indicates a marine salt source. Marine salt from the Taiwan Strait, about 30 km from the THU sampling site, was the main cause of this result. Pacyna (1998) illustrated that industrial metallurgical processes produce the large emission of Cu. High loading of Cu (0.957) for factor 3 indicated that emissions of smelter industry from metallurgical procedure were also observed in this area.

5. Metallic element concentrations of $PM_{2.5}$ and coarse $PM_{2.5\text{-}10}$ during daytime and nighttime period

Daytime and nighttime period sampling programs were carried out by a versatile air pollutant system to collect the fine ($PM_{2.5}$) and coarse ($PM_{2.5\text{-}10}$) particulates simultaneously at a traffic sampling site in front of Hungkuang University during August to October 2003. Chemical analyses of metallic elements were accomplished by a flame atomic absorption spectrophotometer coupled with hollow cathode lamps. Statistical methods such as correlation coefficients and principal component analysis were used to compare chemical components and to find the possible emission sources at this traffic sampling site. The variations of metallic element concentrations on fine and coarse particulates during daytime and nighttime were also discussed in this study.

Table 5-1 shows the sampling information at the CCRU sampling site in central Taiwan during August to October 2003. The average temperatures for daytime and nighttime sampling periods were 28.3 and 24.3 ºC, respectively. The average wind speed ranged from 0.5 to 1.8 m sec^{-1} during the sampling periods. After regression analysis, no obvious correlation coefficients were found among fine particulates, coarse particulates, atmospheric temperature, and wind speed in either daytime or nighttime periods.

The average metallic element concentrations of fine and coarse particulates during daytime and nighttime during August to October 2003 are shown in Fig. 5-1. In general, metallic element concentrations in fine particulates were higher than in coarse particulates except for the crustal elements Fe and Mg. With regard to the variations of daytime and nighttime sampling periods, the mean metallic concentrations of fine particulates were in the following order: Fe (891.2) > Zn (641.3 > Cr (300.9) > Cu (275.5) > Mg (254.6) > Mn (41.2) and Fe (974.5) > Zn (532.5) > Mg (324.1) > Cr (289.4) > Cu (256.9) > Mn (64.8) in ng m^{-3}, respectively. In the daytime sampling period, the metallic element Fe and Zn were the predominant constituents in the fine particulates. In general, the metallic elements concentrations were higher in daytime than nighttime sampling periods.

6. Mass size distribution and dry deposition flux during incense burning at Tzu Yun Yen temple

Figure 6-1 and 6-2 displays the mass size distribution during incense burning at Tzu Yun Yen temple. Comparing mass size distribution during incense burning of two periods shows that those for Zhong Yuan Jie and the 1st or 15th of nong li for each month (Chinese lunar calendar), were higher than non-Zhong Yuan Jie and non-1st or 15 th days, respectively. It found that the average mass size distributions are bimodal with the major peaks within 0.56-1 µm and 5.6-10µm, respectively during non-Zhong Yuan Jie and non-1st or 15 th days. It also found that the average mass size distributions are bimodal with the major peaks within 0.18-0.32 µm and 5.6-10µm, respectively during Zhong Yuan Jie and the 1st or 15th of nong li for each month (Chinese lunar calendar) at Tzu Yun Yen temple. The results how that fine suspended particulate concentrations increase at Tzu Yun Yen temple during Zhong Yuan Jie and the 1st or 15th of nong li for each month (Chinese lunar calendar).

Figure 6-3 displayed average mass size distribution during incense burning at Tzu Yun Yen temple. It showed that the average mass size distributions are bimodal and with the major peak within 0.32-0.56 µm and 5.6-10 µm, respectively during incense burning period at Tzu Yun Yen temple. The results yield here indicated that fine ($PM_{2.5}$) suspended particulate concentrations were major particle type at Tzu Yun Yen temple incense burning period in this study.

Figure 6-4 exhibited average cumulative particle size distribution of total aerosols during the incense burning at Tzu Yun Yen temple. The results were clearly shown average mass median aerodynamic diameter (MMAD) and geometric standard deviation (σg) for this study. The average mass median aerodynamic diameter (MMAD) of suspended particles is 0.32 µm during the incense burning at Tzu Yun Yen temple in this study. In addition, average geometric standard deviation (σg) were 7.14 during the incense burning at Tzu Yun Yen temple.

Table 6-1 compares the dry deposition flux for the indoor and outdoor environment at Tzu Yun Yen temple during the burning incense period. The results also indicate that almost the average dry deposition flux in the indoor environment is lower than in the outdoor environment at Tzu Yun Yen temple. The dry deposition flux ranged from 18 to 88 mg $m^{-2}day^{-1}$ and from 56 to 731 mg $m^{-2}day^{-1}$ in the indoor and outdoor environment, respectively. In general, the average dry deposition flux (59 mg $m^{-2}day^{-1}$) in the indoor environment was lower than in the outdoor environment (averaged 207 mg $m^{-2}day^{-1}$) in this study. The mean dry deposition indoor/outdoor flux ratios were 28 %.

Table 6-2 showed averaged mass dry deposition flux, metallic elements flux, and indoors/outdoors ratio (%) for the indoor and outdoor environment at Tzu Yun Yen temple during the incense burning periods. The results also indicate that almost the average dry deposition flux in the indoor environment is lower than in the outdoor environment at Tzu Yun Yen temple. The average dry deposition flux was 80.2 mg $m^{-2}day^{-1}$ and 202.7 mg $m^{-2}day^{-1}$ in the indoor and outdoor environment, respectively.

The mean dry deposition flux indoor/outdoor ratios were 39.6% at Tzu Yun Yen temple in this study. Averaged elements fluxes were 0.03, 0.15, 5.35, 0.15, 0.08, 0.05, and 0.08 $mgm^{-2}day^{-1}$ for Cr, Zn, Fe, Pb, Mn, Ni, and Cd at the indoor environment, respectively. And Averaged elements fluxes were 0.01, 0.03, 0.11, 5.75, 0.07, 0.08, 0.06, and 0.04 $mgm^{-2}day^{-1}$ for Cu, Cr, Zn, Fe, Pb, Mn, Ni, and Cd at the outdoor environment, respectively. The data provided here also indicated that element Fe were higher than anthropogenic elements (Zn, Pb, Mn, Ni, and Cd) in the dry deposition flux mode at Tzu Yun Yen temple in this study. In general, mean indoor/outdoor ratios for dry deposition flux of metallic elements were 91%, 138%, 93%, 222%, 101%, 95%, and 208% for Cr, Zn, Fe, Pb, Mn, Ni, and Cd at this temple, respectively. Results also indicated that the major metallic elements dry deposition at Tzu Yun Yen temple indoor environment were Zn, Pb, and Cd.

Conclusion

1. Average downward dry deposition flux, TSP, PM10 concentrations obtained in the Taichung harbor were about 0.51, 0.3, and 3.4 times as those values obtained by traffic sampling site. Three major soluble inorganic species concentrations (sulfate + nitrate + ammonium) accounted for 59.8% and 80.6% of the $PM_{2.5}$ and $PM_{2.5-10}$ mass concentrations at Taichung harbor sampling site in central Taiwan.
2. Average dry deposition velocity for mass, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, and Ca^{2+} were 9, 3.8, 0.3, 0.25, 0.46, 0.18, 0.51 and 2.28 (cm sec^{-1}) at the Taichung harbor sampling site, respectively.
3. The summer/winter flux ratios for Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Mg^{2+}, Ca^{2+} ,and Na^+ were 0.8, 0.3, 0.7, 1.3, 0.8, 0.8, and 0.6, respectively at TH. In addition, the summer/winter flux ratios for Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Mg^{2+}, Ca^{2+} ,and Na^+ were 0.7, 0.8, 0.8, 1.4, 0.9, 0.7, and 0.5, respectively, at Wuchi. And that the NH_4^+, NO_3^- and SO_4^{2-} showed higher concentrations in winter, and lower in summer for both TH and Wuchi sampling sites.
4. The annual average Vd of Cl^-, NO_3^-, and SO_4^{2-} were 1.8 ± 0.3, 0.2 ± 0.1, and 0.2 ± 0.0 cm sec^{-1} at TH and 1.7 ± 0.4, 0.3 ± 0.2, and 0.2 ± 0.1 cm sec^{-1} at Wuchi. In addition, the annual average Vd of NH_4^+, Na^+,Ca^{2+}, and Mg^{2+} were 0.1 ± 0.0, 1.8 ± 0.5, 2.5 ± 0.6 and 1.1 ± 0.3 cm sec^{-1} at TH and 0.2 ± 0.1, 1.7 ± 0.5, 2.1 ± 0.4 and 1.0 ± 0.3 cm sec^{-1} at Wuchi.
5. Concentrations of total suspended particulate mass in the daytime period (averaged 996.2$\mu g/m^3$) were higher than in nighttime period (averaged 560.7μg/m3). Furthermore, the average downward dry deposition fluxes (averaged 26.22$\mu g/m^2$ s) were also about two times as that of upward dry deposition fluxes (averaged 12.11$\mu g/m^2$ s) in the nighttime period.
6. PM_{10} concentration of metallic elements Pb, Cu, Mn, Cr and Ni was obtained highest concentrations than any other Asia countries.
7. Traffic emission was the major source for these metallic elements(Fe, Zn and Pb). Moderate correlation coefficients were also observed with Fe, Zn and Mn, which indicate that emission from soil/resuspended and were a possible contributor at the THU sampling site. At the TIP sampling site, high correlation coefficients were also obtained for the metallic elements Fe and Zn indicating that same source was the major one at TIP.

8. Higher loading of Fe (0.901), Zn (0.785), Pb (0.770), and Mn (0.705) were contributed by traffic emission and the soil source. Taijunggang Road near THU contains heavy traffic flow, so it was responsible for this result. The effect of soil dust in the THU sampling site was also significant. And high loading of Mg (0.940); this phenomenon indicates a marine salt source. Marine salt from the Taiwan Strait, about 30 km from the THU sampling site, was the main cause of this result.
9. The mean metallic concentrations of fine particulates were in the following order: Fe (891.2) > Zn (641.3 > Cr (300.9) > Cu (275.5) > Mg (254.6) > Mn (41.2) and Fe (974.5) > Zn (532.5) > Mg (324.1) > Cr (289.4) > Cu (256.9) > Mn (64.8) in ng m^{-3}, respectively. In the daytime sampling period, the metallic element Fe and Zn were the predominant constituents in the fine particulates. In general, the metallic elements concentrations were higher in daytime than nighttime sampling periods.
10. The average dry deposition flux (58.5 mg $m^{-2}day^{-1}$) in the indoor environment(temple) is lower than that measured in the outdoor environment (averaged 206.7 mg $m^{-2}day^{-1}$). The mean mass dry deposition indoor/outdoor flux ratio was 28.3 % in this study. The mean indoor/outdoor ratios for dry deposition flux of metallic elements were 91%, 138%, 93%, 222%, 101%, 95%, and 208% for Cr, Zn, Fe, Pb, Mn, Ni, and Cd at this temple, respectively. Results also indicated that the major metallic elements dry deposition at Tzu Yun Yen temple indoor environment were Zn, Pb, and Cd.
11. The average mass size distributions are bimodal with the major peaks within 0.18-0.32 μm and 5.6-10μm, respectively during Zhong Yuan Jie and the 1st or 15th of nong li for each month (Chinese lunar calendar) at Tzu Yun Yen temple. The results also showed that fine suspended particulate concentrations increase at Tzu Yun Yen temple during Zhong Yuan Jie and the 1st or 15th of nong li for each month (Chinese lunar calendar).
12. Average mass size distribution during incense burning at Tzu Yun Yen temple was also studied. It showed that the average mass size distributions are bimodal and with the major peak within 0.32-0.56 μm and 5.6-10μm, respectively during incense burning period at Tzu Yun Yen temple. And the average mass median aerodynamic diameter (MMAD) and geometric standard deviation (σg) of suspended particles are 0.32 μm, 7.14 during the incense burning at Tzu Yun Yen temple in this study.

Acknowledgements

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Date	TSP concentration (μg m^{-3})						
	Na^{+}	NH$_4^{+}$	Mg$_2^{+}$	Ca$_2^{+}$	Cl^{-}	NO$_3^{-}$	SO$_4^{2-}$
February(n=1)	2.31	1.76	2.62	14.27	1.39	10.33	27.9
March(n=2)	2.19±0.93	1.25±0.52	2.81±1.17	15.32±7.52	1.25±0.53	9.82±3.66	27.23±7.29
April(n=3)	1.93±1.08	2.62±0.79	3.01±2.06	11.62±7.53	1.43±0.72	8.25±2.21	28.31±9.21
May(n=3)	1.25±0.52	1.57±0.47	1.97±0.52	18.84±10.39	1.15±0.45	7.91±4.82	26.05±11.29
June(n=3)	1.65±0.28	1.93±1.05	2.04±0.73	12.72±6.25	1.3±0.58	9.18±3.72	25.33±12.62
July(n=2)	2.24±0.64	1.24±0.63	2.36±0.95	15.5±7.18	1.43±1.02	8.25±5.28	24.25±13.62
August(n=2)	1.97±0.72	2.11±0.73	1.72±1.12	14.25±5.47	1.72±0.73	7.42±3.71	25.23±11.83
Average	1.93±0.67	1.64±0.82	2.36±1.21	14.65±7.25	1.38±0.45	8.73±3.25	26.32±12.73

Table 1-1

Ambient air particulate concentrations at harbor sampling site in Taichung

Date	Total suspended particulate concentration (μg m^{-3})	Dry Deposition flux Downward (μg m^{-2}sec^{-1})	Coarse particle concentration (μg m^{-3})	Fine particle concentration (μg m^{-3})
March (n=3)	296.39	19.64	43.31	176.04
April (n=3)	271.25	18.79	54.92	149.56
May (n=3)	197.30	19.34	37.43	124.79
June (n=2)	193.24	27.05	57.53	86.30
July (n=2)	190.49	22.70	30.84	70.73
August (n=2)	175.67	21.01	22.16	50.14
Average	212.62	21.45	40.50	101.13
STDEV	44.76	5.02	22.33	45.15

Table 1-2

Average dry deposition flux (Downward), and TSP concentration for water- soluble ionic species at Taichung harbor.

Dry Deposition flux Downward (µg m-^{2}sec^{-1})					
Na^+	NH_4^+	Mg_2^+	Ca_2^+	Cl^-	NO_3^-
4.35	11.72	5.28	5.42	5.89	2.89
5.24±2.53	12.92±4.21	4.32±2.14	6.83±2.52	6.11±3.72	4.32±1.22
3.86±1.72	10.52±5.82	4.71±1.94	7.24±3.24	5.10±2.88	5.21±2.01
3.26±1.18	9.72±3.97	5.58±3.62	6.52±4.12	4.75±1.52	3.72±1.42
4.17±2.01	11.03±5.24	3.62±1.04	5.37±3.72	5.12±1.72	4.57±1.57
4.82±1.86	9.74±4.52	5.02±2.26	6.26±4.54	4.83±1.02	5.23±2.25
3.92±1.83	9.04±3.68	4.73±1.96	8.12±4.29	4.98±1.84	3.13±1.62
4.23±1.88	10.67±4.52	4.75±2.08	6.54±3.73	5.25±1.54	4.15±2.54

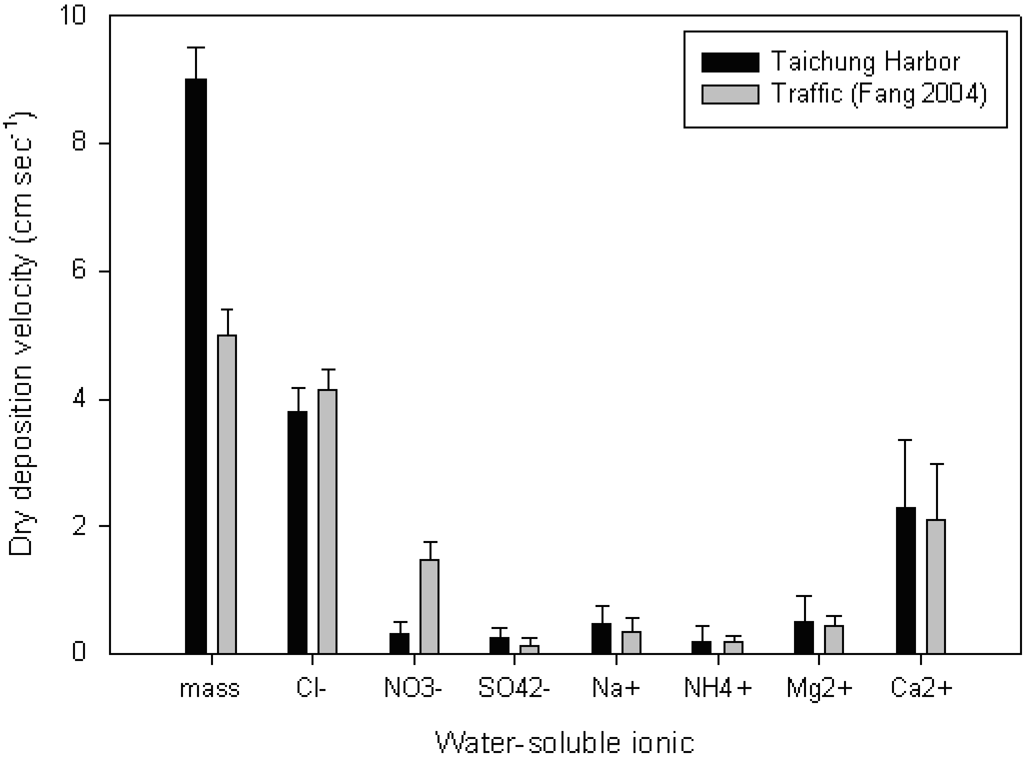
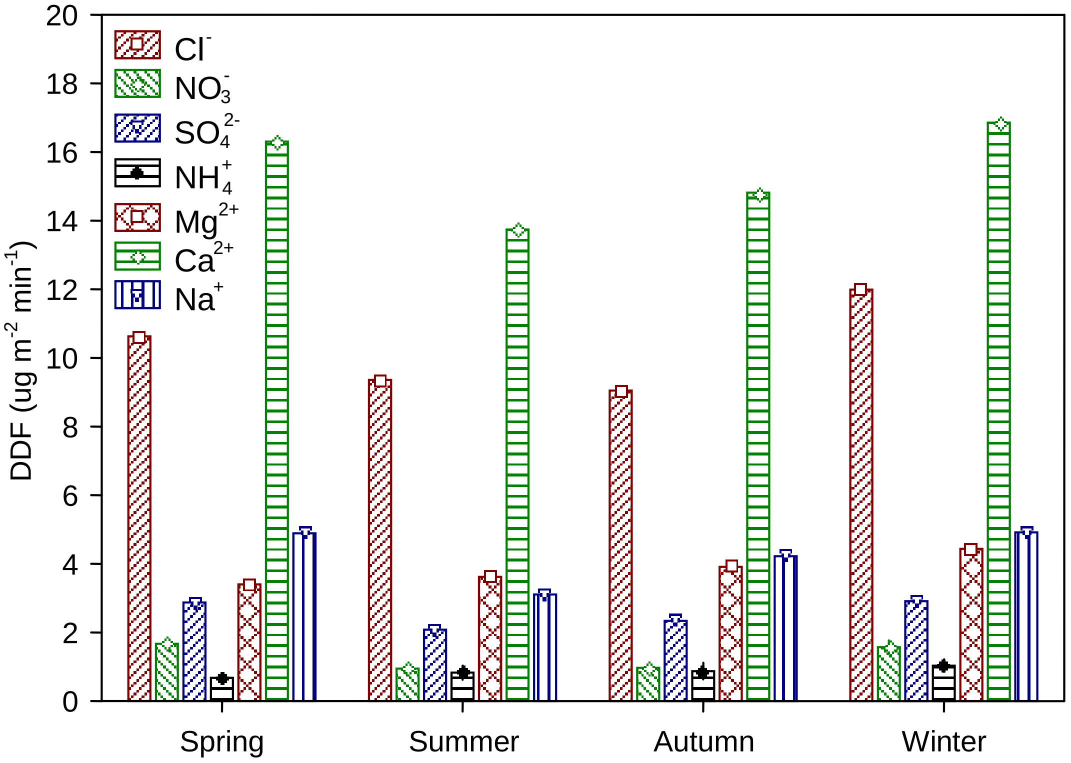
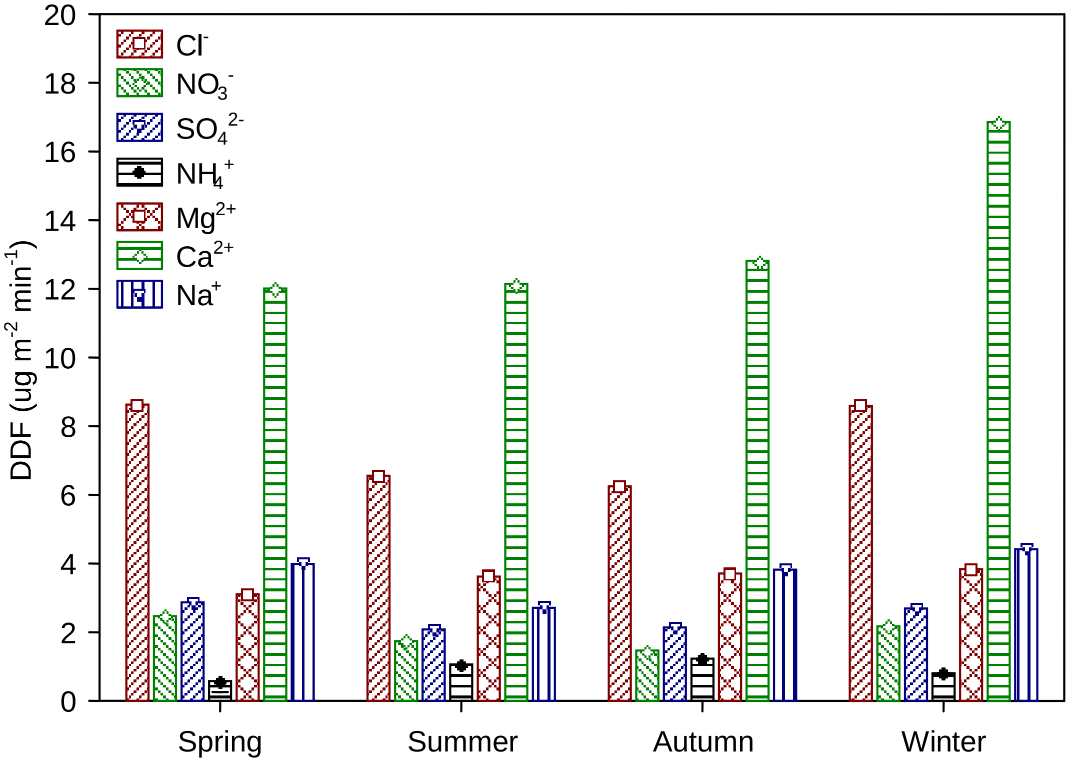


Fig. 1-2
Average dry deposition velocity for mass and water- soluble ionic species at Taichung harbor and traffic sampling site.

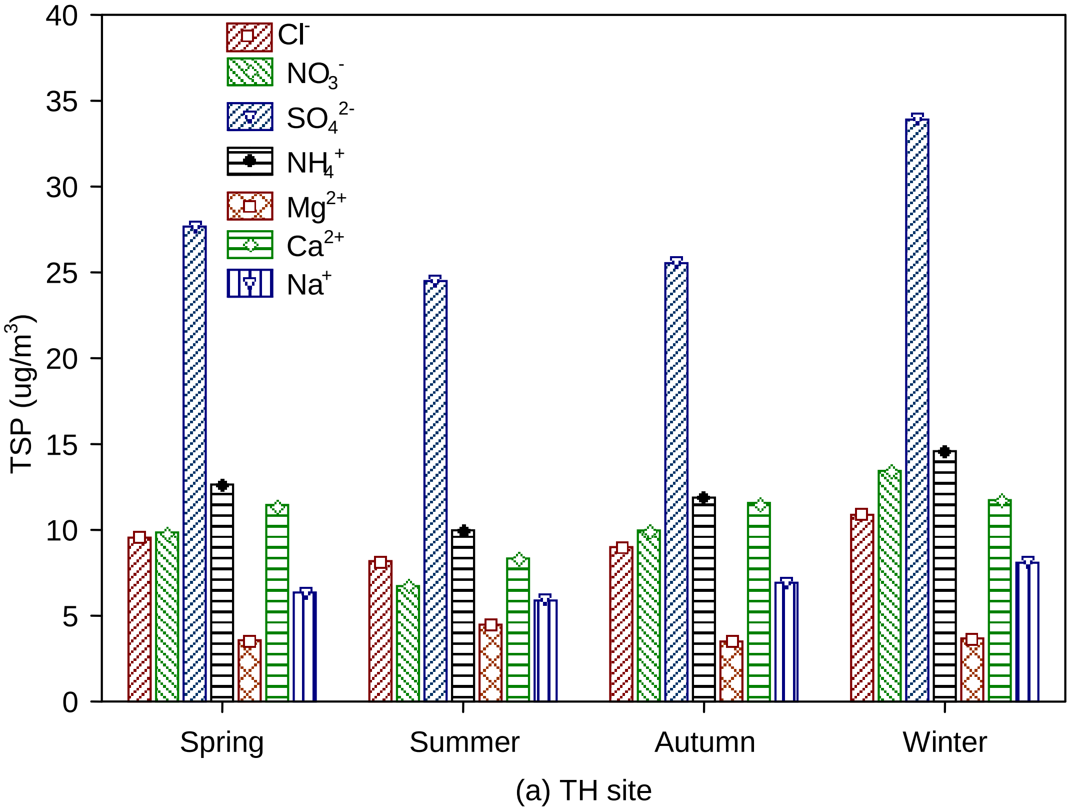


(a) TH site



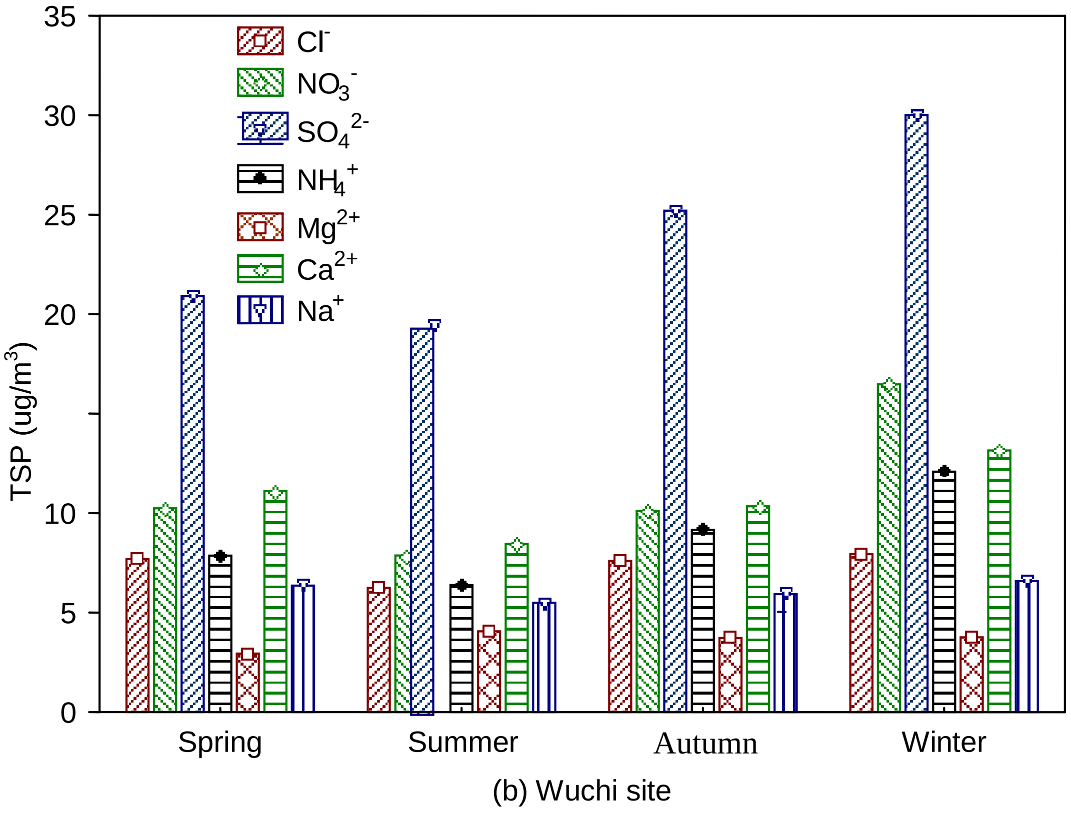
(b) Wuchi site

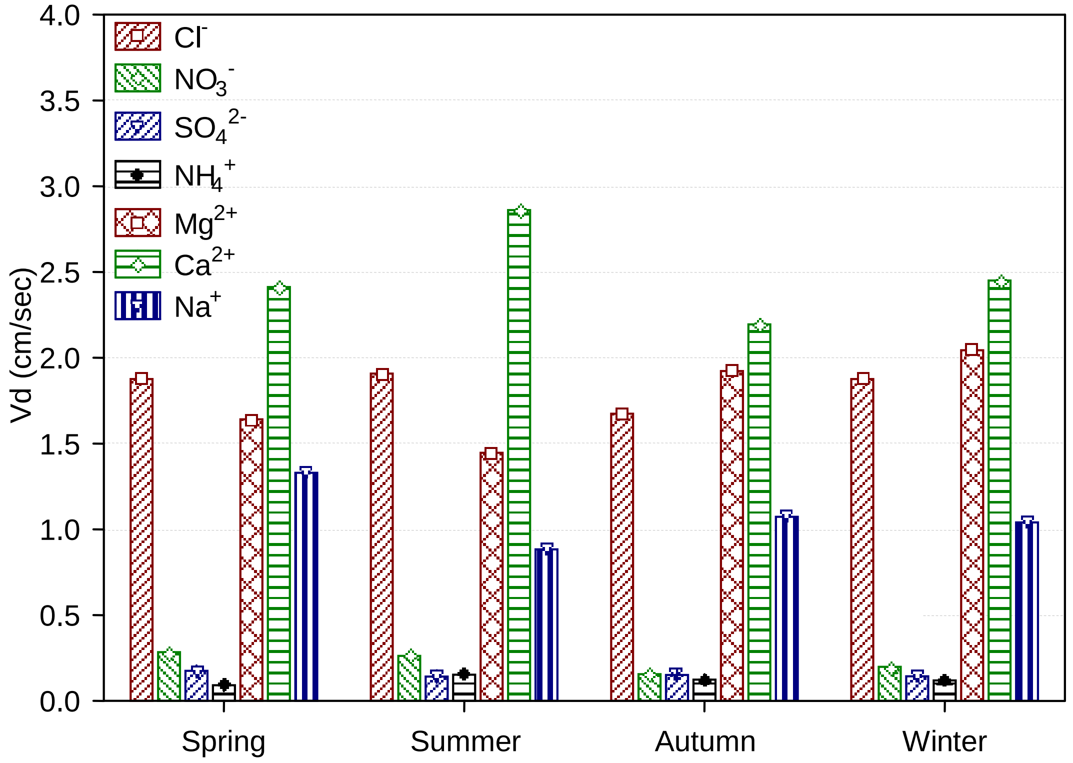
Fig. 2-1. Seasonal variations of dry deposition fluxes (μg m^{-2} min^{-1}) for soluble ions at TH and Wuchi sampling sites.



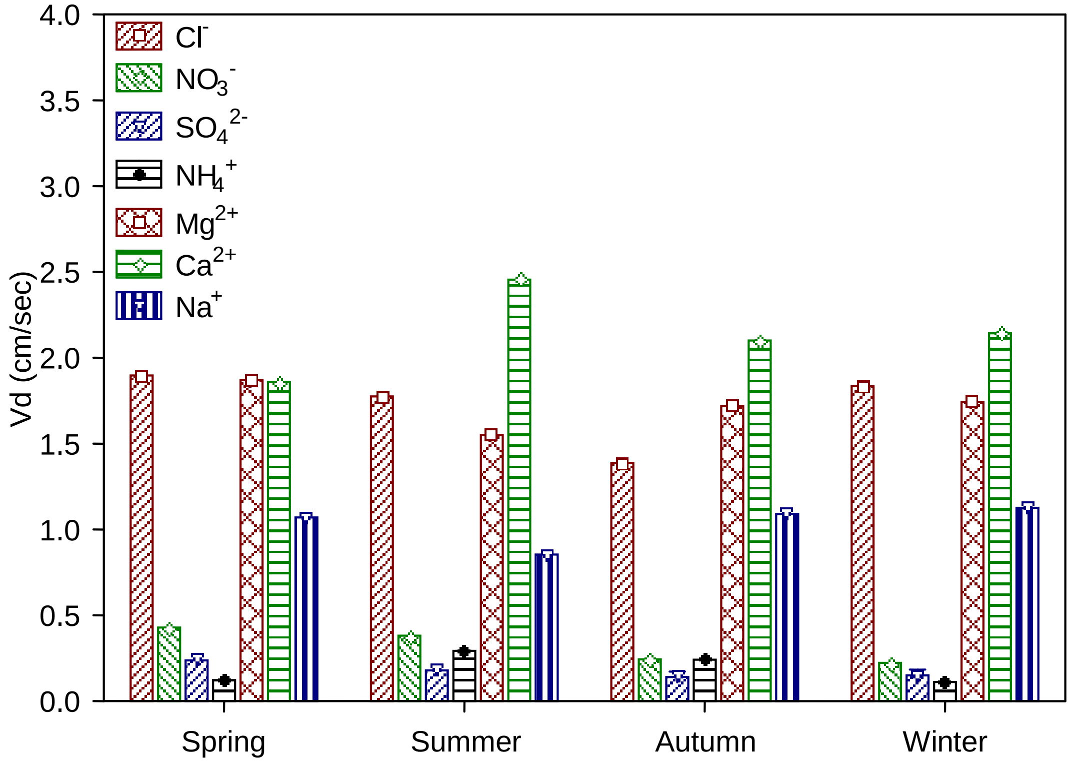
(a) TH site

Fig. 2-2. Seasonal variations of TSP concentrations for soluble ions at TH and Wuchi sampling sites.





(a) TH site



(b) Wuchi site

Fig. 2-3. Seasonal variations of deposition velocities for soluble ions at TH and Wuchi sampling sites.

Table 3-1

Bulk metal element samples of suspended particulate collected in different areas around Asia.

Location	City	Character	Size	Mass ($\mu g\,m^{-3}$)	Pb ($ng\,m^{-3}$)	Cu ($ng\,m^{-3}$)	Zn ($ng\,m^{-3}$)	Fe ($ng\,m^{-3}$)	Mn ($ng\,m^{-3}$)	Cr ($ng\,m^{-3}$)	Ni ($ng\,m^{-3}$)	Reference
China	Hong-Kong	Airborne	TSP	79	79	88	140	1421	-	-	-	Lau and Luk (2000)
		Traffic	PM_{10}	83.5	98740	35380	340	860	23070	6850	8620	
			$PM_{2.5}$	50.9	76860	17320	290	250	9960	2430	5340	
		Industry	PM_{10}	73.1	100520	63530	460	790	26080	5750	9580	Ho et al. (2003)
			$PM_{2.5}$	57.4	91620	36780	380	480	19720	4510	6000	
		Urban	PM_{10}	80	62750	15330	130	620	20620	4970	8270	
			$PM_{2.5}$	42.4	60130	9710	120	190	9410	4190	6330	
	Shanghai	University	$PM_{2.5}$	62.4	270	-	-	820	-	-	-	Ye et al. (2003)
		Urban	$PM_{2.5}$	67.6	280	-	-	900	-	-	-	
India	Sakinaka Mumbai	Traffic junction	SPM	1176	1060	370	-	165500	850	-	-	Kumar et al., 2001
	Gandhinagar		SPM	1031.9	820	1550	-	265500	1470	-	-	
Indonesia	Bukit Tinggi	Tropical jungle	$PM_{2.5}$	4.5	1.22	< 0.41	0.71	2.6	0.121	-	-	Maenhaut et al. (2002)
			$PM_{2.5\text{-}10}$	4.8	< 0.3	< 0.16	0.83	14.8	0.57	-	-	
	Pontianak	rural	$PM_{2.5}$	9.4	8.7	0.22	2.2	4.7	0.34	-	-	
			$PM_{2.5\text{-}10}$	12	4.2	0.56	2.7	53	1.77	-	-	
Japen	Sapporo	Urban city	TSP	-	43.9	20.9	149	625	16.8	2.61	3.81	Var et al. (2000)
	Tokyo		TSP	-	125	30.2	299	677	40.1	6.09	5.63	

Table 3-1

Bulk metal element samples of suspended particulate collected in different areas around Asia. (Continue)

Location	City	Character	Size	Mass $(\mu g\ m^{-3})$	Pb $(ng\ m^{-3})$	Cu $(ng\ m^{-3})$	Zn $(ng\ m^{-3})$	Fe $(ng\ m^{-3})$	Mn $(ng\ m^{-3})$	Cr $(ng\ m^{-3})$	Ni $(ng\ m^{-3})$	Reference
Korea	Taejon	Industrail	TSP	115	260	54.9	220	1839	66.1	31.8	33.6	Kim et al. (2002)
			PM_{10}	72.2	195	32.4	277	1577	41.8	39.3	42.6	
	Seoul	urban	$PM_{2.5}$	-	96.4	27.8	163	743	39	13.7	19.6	Kim et al. (2003)
			PM10	-	124	50.1	302	2321	94.2	18.8	47.8	
Taiwan	Taichung	rural	$PM_{2.5}$	23.6	26	-	61	581	-	-	11	Fang et al. (2002)
			$PM_{2.5\text{-}10}$	16.2	3	-	15	1479	-	-	2	
			TSP	84.1	39	-	105	2700	-	-	18	
		Temple	< 2.5	75	88	32	392	894	81	360	54	Fang et al. (2003)
			$PM_{2.5\text{-}10}$	28	120	14	119	568	17	147	73	
		Traffic juntion (daytime)	TSP	981	180	240	1060	1710	110	-	-	Fang et al. (2004)
		Traffic junction (nighttime)	TSP	551	180	230	860	1660	70	-	-	
	Kaoshiung	Inland urban	PM_{10}	167	150	-	190	1730	50	-	30	Chen et al. (2003)
		Inland industral	PM_{10}	147	80	-	320	2090	70	-	90	
		Coastal industral	PM_{10}	181	190	-	540	2140	70	-	40	
		Coastal urban	PM_{10}	175	340	-	340	1740	60	-	30	
Vietnam	Ho Chi Minh	Urban	PM_2	32	73	3	326	1222	52	-	-	Hien et al.(2001)
			$PM_{2\text{-}10}$	16	79	2	245	261	14	-	-	
			TSP	73.6	146	-	203	2904	-	-	-	

Table 4-1
Correlation matrix of TSP metallic elements measured at the TIP and THU sampling sites (N=28)

TIP	Temp.[a]	W.S.[b]	R.H.[c]	P.[d]	Fe	Zn	Pb	Cu	Mg	Mn	THU	Temp.	W.S.	R.H.	P.	Fe	Zn	Pb	Cu	Mg	Mn
Temp.	1										Temp.	1									
W.S.	-0.45	1									W.S.	-0.5	1								
R.H.	-0.23	0.04	1								R.H.	-0.14	0.13	1							
P.	-0.67	0.32	-0.01	1							P.	-0.76	0.35	-0.09	1						
Fe	-0.21	0.14	-0.25	0.24	1						Fe	0.29	-0.16	-0.5	-0.06	1					
Zn	0.05	0.12	-0.30	-0.04	0.72	1					Zn	0.38	0.23	-0.31	-0.19	0.71	1				
Pb	-0.08	-0.21	-0.09	0.07	0.35	0.31	1				Pb	-0.05	0.36	-0.09	0.26	0.56	0.57	1			
Cu	-0.07	-0.11	-0.39	0.19	0.16	0.14	0.19	1			Cu	-0.07	-0.58	-0.13	-0.15	-0.16	-0.45	-0.39	1		
Mg	0.15	0.18	-0.27	0.13	0.30	0.14	0.11	0.25	1		Mg	-0.03	0.22	-0.59	0.10	0.28	0.28	-0.13	-0.36	1	
Mn	-0.25	-0.02	-0.40	0.28	0.33	0.41	0.40	0.56	0.15	1	Mn	0.05	-0.18	-0.55	0.09	0.66	0.50	0.30	0.01	0.48	1

a: Atmospheric temperature (?) b: Wind speed (m/s) c: Relative humidity (%) d: Atmospheric pressure (hpa)

Table 4-2
Factor analysis on TSP element concentrations data set (N=28)

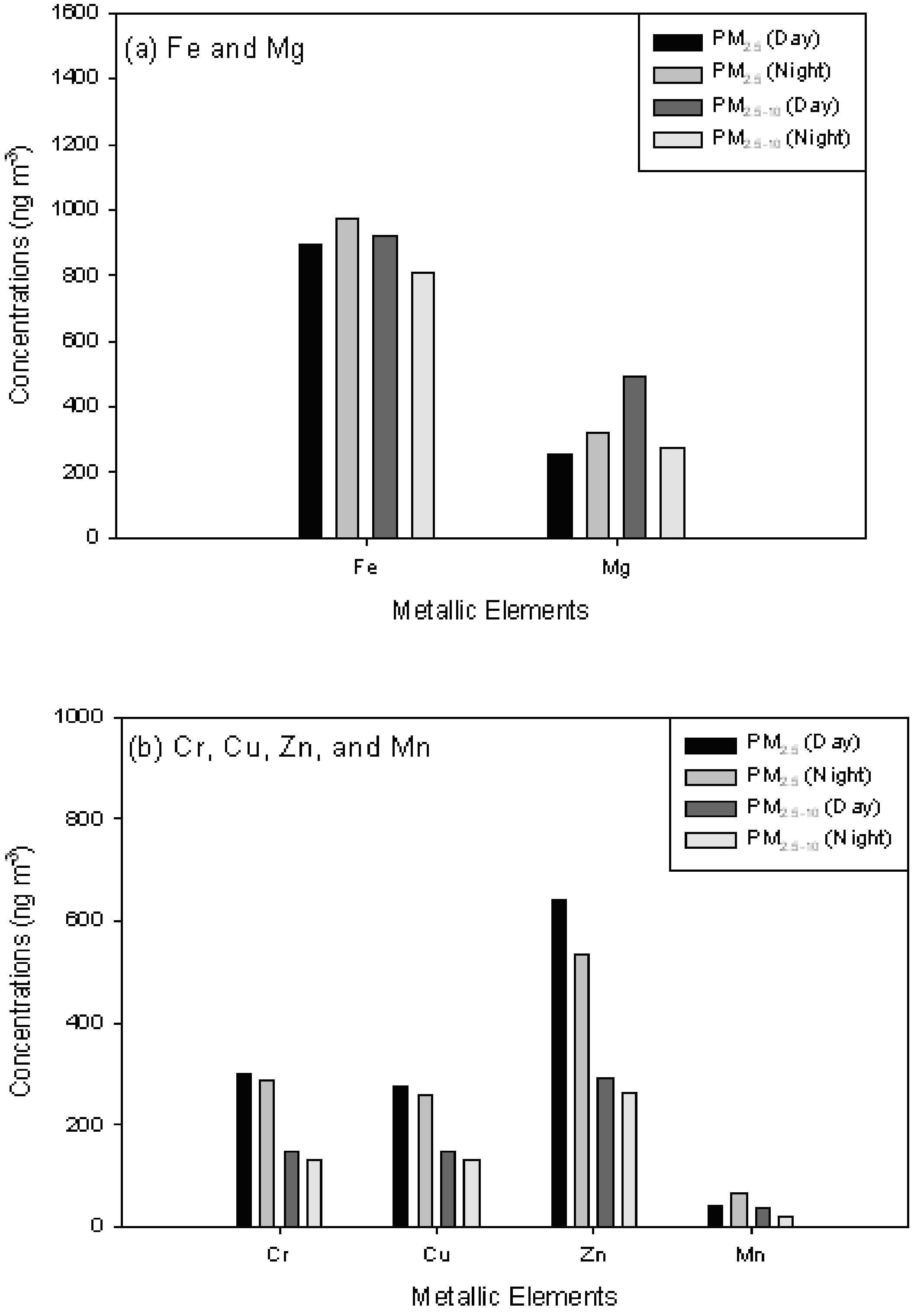
TSP	TIP		THU		
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 3
Mg	0.332	0.290	-	0.094	**0.940**
Mn	**0.764**	0.361	0.266	**0.705**	0.551
Fe	**0.903**	-	-	**0.901**	0.202
Zn	0.104	**0.899**	-	**0.785**	0.153
Pb	0.351	0.509	-	**0.770**	-
Cu	0.098	**0.880**	**0.957**	-	-
Eigenvalue	1.149	2.565	1.102	2.941	1.24
Variance (%)	19.157	42.744	18.363	49.009	20.669
Cumulative (%)	61.902	42.744	88.041	49.009	69.678
Origin	Soil/Resuspended	Industrial/Traffic	Smelter	Traffic, Soil	Marine salt

Note: Only factor loading values with moduli larger than 0.1 are presented and the factor loading values with moduli higher than 0.7 are in bold.

Table 5-1
Sampling information at the CCRU sampling site during August to October 2003 by using Versatile Air Pollutant System in central Taiwan

Date	Fine ($\mu g\ m^{-3}$)		Coarse ($\mu g\ m^{-3}$)		Prevailing wind (deg)		Average Wind Speed ($m\ s^{-1}$)		Temperature ( )	
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
08/25-26	26.9	31.9	17.4	18.5	174.1	158.4	1.1	0.2	30.4	26.9
08/26-28	11.3	25.9	5.3	16.6	225.4	190.5	0.9	0.2	31.5	27.3
08/28-30	32.4	29.9	22.2	7.8	209.9	161.8	1.0	0.1	31.5	27.5
2009/4/5	47.5	63.7	23.3	45.5	138.1	187.2	1.0	0.2	30.3	27.2
2009/9/10	25.9	-	18.1	-	57.5	-	2.5	-	29.9	-
09/16-18	42.8	49.5	16.2	49.7	97.1	162.4	1.0	0.0	29.9	27.0
09/22-24	25.5	19.0	27.6	15	98.8	120.0	1.4	0.1	27.6	25.0
10/17-19	51.6	37.7	13.1	15.3	62.5	108.0	2.9	1.2	25.0	20.6
10/19-21	42.5	38.7	36.7	25.3	65.3	132.4	2.5	0.3	26.0	20.5
10/22-24	26.4	47.9	10.9	52.8	59.2	60.8	3.8	2.2	23.7	19.8
10/27-28	75.5	65.3	34.1	43.8	142.0	159.9	1.6	0.1	25.4	21.2
Average	37.1	41.0	20.4	29.0	120.9	144.1	1.8	0.5	28.3	24.3
STDEV	17.4	15.5	9.6	17.0	61.5	39.5	1.0	0.7	2.8	3.3

Fig. 5-1. Average metallic element concentrations of fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particulates during daytime (09:00-21:00) and nighttime (21:00-09:00) by using versatile air pollutant system at the CCRU sampling site.



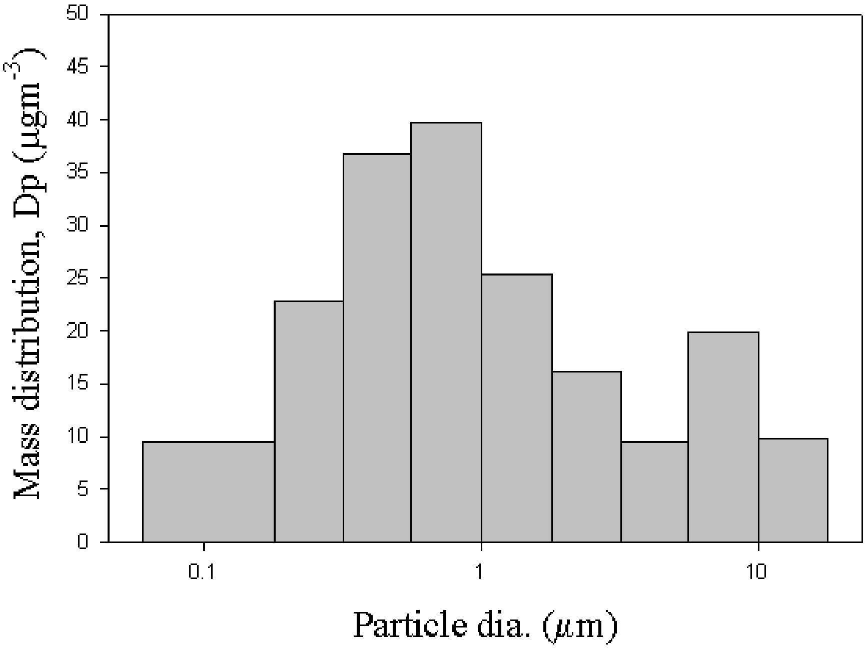


Figure 6-1

The mass distribution during non-Zhong Yuan Jie and non-1st or 15th for each month of the Chinese lunar calendar (nong li) period (n=20) at Tzu Yun Yen temple.

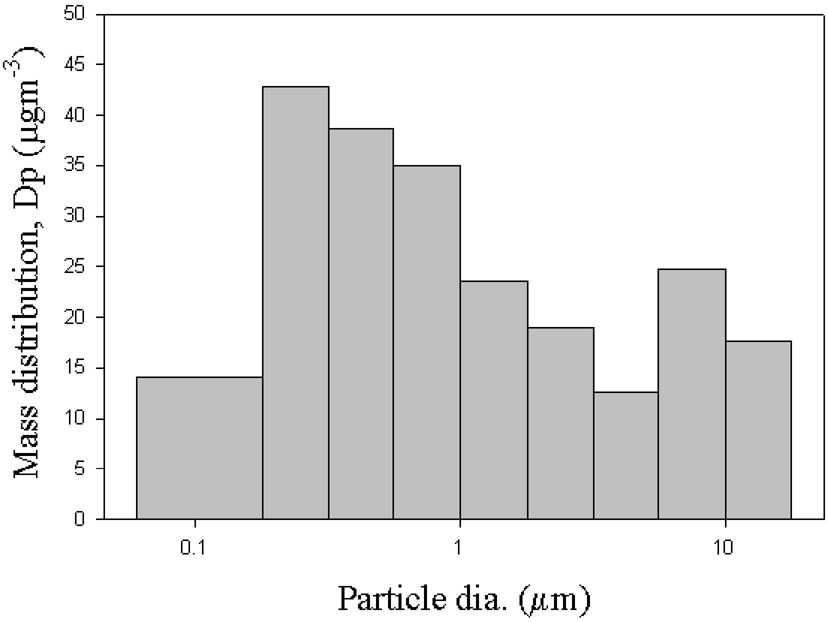


Figure 6-2

The mass distribution during Zhong Yuan Jie and the 1st or 15 th for each month of the Chinese lunar calendar (nong li) period (n=6) at Tzu Yun Yen temple.

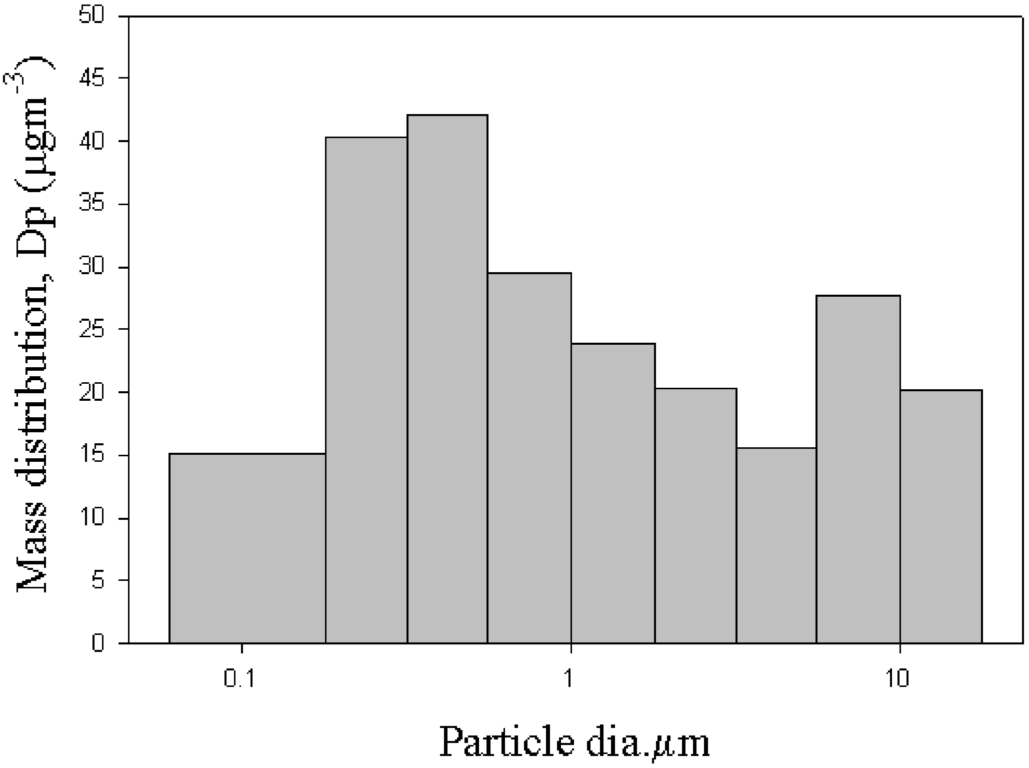


Figure 6-3

Average cumulative particle size distribution of total aerosols during incense burning period (n=26) at Tzu Yun Yen temple.

Table 6-1

One day mass dry deposition flux indoors and outdoors at Tzu Yun Yen temple in central Taiwan.

	Dry deposition flux (mg m^{-2} day^{-1})		Indoor/ Outdoor
Sampling date (2001 to 2002)	Outdoor (n=16)	Indoor (n=26)	(%)
Max	55.6	18.1	33.6
Min	730.8	88.4	12.0
Mean	206.7	58.5	28.3
SD	156.5	25.4	35.1

Table 6-2

Compares averaged dry deposition metallic elements flux (mg $m^{-2} day^{-1}$), and indoors/outdoors ratio (%) for the indoor and outdoor environment at Tzu Yun Yen temple sampling site.

		Cadmium (Cd)	Nickel (Ni)	Manganese (Mn)	Lead (Pb)	Iron (Fe)	Zinc (Zn)	Chromium (Cr)	Copper (Cu)
Indoors environment	Mean	0.077	0.053	0.076	0.153	5.349	0.152	0.031	-
(n=20)	SD*	0.066	0.046	0.056	0.145	2.982	0.134	0.024	-
Outdoors	Mean	0.037	0.056	0.075	0.069	5.747	0.110	0.034	0.012
environment (n=15)	SD*	0.022	0.042	0.056	0.052	3.137	0.058	0.018	0.005
Indoors/ Outdoors	Average ratio	208.1%	94.6%	101.3%	221.7%	93.1%	138.2%	91.2%	-

*: Standard deviation

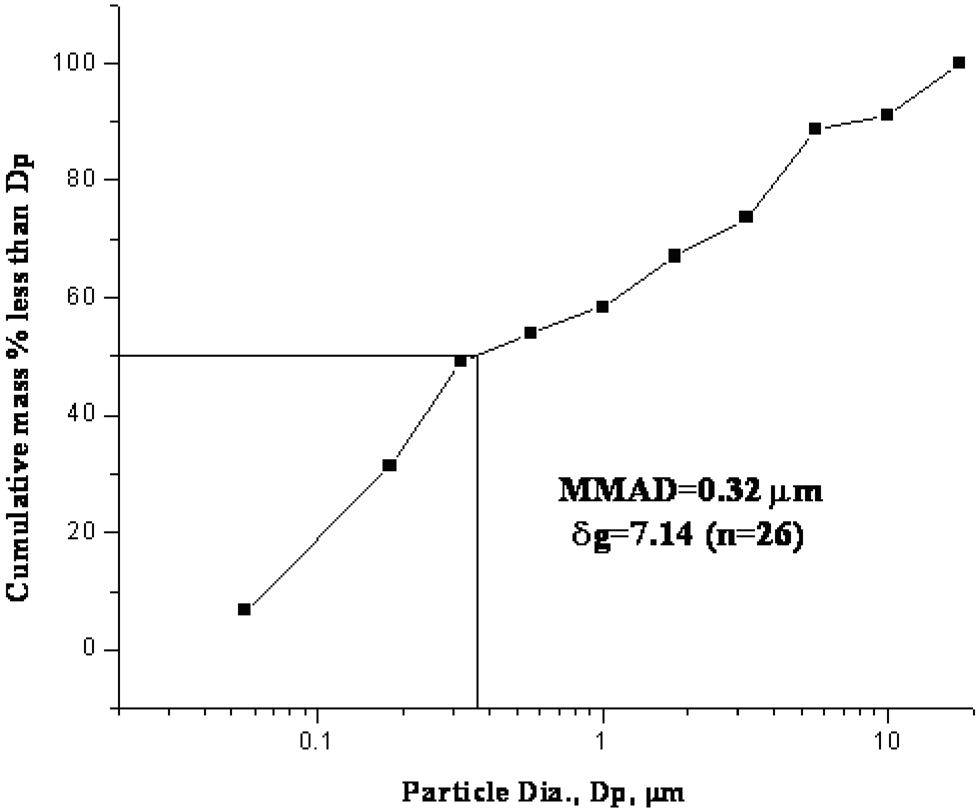


Figure 6-4

Average cumulative particle size distribution of total aerosols during incense burning period (n=26) at Tzu Yun Yen temple.

SOLID WASTE MANAGEMENT IN DEVELOPING COUNTRIES: A CASE STUDY IN TURKEY

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Handling of solid wastes has been a serious problem for all the countries in all over the world. Increase in the population, change in the life standard and life style, industrialization and production of new products contributed to the increase of the amount of solid wastes and consequently the problems generated by them.

Economically developed countries, being aware of the significance of the problems, established regulatory programs while economically developing countries continued to handle the solid wastes in a very primitive way such as dumping them into "open dumps". Therefore, economically developing countries should establish "solid waste management programs", publish related regulations and strictly control the application of them. For the protection of the environment and sustainable development, they should also develop recycling/recovery programs and start conducting studies for the amount and quality of the solid wastes.

Turkey as a developing country has more than 3000 open dumps. İstanbul, being a densely populated Metropolitan City, has faced serious disasters such as "Hekimbaşı Open Dump accident" from the mal-management of the solid wastes up to recent years (Kocasoy, Curi, 1995). By the publication of the Solid Waste Control Regulation of Turkey in 1991 and 1999, municipalities have started to abandon and rehabilitate the existing open dumps and construct sanitary landfills according to the standards. The Municipality of the Metropolitan City of İstanbul has constructed six transfer stations and two sanitary landfills since 1995.

The improvements and the lacking points in the solid waste management at İstanbul, Turkey has been evaluated as a case study.

INTRODUCTION

The proper management of solid waste is one of the major problems which contemporary communities are facing today. Increase in the population as well as the changes in habits and the way of living, increase in the personal income, industrialization and production of new products have increased the amount and the complexity of solid waste generated. Management of solid waste is a serious problem especially in the densely populated areas such as the Metropolitan City of İstanbul. Problems started to arise when increasing urbanization of the society enforced people to live closer to wastes. The increasing levels of awareness with higher perception of nuisances caused by waste disposal and environmental risks, problems of economic activities caused by obstacles which originate from improper waste management are some of the factors made the upgrading of the quality of waste disposal requirements necessary (Cossu, 1989).

In order to find some reasonable solutions for these problems, solid waste management programs were developed. "Solid Waste Management" can be defined as the discipline associated with the control of generation, storage, collection, transfer and transport, processing and disposal of solid wastes in a manner that is in accordance with the best principles of public health, economics, engineering, conservation, aesthetics and other environmental considerations, and that is also responsive to public attitudes.

The establishment of a national regulatory control program with appropriate legislation, regulations, ordinances and licenses is the most important step in the protection of human health and the environment. In the countries where regulatory programs are established, clear improvement in waste management practices has occurred while in those countries without any regulatory programs many instances of environmental damage and public health problems have been cited (Skinner, 1993).

Solid wastes comprise all the wastes arising from human and animal activities that are normally solid and discarded as useless or unwanted (Tchobanoglous, 1993). Solid wastes are generated at the starting with the process of the mining of materials and thereafter generated at every step in the process as raw materials are converted to goods for consumption. The best way to reduce the amount of waste that must be disposed of is to limit the consumption of the virgin raw materials and to increase the rate of recovery and reuse of the waste materials.

Solid waste is a very heterogeneous material including organic wastes such as food remains, recyclable material like paper, plastic, glass and some kind of metals and industrial wastes (Curi, 1993). The characteristics of solid waste change not only according to its sources, but also according to the seasons, countries and even according to the different regions within the same country, mostly resulting from different socio-economic conditions. As an example the composition of solid wastes of different countries is given in Table 1.

Table 1. The percentage distribution of municipal solid waste composition in different countries (Kocasoy, 2002; ISTAÇ, 2006)

Type of Wastes	France	Italy	Japan	South Africa	Turkey	UK	USA
Food remains (%)	25.0	20.0	20.0.0	31.0	45.0	23.4	29.0
Paper and cardboard (%)	30.0	28.0	37.0	33.0	15.5	33.9	35.6
Glass (%)	12.0	11.0	16.0	12.0	3.8	14.4	8.4
Plastics (%)	6.0	8.0	17.0	7.0	9.5	4.2	7.3
Metals (%)	5.0	3.0	6.0	7.0	2.2	7.1	8.9
Textile (%)	4.0	1.0	3.8	-	5.6	4.1	2.0
Ash (%)	-	2.0	0.2	1.0	15.0	-	0.1
Other (%)	18.0	27.0	-	9.0	3.4	12.9	8.7

Since the most widely used method for the solid waste disposal is the landfilling and the generated leachate is one of the main sources for the contamination of the ground water, it is very important to determine the characteristics of the solid wastes before the determination of the disposal method of them. The characteristics of solid wastes according to the characteristics of eluates are given in Table 2.

Table 2. Waste classification of solid wastes according to eluate characteristics (Murat, 1996)

Parameter	Hazardous Waste Limits	Noninteractive Waste Limits
pH	4-13	4-13
TOC	40-200 mg/L	< 200 mg/L
Arsenic III	0.2-1.0 mg/L	< 0.1 mg/L
Lead	0.4-2.0 mg/L	The Sum of These Metals Should not Exceed 5 mg/L[1]
Cadmium	0.1-0.5 mg/L	
Chromium VI	0.1-0.5 0 mg/L	
Copper	2-10 mg/L	
Nickel	0.4-2.0 mg/L	
Mercury	0.02-0.1 mg/L	
Zinc	2-10 mg/L	
Phenol	100-200 mg/L	< 10 mg/L
Fluoride	10-50 mg/L	< 5 mg/L
Ammonium	0.2-1.09 mg/L	< 50 mg/L
Chloride	1.2-6.0 g/L	< 0.5 mg/L
Cyanide[2]	0.2-1.0 mg/L	< 0.1 mg/L
Sulphur[3]	0.2-1.0 g/L	< 1.09 mg/L
Nitrite	6-30 mg/L	< 3 mg/L
Solvents	0.02-0.10 mg/L	< 10 μg/L
Insect Killers[4]	1.5 μg/L	0.5 μg/L
Lipoph Substances	0.4-0.2 mg/L	1 mg/L

[1] None of these metal values will exceed the minimum concentration limit for hazardous waste alone

[2] Easily found

[3] If it is possible 500 mg/L

[4] Chlorinated

FINAL DISPOSAL OF SOLID WASTES IN TURKEY

Today in most part of the world solid wastes are either dumped in open dumps/sanitary landfills or incinerated. As incineration and sanitary landfilling are money consuming -both as the initial investment and during the operation- they are mostly used in economically developed countries, while open dumping, that has no cost at all, is preferred by economically developing countries like Turkey. As a case study the background, existing situation and the planned solid waste management in Turkey is presented in the following sections.

In parallel to the increase in population by the change of the standard of life and the consuming habits of the people, the amount and the types of the solid waste generated in Turkey has been continuously changing. There had not been dependable statistical data about the amount of the solid waste generated. Data available was collected by individual investigators for a certain period for the research area. Since these data were not put in a data bank, it is also very difficult to obtain them. In order to get such kind of inventory, "the Institute of Statistics of Turkey" started to collect data about the municipal solid waste systematically after the publication of the Solid Waste Regulation in 1991. Later in 1999 this Regulation was revised and published in the Official Gazette (Ministry of Environment, 1991; Ministry of Environment, 1999).

After the publication of the Solid Waste Control Regulation in 1991, the municpalities started to establish solid waste management programs including just the collection and transportation and disposal of the solid waste, but they did not prepare any program for the recycling and recovery of the solid wastes at that time. Later at 2005, the Regulation about the recoverable packaging materials was published by the Ministry of Forestry and Environment (Ministry of Environment and Forestry, 2005).

In Turkey the traditional practice for the disposal of solid wastes has been dumping them either in seas or into "open dumps". There are more than 3000 open dumps in Turkey. They are neither compacted nor covered. The open dumps do not have any leachate or methane gas collection systems and they continuously pollute the environment and have the potential to cause serious problems to the public health. Serious accidents like sliding down of the solid wastes piled at a wrong slope and the explosion of the methane gas causing the death of the 39 people at the Ümraniye Open Dump in İstanbul at April 28, 1995 is an example of the disasters that these open dumps are causing. Another accident in İstanbul was the sliding of a huge mass of solid waste from the Kemerburgaz Open Dump to the by-passing road at May 23, 1996. The existing open dumps should be immediately closed and rehabilitated in order not to face more severe accidents in future.

Waste Management in the Metropolitan City of İstanbul

İstanbul is placed on two continents and acts as a bridge between the Europe and the Asia. Handling the solid waste properly is very significant especially for the cities like İstanbul whose population is continuously increasing because of the migration from rural areas and other cities. Today the population of İstanbul has reached to almost 15 million and is expected to reach to17 million by the year 2020. As a result of the increase in the population, 10 000 tons of municipal solid waste is generated per day in the city of İstanbul. 6 500 and 3 500 tons of these solid wastes are generated in the European and the Asian Sides of İstanbul respectively. The residential areas, hotels, offices, commercial areas, street cleanings, parks and recreational areas, are the sources of the solid wastes generated. The annual waste generation estimations for the future are given in Table 3. According to the Table 3, the solid waste production per capita is 0.66 kg/day in the European Side while it is 0.56 kg/day in the Asian Side and the average for the whole city is 0.63 kg/day (Curi, Ekinci and Kocasoy, 1998).

Table 3. Annual solid waste production in İstanbul (millions of tones) (Curi, Ekinci and Kocasoy, 1998)

Location	Years			
	1990	2000	2010	2020
European Side	1.11	1.71	2.34	3.01
Asian Side	0.55	0.97	1.35	1.74
Total	1.66	2.68	3.69	4.75

The physical and the chemical properties of the solid wastes of İstanbul change from region to region and also from season to season. Therefore the composition of the solid waste generated in İstanbul is determined by dividing the city into five regions according to the socio-economic level of the inhabitants and the type of the fuel used for heating in the district.

Region 1 : Commercial districts.
Region 2: Low socio-economic level, shanty houses, using coal or wood for heating. 30 % of the population is living in this region.
Region 3 : High socio-economical level, using solid fuel. 20 per cent of the population is living in this region.
Region 4 : High socio-economical level, using liquid fuel. 20 per cent of the population is living in this region.
Region 5 : Normal-average socio-economical level, using solid fuel. 30 per cent of total population is living in.

The unit weight and the composition of the solid wastes generated at different regions are given in Tables 4 and 5 respectively.

Table 4. The unit weight of the solid wastes in different regions and months (kg/m^3)

Month/Year	Region 1			Region 2			Region 3			Region 4		
	1981	1992	1996	1981	1992	1996	1981	1992	1996	1981	1992	1996
April	451	366	409	445	273	409	566	196	164	313	176	139
September	451	302	239	403	240	239	302	197	131	353	177	175

Table 5. The composition of solid waste generated at different regions (Baştürk, 1997)

Region	Water Content (%)	Organic Material (%)	C/N	Calorific Value (kJ/kg)
1	49.8	54.7	30.7	3 325
2	37.4	36.5	33.3	3 125
3	38.4	40.7	35.7	3 371
4	57.6	65.6	22.6	3 841

Wastes of İstanbul had been dumped into the seas until 1953. Then the disposal of the solid wastes into open dumps became a common practice till the publication of the Solid Waste Control Regulation in 1991. İstanbul had five open dumping areas, named Kemerburgaz, Halkalı, Ümraniye, Aydınlı, Yakacık and the Princess Islands. The solid wastes of the islands were dumped into the four dumping areas at the islands because the Municipality of did not collect the solid wastes of the Princess Islands although it was its responsibility. Lately the solid wastes of the islands have been transported to the dumping areas of the main land.

According to the Solid Waste Control Regulation the district municipalities are responsible for the collection and transportation of all municipality solid wastes to the transfer stations while the Metropolitan Municipality is responsible only for the collection of solid wastes from the main streets, public parks and then the management of the all solid wastes after they are brought to the transfer stations. The Metropolitan Municipality is also responsible for the construction and the operation of the final disposal areas.

After the publication of the Solid Waste Control Regulation in 1991, open dumping areas in İstanbul were legally closed and the rehabilitation activities were completed. Also the Metropolitan Municipality has started to construct transfer stations and sanitary landfills according to the international standards. Six transfer stations and two sanitary landfills have been constructed since 1995.

The transfer stations, Halkalı, Baruthane and Yeni Bosna with 53, 65 and 50 silos respectively and a total capacity of 7 500 ton/day are located at the Asian Side. The other three transfer stations, Aydınlı, Hekimbaşı and Küçük Bakkalköy, having 55, 69 and 45 silos and the total capacity of 7500 ton/day are in the European Side. The volume of the silos is 32m^3. The distance of the transfer stations to the sanitary landfills are between 38 and 51 kilometers. Collected solid wastes are brought by trucks to the transfer stations and emptied into the vertical silos and pressed reducing the volume by 20 per cent and then the silos are carried to the solid waste final removal areas.

There have been two sanitary landfills in operation in İstanbul since 1995. One, called Odayeri, is located in the European Side and the other one, named Kömürcüada, is at the Asian Side. Odayeri sanitary landfill has an available area of 14 ha, but it has the project area of 2 000 ha. for the future developments. It has the capacity of storing 4 500 ton/day solid waste. The area of the other sanitary landfill, Kömürcüada, is 6 ha, but additional 50 ha is reserved for the future. The target is 198 ha for the next 25 years. The base of the landfill areas was made impermeable (10^{-8}) by a layer of clay of 60 cm thickness and a high density polyethylene (HDPE) membrane of 2 mm thickness. Leachate collection pipes were installed on the impermeable layer and the collected leachate is transferred to the treatment plants. Also gas collection chimneys were placed at every 50 m and it is planned to convert the collected gas into electric energy in the future.

Compacted solid wastes in silos are transported from the transfer stations to the sanitary landfills by trucks and emptied to specially built platforms from where they are placed in prepared cells by bulldozers and are pressed by compressors. At the end of the daily storage operation, the cells are covered with soil. Every day 4 500 ton of waste is brought to Odayeri and 3 000 ton of solid waste is brought to the Kömürcüada sanitary landfill. The rest of the solid waste is dumped in open dumps.

The industrial solid wastes are not collected by the Municipality. It is the responsibility of the industry itself to collect and transport their domestic solid waste to the disposal sites and their hazardous wastes to the incineration plant located at Kocaeli. Since there was not any efficient control, most of these hazardous wastes have been transported and disposed in the open dumps that municipality wastes were dumped up to recent times.

The health-care wastes on the other hand are collected and transferred to the incineration plant separately by the Municipality. The management of the health-care wastes in Turkey is conducted according to the Turkish Medical Wastes Control Regulation that was adopted in 1993 and revised in 2005 (Ministry of Turkey, 1993; Ministry of Environment and Forestry of Turkey; 2005).

Recycling and Recovery of the Solid Wastes in Turkey

The developed countries, realizing that the natural resources are not limitless and energy shortage is becoming more and more significant, try to find new efficient methods for the recovery and recycling of valuable materials thrown away as solid waste. On the other hand the economically developing countries do not realize that having recycling and recovery programs will help the development and strengthening of the industry and the economy. Recovery of materials such as iron, steel, copper, lead, paper, plastic and glass will decrease the amount of the foreign currency paid for the import of these materials from other countries. Another advantage of the recovery of valuable materials is the saving energy. There is no doubt that recycling of these valuable materials contribute to the economy of the country. Presently in Turkey the recycling/recovery of valuable materials from the solid waste is conducted in a very primitive way. The separation of valuable materials is conducted in a few steps such as;

- glass bottles and newspapers are collected separately at residential areas and sold to the salesman. In the Metropolitan cities this process is conducted by the doorkeepers;
- solid wastes collected in the street containers are sorted by the scavengers and sold to the companies. During this process the solid waste is spread around contaminating the environment. The wastes sorted are also contaminated with the oil and food remains.
- solid wastes transported to the disposal areas are sorted by people working in the open dumps at very unhealthy conditions and sold to the owner of the disposal area to be sold later to the factories processing these materials. Since these materials are also contaminated some of them can not be recycled/recovered and the remaining ones should be cleaned before processing which increases the cost of process (Curi, 1994).

The sorting process applied is not effective. All these materials should be collected separately at source and transferred to the recycling/recovery centers in order to gain economic contribution. Most of the recyclable/recoverable valuable materials are wasted and disposed in the landfill areas shortening the life time of the disposal site.

Only a small amount of these recyclable/recoverable materials are recovered and Turkey is importing scrap wastes from other countries. According to a research conducted by the author, even if the 70% of the recoverable materials of the solid wastes of İstanbul are recovered, it will supply the local demand for scrap and for some items like paper will exceed the demand and can be exported. Thus besides having income from the recovery of wastes, Turkey will save foreign currency for the import of the wastes to supply the local demand.

Economically developed countries developed many methods for recycling the wastes and reusing them with the view of preventing the waste of resources, improving the living conditions and avoiding any possible energy crisis to arise soon. With this purpose, “Regulation on Packaging and Packaging Waste” has been enacted after being published in the Official Gazette dated 30.07.2004 with No. 25538 in order to reuse and recycle the packaging wastes in Turkey. Within the scope of this Regulation, the obligations and targets of market providers, municipalities and the public are determined in terms of where, how, when and under which type of collection the packaging wastes will be collected, where they will be separated, where the recyclable materials will be processed, how the consumers will be trained, opinions and criticism of the consumers, establishment of the e-packaging line, training of collectors, integration of the street collectors into the system as well as the benefits to be provided by the collection of packaging wastes. By the publication of this Regulation, packaging waste is aimed to be sorted at source and collected by the private companies which has license from the Ministry of Environment and Forestry (Ministry of Environment and Forestry, 2004).

The data about the recyclable/recoverable materials in the metropolitan cities of Turkey are given in Tables 6 and 7.

Table 6. The percent distribution of the recyclable/recoverable materials in the metropolitan cities of Turkey (Summer) (DIE, 1995; Metin, *et al*, 2003)

City	Paper and Cartoon (%)	Metal (%)	Glass (%)	Nylon (%)	PET and PVC (%)	Textile (%)	Battery (%)	Rubber (%)
Adana	81.80	3.15	4.69	4.85	1.16	3.15	0.07	1.13
Ankara	58.33	8.56	12.52	11.23	4.16	3.00	0.16	2.04
Bursa	45.98	8.50	12.00	15.00	8.99	7.99	0.12	1.42
Diyarbakır	39.36	11.89	8.00	20.91	9.00	3.91	0.69	6.27
Gaziantep	39.81	7.99	21.00	20.63	3.16	5.73	0.33	1.34
İskenderun	36.42	5.60	25.79	18.70	2.09	7.13	011	4.17
İstanbul	48.11	8.27	15.91	14.81	7.08	4.20	025	1.37
İzmir	44.94	10.04	24.70	11.76	0.06	3.68	0.47	1.35
Kayseri	34.67	16.46	8.80	15.87	11.70	2.80	1.76	7.95
Konya	33.76	15.89	12.88	21.12	6.15	9.04	0.36	0.80
Samsun	43.76	5.23	16.73	12.12	5.75	11.82	0.31	4.30

Table 7. The percent distribution of the recyclable/recoverable materials in metropolitan cities of Turkey (Winter) (DIE, 1995)

City	Paper and Cartoon (%)	Metal (%)	Glass (%)	Nylon (%)	PET and PVC (%)	Textile (%)	Battery (%)	Rubber (%)	Bones (%)
Adana	36.9	9.9	22.3	11.8	4.6	6.5	0.02	4.27	3.42
Ankara	51.7	8.8	16.4	14.7	5.2	1.9	0.01	0.150.	0.00
Bursa	29.9	13.2	30.2	15.3	6.0	2.8	0.22	2.08	0.23
Diyarbakır	14.5	5.9	19.7	7.5	4.8	3.7	4.56	7.01	32.38
Gaziantep	11.29	30.9	15.0	14.20	10.4	7.6	3.53	2.25	5.01
İskenderun	27.5	10:0	23.3	12.6	9.1	10.2	1.06	2.45	3.91
İstanbul	45.3	10.8	15.5	13.0	7.3	4.3	0.54	1.98	1.27
İzmir	42.87	7.2	23.6	14.4	4.6	5.7	0.05	1.26	0.34
Kayseri	16.6	29.6	12.0	22.1	11.3	3.4	0.57	1.68	2.93
Konya	24.4	9.5	20.1	17.8	2.8	16.5	0.87	2.76	5.25
Samsun	29.2	10.5	31.2	17.2	5.2	4.6	0.51	0.64	0.00

NATIONAL SOLID WASTE MANAGEMENT POLICY OF TURKEY

The State Planning Department and the Ministry of Environment established a National Policy about the management of solid wastes within the scope of the National Environmental Plan at 1998. In the establishment of the National Policy the following suggestions are made to improve the existing situation in the solid waste management:

- Legislation :
    - Legislation about the solid waste management should be reviewed, contradictions with the other regulations should be corrected and the authorities and the responsibilities of different institutions should be clearly identified;
    - Legislation should be made to be in compliance with the European Union Directives;
    - Application of the legislation and the regulations should be strictly controlled and the violators should be punished;
    - Environmental Impact Assessment (EIA) studies should be required before the selection of the location of the sanitary landfill areas.
- Inventory:
    - Data collection and analyze methods should be standardized and a data bank should be established;
    - Collection of data about the solid waste should be continued.

- Waste Minimization:
    - The "Solid Waste Disposal Tax" should be charged according to the amount of the solid waste generated;
    - Recycling/recover programs should be prepared according to the Regulation on Packaging and Packaging Waste and recycling/recovery centers should be established;
    - Public should be educated and public awareness should be created to minimize the waste generation and to use recyclable/reusable materials.
- Final Disposal of Solid Wastes :
    - Before deciding to construct incinerators the composition and the calorific values of the solid wastes to be incinerated should be determined.
    - Composting solid wastes should be encouraged in the rural areas;
    - Studies should be made to determine the soil quality to find out the demand for the compost;
    - Cost/benefit analyses should be made before deciding the construction of compost plants;
    - Conversion of gasses generated at the sanitary landfill areas to the energy should be applied after the cost/benefit analysis should be made;
    - Necessary funds should be established to construct the sanitary landfill areas as required by the Solid Waste Control Regulation;
    - An operational and control method should be decided for the sanitary landfills and incinerators.
- Rehabilitation of Open Dumps :
    - The risks of the existing open dumps should be determined;
    - According to the risks involved a rehabilitation program should be prepared (immediately, in the short run, in the long run);
    - The necessary finance should be supplied for the rehabilitation of these areas.
- Organizational Structure:
    - An organizational structure should be made for the efficient collection, transportation and disposal of solid wastes (Curi, Ekinci, Kocasoy, 1998).

CONCLUSION

Management of the solid waste is still continuing to be a problem for all the countries in the world. Since handling and disposal of solid waste is an expensive process, most of the countries are trying to minimize the generation of solid waste, encouraging the recycling/recovery of valuable components and conversion of them into useful products such as compost or energy. Consequently the amount of the solid wastes to be dumped will be less which means that the expenses of the solid waste management will be less. The most common and the cheapest method to dispose the solid waste are landfilling. Selection of the sanitary landfill area should be made carefully after conducting Environmental Impact Assessment (EIA) studies and the sanitary landill should be prepared and constructed according to the standards in order not to cause any environmental problems. An integrated solid waste management should be prepared and applied in order to minimize the usage of natural resources solid waste generated and to handle the solid wastes efficiently.

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MANAGEMENT OF HAZARDOUS ROAD DERIVED RESPIRABLE PARTICULATES USING MAGNETIC PROPERTIES OF TREE LEAVES

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The magnetic properties of tree leaves along with their ecological, economical and aesthetic importance can be used to control road derived respirable particulates. Isothermal remanent magnetization (IRM300 mT) of three different tree leaves viz. Mango (Mangifera indica), Sisso (Dalbergia sisso) and Banyan (Ficus benghalensis) were determined and IRM300 mT normalized for the leaf area. The normalized 2-D magnetization of leaves as shown by results is dominantly controlled by leaf morphology and traffic density. Banyan leaf has highest 2-D magnetization and Sisso leaf having least 2-D magnetization suggesting greater ability of Banyan tree leaves to reduce magnetic particulates .The particle size of the magnetic grains falls in the category of PM2.5, a particle size hazardous to human health due to its capacity to be inhaled deeply into the lungs.

Keywords: Magnetic properties; IRM300 mT; Aesthetic; Keystone species; Background magnetization.

1. Introduction

It has been now well established that particulate matter (PM) in urban air contribute significantly to adverse health effects (Pope et al., 2002; WHO, 2003; USEPA, 2004). A strong positive correlation have been demonstrated between fine-grained (<10 mm) particulate matter and the risk of respiratory and circulatory morbidity and mortality. Magnetic minerals derived from vehicular combustion and street-trams are mainly maghemite and metallic iron grain having size range of 0.1– 0.7 mm (Muxworthy et al., 2002). Ultrafine (<0.1 mm, PM0.1) and aggregate (<1 mm, PM1.0) particulates are confirmed to have serious health effects than fine (<2.5 mm, PM2.5) materials (Harrison and Yin, 2000; Wichmann and Peters, 2000). Moreover, in aerosols, magnetite is associated to other heavy metals like zinc, cadmium and chrome (Georgeaud et al., 1997) and to mutagenic organic compounds (Morris et al., 1995), also dangerous to human health.

In atmosphere, magnetic minerals are derived from combustion processes, such as industrial, domestic or vehicle emissions (Hunt et al., 1984; Flanders, 1994) or from abrasion products from asphalt and from vehicles brake systems (Hoffmann et al., 1999). The magnetic fine particles mostly consist of spherules and grains of irregular shapes that contains variable amounts and grain size of magnetite and hematite, which depends upon the fuel type, and the temperature of combustion (Matzka and Maher, 1999). Magnetic properties of soils (Hay et al., 1997; Hoffmann et al., 1999; Hanesch et al., 2001; Leocoanet et al., 2001; Shu et al., 2001), filters (Muxworthy et al., 2001; Xie et al., 2001) and leaves (Georgeaud et al., 1997; Matzka and Maher, 1999) have been used for identifying spreading of pollution derived from vehicular or industrial emissions.

Iron often occurs as an impurity in fossil fuels during industrial, domestic or vehicle combustion, carbon and organic material are lost by oxidation whilst the iron forms a non-volatile residue, often comprising glassy spherules (due to melting). These spherules are magnetic, with magnetizations easily measurable. It has been shown that combustion processes simultaneously release hazardous substances and magnetic particles into the atmosphere. In addition to these combustion-related particles, vehicles, via exhaust emissions and abrasion/corrosion of engine and/or vehicle body material (Olson and Skogerboe, 1975), can generate non-spherical magnetite particles.

In bio-monitoring studies the spatial mapping of PM loads via environmental magnetic techniques has been shown to be quick, non-destructive and inexpensive (Matzka and Maher, 1999; Jordanova et al., 2003; Moreno et al., 2003; Hanesch et al., 2003; Urbat et al., 2004; Gautam et al., 2005) Leaves with large surface areas per unit of weight and favorable surface properties having waxy coating and long lifespan, like conifer needles or evergreen tree leaves, are considered as good accumulators of particulate matter from the atmosphere (Alfani et al., 2000, Freer-Smith et al., 1997). Measured magnetization levels within a geographical region depend on the type of plant surface, its age, and its surface characteristics, as well as on local emission levels and distance from emission source (Flanders, 1994).

2. Sampling methods

The city of Varanasi (82° 15’E to 83° 30’E and 24° 35’N to 25° 30’N, India), and its surrounding area, is characterized by little industry but, due to more than 10 million inhabitants, a substantial volume of traffic exists. The leaf samples were collected from national highway having high traffic density, rural road having low traffic density and garden in the city.

Mango (Mangifera indica), Banyan (Ficus benghalensis) and Sisso (Dalbergia sisso) were selected for sampling. Leaves were collected from one species of tree to avoid the possibility of species-dependent differences in dust absorbency. Each sample consisted of six leaves, taken from the outer canopy at a height of 2-3 m and packed into 10 cc plastic sample pots. To maintain uniformity in leaves age, only the oldest leaves of the newest twig growth were collected. To determine the reliability of the method, two samples were taken for every sampling position and their mean value and deviation calculated. Consequently, the calculated magnetizations for each sample point are based on the measurement of 12 leaves.

3. Measurements

The samples were magnetized with a pulsed magnetic field of 300 mT, the isothermal remanent magnetization (IRM300 mT) was then measured with a CCL cryogenic magnetometer having the sensitivity of 10-10Am2 (the weakest leaf samples had magnetizations of ~10-9 Am2). Area of individual leaf was calculated by digitizing their computer-scanned images.

The 2D-magnetization was calculated as the magnetic moment per leaf area (and not per unit mass since magnetic materials in plants is found mainly on the surface), in units of Amperes (A=Am2/m2). A small number different tree leaves, representative of different sampling locations were used to measure 2-D magnetization. After measurement of 2-D magnetization the leaves were cleaned with water, detergent and ultrasonics, to determine their ‘background' magnetization.

4. Results

The 2-D values of leaves from different trees at different locations and their background magnetization are shown in Table 1. The magnetizations values are least for garden trees, higher for rural roadside trees and highest for trees nearby to national highway. This magnetic pattern is in accordance with the report of Impens and Delcarte (1979) for total dust interception by roadside trees. Maximum 2-D values were for Banyan leaves and least for Sisso leaves. Percentage IRM300 mT after cleaning by detergent and subsequent ultrasonic clearing removes 88%, 84% and 85% for Banyan, Sisso and Mango leaves respectively. The residual magnetization may be due to imperfect cleaning of the leaf, incorporation of some dust particles, or a non-airborne, biogenic magnetic contribution.

5. Discussions

The magnetic properties of roadside tree leaves are due to magnetic particles present in road dust. These particles are primarily non-spherical which comes from rust and attrition of vehicles, pipes and other iron and steel surfaces (Flanders, 1994). Moving vehicles would re-suspend these magnetic particles to be deposited on leaf surfaces. Thus, roads having high traffic density would re-suspend more road dust leading to higher magnetization of tree leaves. The required magnetic field to demagnetize IRM300 mT is greater than 40 mT, which indicate that the size of magnetic particle ranges from 0.03-0.3 μm (Haider et al; 1996).

As shown by results Banyan leaves have high magnetization indicating their ability to capture more road-derived particulates. Their ability to capture more particulates is because of large surface area, waxy coating, ovate shape, long life span and thick nature of leaves. These properties are missing in Sisso leaves and thus have poor dust interception efficiency. Leaving aside large surface area and ovate structure, other leaf properties are found in Mango leaves and thus better than Sisso for road dust interception.

Besides their particulates removing capability, these trees can be suggested for plantation because of their ecological, aesthetic and economical importance. Banyan tree is a keystone species and have high ecological importance. In addition, Banyan tree have much religious importance. On the other hand, both Sisso and Mango have economical importance.

Table 1

IRM300 mT values of sampled leaves of different trees for different locations versus ‘background' IRM300 mT of the subsequently cleaned leaves. Leaf samples from trees nearby to highway show much higher 2D-magnetizations than those from the rural road and garden.

Sample location	2-D magnetization (10^{-6} A)			2-D magnetization after cleaning of leaf (10^{-6} A)			% magnetization removed by clearing		
	Banyan	Sisso	Mango	Banyan	Sisso	Mango	Banyan	Sisso	Mango
1.Remote rural road	15.53	12.53	13.13	1.85	1.97	1.97	88.08	84.27	84.99
2.Company garden (Maidagin)	12.18	10.30	11.33	2.67	2.07	2.37	78.07	79.9	79.08
3. National highway	69.78	55.28	57.38	15.42	12.31	13.51	77.9	77.7	76.45

6. Conclusions

1. The magnetization of leaves is controlled by their morphology, surface area, surface characteristics and age.
2. High leaf magnetizations are found for trees which are nearby to highway and least for garden trees indicating that vehicle and road derived particles are the cause of leaf magnetization.
3. The grain size of the particles is of the order of 0.3-3 mm, a size of potential hazard to human health because of its capacity to be respired deeply into the lungs.
4. Keeping aesthetic, ecological and economical importance in mind Banyan tree is best to control road and vehicles derived magnetic particulates.

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RAPID MEASUREMENT OF APPLE VINEGAR’S ADDED SODIUM METABISULFITE BY ULTRASONIC METHOD

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Ultrasonic velocities and densities of sodium metabisulfite+apple vinegar in the temperature range 293.15-313.15K have been measured. Changes in ultrasonic parameters as changes sodium metabisulfite compositions in apple vinegar were studied. Change in concentration of 0.001 molal of sodium metabisulfite+ apple vinegar cause quite change of ultrasonic parameters. These results indicated that the power and usefulness of ultrasonic measurement to monitor sodium metabisulfite in apple vinegar.

1. Introduction

Sodium metabisulfite is most generally used as a preservative in food products, such as biscuit, chocolate, sausage, jam, salami, apple viegar’s and in many alcoholic liquor like as beer, wine, champagne. Recent studies showed that sodium metabisulfite can induce chromosomal aberration and sister chromatic exchanges in human lymphocytes [Rencüzoğullari et.al., 2001]. These suggested that sodium metabisulfite has cytotoxic and genotoxic effect. Therefore, the knowledge of sodium metabisulfite compositions in apple viegar is of particular interest. Spectroscopic and chromatographic methods are used to monitor quality of apple vinegar. These methods have specific drawbacks, for example high cost and time consumption. In recent years, Ultrasonic method has been applied to food industry (McClements, 1991; Pendse, Strout, Shanna, 1993; Dukhin, & Goetz, 1996a; Dukhin, & Goetz, 1996b; Dukhin, Goetz, 1996c; McClements, 1997; Dukhin, & Goetz, 1998; Mohanan et al., 2002; Roger, Balaban & Teixeira, 2003; Resa, Elvira, & Montero de Espinosa, 2004). In the ultrasonic method, the attenuation and/or ultrasonic velocity are measured. Ultrasonic velocity, compared to attenuation, is more sensitive to variation of chemical compositions and temperature.

In this work, we measure the densities and ultrasonic velocity of sodium metabisulfite+ apple vinegar from T=(293.15 to 313.15K) at intervals of 5K over the entire composition range. The isentropic compressibility, specific acoustic impedance and Rao’s molar sound function were calculated from experimental values of densities and ultrasonic velocity. The results are fitted to linear type equations with standard deviation are given in table 2.

2. Materials and methods

Pure apple vinegar was obtained from Kükrer Gıda Ltd. Şti (Eskişehir, Republic of Türkiye). Sodium metabisulfite (E-223) were used as received without further purification. The samples in this research were determined by measurement of mass. All the mass measurements were prepared using electronic balance (Scaltec, SBC22) accuracy 0.01mg. The densities and speed of sound of the samples were measured using a vibrating tube densimeter and sound analyzer, Anton Paar DSA-5000, automatically thermostat at □ 0.01 K. These measurements ware repeated three times.

This paper shows last measurement. The calibration of the apparatus was carried out with air and deionised double-distilled water. The uncertainty of the measurements was estimated to be ±5×10−6 gcm−3 for density and ±0.5ms−1 for speeds of sound; the respective reproducibility was ±1×10−6 gcm−3 and ±0.01ms−1. The precision of the temperature measurements was ±0.001 K.

3. Results and discussion

Specific acoustic impedance, isentropic compressibility and Rao's molar sound function were calculated using the experimental data density and ultrasonic velocity by the following equations.

The specific acoustic impedance Z was calculated using the equation

$$Z=\rho u \qquad (1)$$

Where ρ and u are the densities and speeds of sound of solution, respectively.

The isentropic compressibility, κ_s, has been calculated using the Newton Laplace's equation:

$$\kappa_s = \frac{1}{\rho u^2} \qquad (2)$$

Rao's molar sound functions (R) (Vigaureux, 1952) was calculated with the expression

$$R=u^{1/3}/\ \rho \qquad (3)$$

These acoustical parameters were fitted to equations of type

$$y=y_o+Aw \qquad (4)$$

where y_o and A are empirical parameter and w mass concentration (%).

Both the concentration and temperature dependence of u, Z, κ_s, and R can be used to following equation :

$$Y= (Y_o+A_1w) + (Y_1+A_2w) (T-273.15) + (Y_2+A_3w)(T-273.15)^2 +(Y_3+A_4w)(T-273.15)^3+(Y_4+A_5)(T-273.15)^4 \qquad (5)$$

Parameter Y_n and A_n are obtained from the least squares methods and given in Table 3.

The standard deviation was calculated using the expression

$$\sigma = \left[\frac{\sum_{i}^{N} \left(Y_{exp} - Y_{pred} \right)^2}{N - m} \right]^{1/2} \tag{6}$$

where Y is the value of the property, N is the number of experimental data and m is number of coefficients.

Table 1
Densities, speeds of sound, specific acoustic impedance, isentropic compressibility and Rao's molar sound functions for metabisulfite+apple vinegar.

Concentration (molal)	ρ (kgm^{-3})	u(ms^{-1})	Z(kgm^{-2}s^{-1})	K_s(TPa^{-1})	R (ms^{-1})(m^{3}mol^{-1})
293.15K					
0.0005	999.647	1485.08	1484556	453.58	0.011413
0.001	1000.585	1486.97	1487840	452.00	0.011407
0.002	1002.515	1490.96	1494710	448.72	0.011395
0.003	1004.346	1494.33	1500824	445.89	0.011383
0.004	1006.222	1497.87	1507190	442.95	0.011371
0.005	1008.124	1501.48	1513678	439.99	0.011359
0.006	1009.944	1505.03	1519996	437.13	0.011347
0.007	1011.879	1508.3	1526217	434.41	0.011334
0.008	1013.771	1511.96	1532781	431.50	0.011322
0.009	1015.643	1515.08	1538780	428.93	0.011308
0.01	1017.329	1518.98	1545302	426.02	0.011299
Concentration (molal)	ρ (kgm^{-3})	u(ms^{-1})	Z(kgm^{-2}s^{-1})	Ks(TPa^{-1})	R (ms^{-1})(m^{3}mol^{-1})
298.15K					
0.0005	998.49	1499.02	1496756	445.70	0.011462
0.001	999.412	1500.76	1499878	444.26	0.011456
0.002	1001.276	1504.32	1506240	441.33	0.011444
0.003	1003.071	1507.22	1511849	438.85	0.01143
0.004	1004.899	1510.38	1517779	436.22	0.011418
0.005	1006.758	1513.57	1523799	433.58	0.011404
0.006	1008.6	1516.64	1529683	431.04	0.011391

Table 1 Cont.

0.007	1010.429	1519.59	1535438	428.59	0.011378
0.008	1012.277	1522.85	1541546	425.98	0.011365
0.009	1014.106	1525.56	1547080	423.70	0.011352
0.01	1015.756	1529.07	1553162	421.07	0.011342
Concentration (molal)	ρ (kgm^{-3})	u (ms^{-1})	Z ($kgm^{-2}s^{-1}$)	Ks (TPa^{-1})	R (ms^{-1})(m^3mol^{-1})
303.15K					
0.0005	997.077	1511.22	1506803	439.15	0.011509
0.001	997.98	1512.8	1509744	437.84	0.011503
0.002	999.804	1515.9	1515603	435.26	0.01149
0.003	1001.561	1518.46	1520830	433.03	0.011476
0.004	1003.351	1521.21	1526308	430.69	0.011462
0.005	1005.17	1524.02	1531899	428.33	0.011449
0.006	1006.972	1526.74	1537384	426.04	0.011435
0.007	1008.762	1529.28	1542680	423.87	0.011421
0.008	1010.568	1532.2	1548392	421.51	0.011408
0.009	1012.358	1534.53	1553494	419.48	0.011394
0.01	1013.969	1537.66	1559140	417.11	0.011383
Concentration (molal)	ρ (kgm^{-3})	u(ms^{-1})	Z($kgm^{-2}s^{-1}$)	Ks(TPa^{-1})	R (ms^{-1})(m^3mol^{-1})
308.15K					
0.0005	995.449	1521.71	1514785	433.83	0.011555
0.001	996.331	1523.15	1517562	432.62	0.011548
0.002	998.12	1525.88	1523011	430.31	0.011534
0.003	999.843	1528.07	1527830	428.33	0.01152
0.004	1001.595	1530.46	1532901	426.25	0.011506
0.005	1003.378	1532.93	1538108	424.12	0.011491
0.006	1005.144	1535.29	1543188	422.08	0.011477
0.007	1006.897	1537.5	1548104	420.13	0.011463
0.008	1008.666	1540.08	1553426	417.99	0.011449
0.009	1010.419	1542.06	1558127	416.19	0.011434
0.01	1011.995	1544.72	1563249	414.12	0.011423
Concentration (molal)	ρ (kgm^{-3})	u(ms^{-1})	Z($kgm^{-2}s^{-1}$)	Ks(TPa^{-1})	R (ms^{-1})(m^3mol^{-1})
313.15K					
0.0005	993.623	1530.62	1520859	429.58	0.011598
0.001	994.482	1531.97	1523517	428.45	0.011592
0.002	996.242	1534.35	1528584	426.37	0.011577
0.003	997.932	1536.16	1532983	424.65	0.011562
0.004	999.649	1538.22	1537680	422.78	0.011548
0.005	1001.397	1540.39	1542542	420.85	0.011533
0.006	1003.127	1542.43	1547253	419.02	0.011518
0.007	1004.848	1544.27	1551757	417.30	0.011503
0.008	1006.582	1546.55	1556729	415.36	0.011489
0.009	1008.302	1548.21	1561063	413.76	0.011473
0.01	1009.844	1550.55	1565814	411.88	0.011461

Table 2

The correlation coefficients (γ), standard deviation (σ) and correlation equations between acoustical parameters and concentrations (m) of metabisulfite+ apple vinegar.

Parameters	Correlation equation	γ	□
293.15K			
□ (kgm^{-3})	□ = 998.7398+1871.4765m	1.0000	0.06
u(ms^{-1})	u = 1483.6286+3533.7883m	0.9998	0.22
Z(kgm^{-2}s^{-1})	Z = 1.4816x10^{6}+6.3736x10^{6}m	1.0000	193.0
□$_s$(TPa^{-1})	□$_s$ = 454.6683-2886.8545m	0.9997	0.23
R(ms^{-1})(m^{3}mol^{-1})	R = 0.0114-0.0122m	0.9998	0.0000
298.15K			
□ (kgm^{-3})	□ = 997.6017+1828.0294m	1.0000	0.05
u(ms^{-1})	u = 1497.7793+3124.4579m	0.9998	0.21
Z(kgm^{-2}s^{-1})	Z = 1.4941x10^{6}+5.913410^{6}m	1.0000	188.57
□$_s$(TPa^{-1})	□$_s$ = 446.6639-2576.4128m	0.9998	0.20
R(ms^{-1})(m^{3}mol^{-1})	R = 0.0115-0.0129m	0.9998	0000000
303.15K			
□ (kgm^{-3})	□ = 996.2096+1788.5914m	1.000	0.05
u(ms^{-1})	u = 1510.1544+2744.527m	0.9998	0.19
Z(kgm^{-2}s^{-1})	Z = 1.5043x10^{6}+5.4854x10^{6}m	1.0000	178.68
□$_s$(TPa^{-1})	□$_s$ = 440.0176-2304.0282m	0.9998	0.17
R(ms^{-1})(m^{3}mol^{-1})	R= 0.0115-0.0135m	0.9998	0.0000000
308.15K			
□ (kgm^{-3})	□ = 994.599+1752.2229m	1.0000	0.05
u(ms^{-1})	u = 1520.8419+2388.9935m	0.9997	0.19
Z(kgm^{-2}s^{-1})	Z = 1.5126x10^{6}+5.0838x10^{6}m	0.9999	187.99
□$_s$(TPa^{-1})	□$_s$ = 434.5827-2061.9834m	0.9998	0.16
R(ms^{-1})(m^{3}mol^{-1})	R = 0.0116-0.0141m	0.9999	000000
313.15K			
□ (kgm^{-3})	□ = 992.7882+1718.166m	1.000	0.05
u(ms^{-1})	u= 1529.9439+2060.121m	0.9996	0.20
Z(kgm^{-2}s^{-1})	Z = 1.5189x10^{6}+4.7101x10^{6}m	0.9999	198.38
□$_s$(TPa^{-1})	□$_s$ = 430.2305-1847.3289m	0.9997	0.15
R(ms^{-1})(m^{3}mol^{-1})	R = 0.0116-0.0146m	0.9999	0.000000

Table 3
The values of parameters of Eq. (5) with standard deviations, σ, for metabisulfite+ apple vinegar

Parametre	ρ (kgm^{-3})	u (ms^{-1})	Z ($kgm^{-2}s^{-1}$)	□$_s$ (TPa^{-1})	R (ms^{-1})(m^3mol^{-1})
Y_o	998.4861	1408.047	1451686	504.796	0.011228
Y_1	0.325	4.5637	-1491.5	-3.427	$7.98x10^{-6}$
Y_2	-0.0219	-0.0397	268.4036	0.055	$1.53x10^{-7}$
Y_3	$3.7.10^{-4}$	$4.98x10^{-6}$	-7.1583	-0.001	$-4.49x10^{-9}$
Y_4	-3.10-6	$1.02x10^{-6}$	0.0607	$3.04x10^{-6}$	$3.98x10^{-11}$
A_1	2417.346	5807.514	159926.1	-5136.95	-0.012601
A_2	-62.1917	-157.4816	1063071	187.301	0.000376
A_3	2.843795	3.1542	-60672.15	-5.569	$-3.04x10^{-5}$
A_4	-0.06688	-0.0575	1380.697	0.110	$7.76x10^{-7}$
A_5	$5.97.10^{-4}$	0.0005	-11.4276	-0.001	$-7.12x10^{-9}$
σ	0.049	0.204	193.08	0.18	$1x10^{-15}$

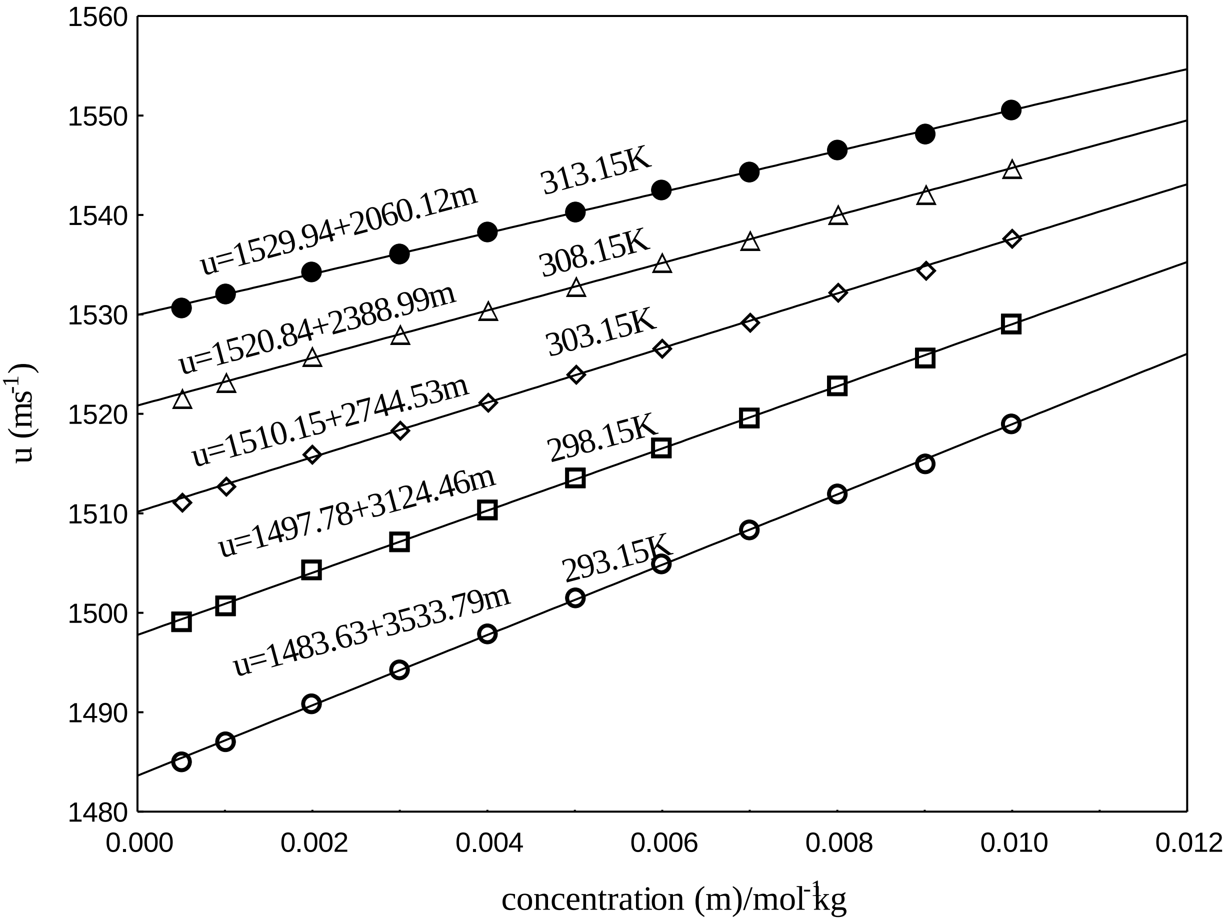

Fig 1. Variations of ultrasonic velocity with metabisulfite concentration in pure apple vinegar at different temperatures.

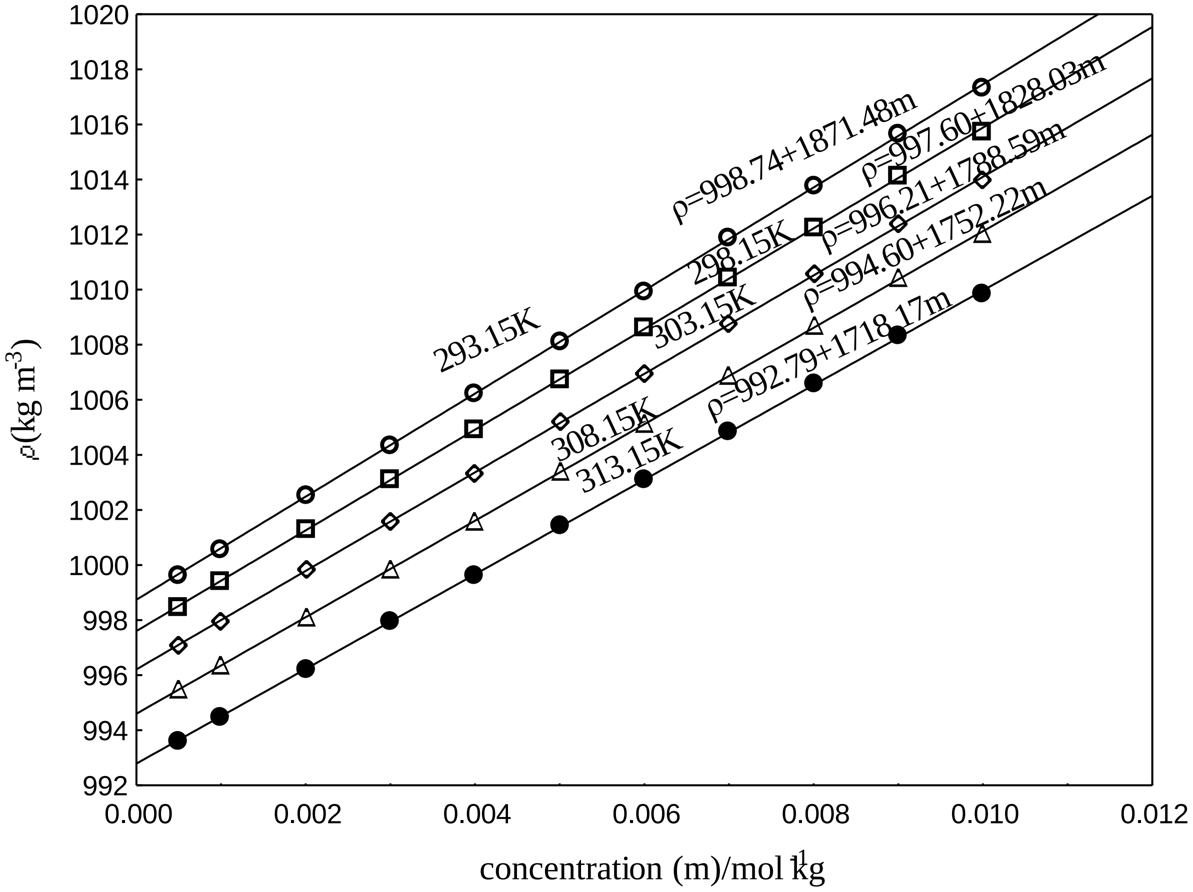

Fig 2. Variations of density with metabisulfite concentration in pure apple vinegar at different temperatures.

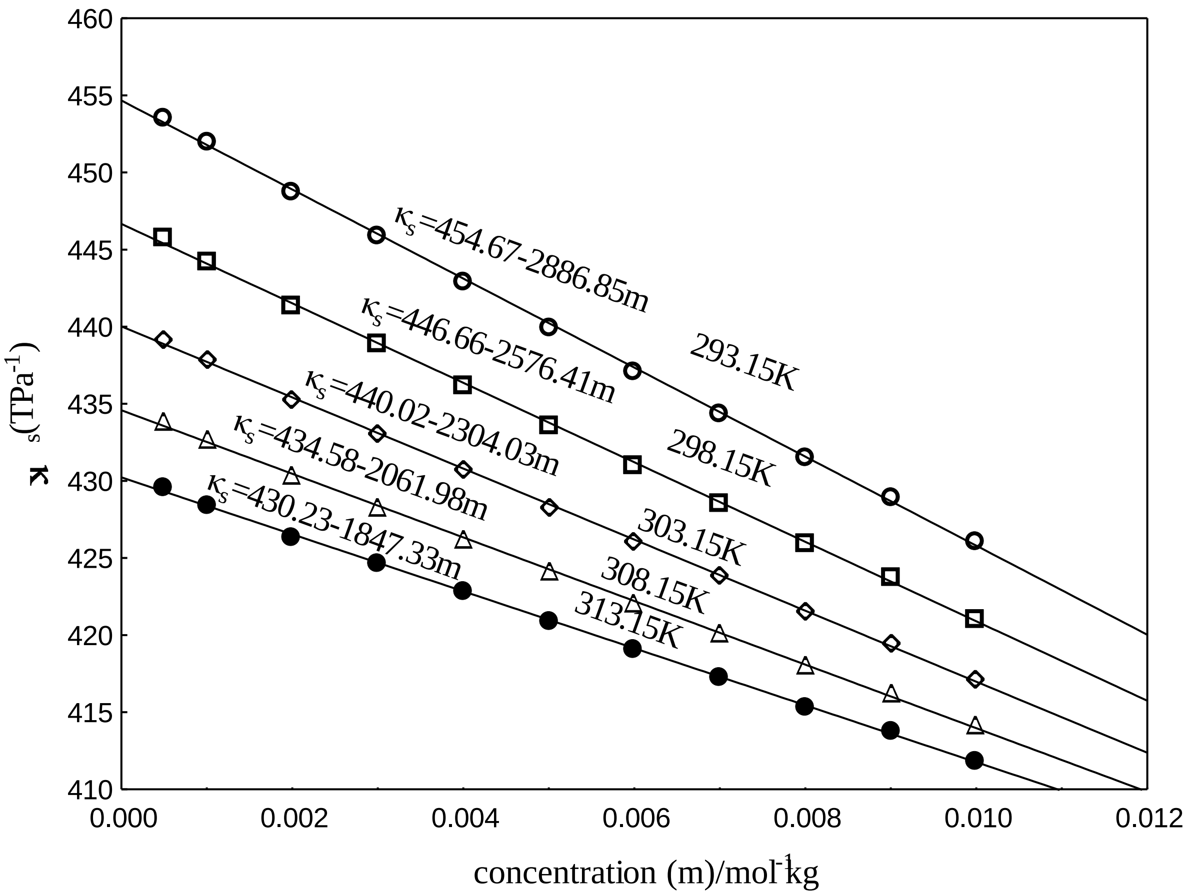

Fig 3. Variations of isentropic compressibility with metabisulfite concentration in pure apple vinegar at different temperatures.

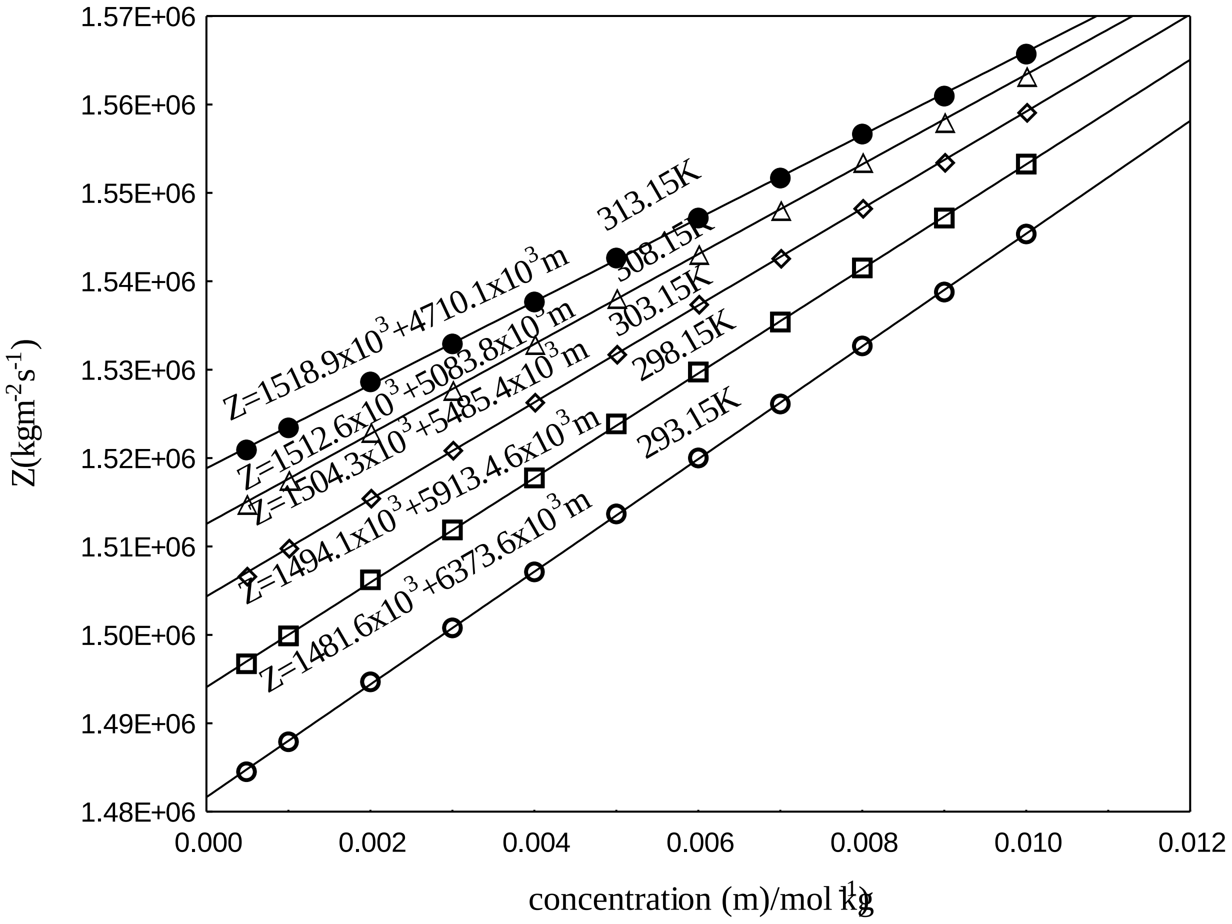

Fig 4. Variations of specific acoustic impedance with metabisulfite concentration in pure apple vinegar at different temperatures.

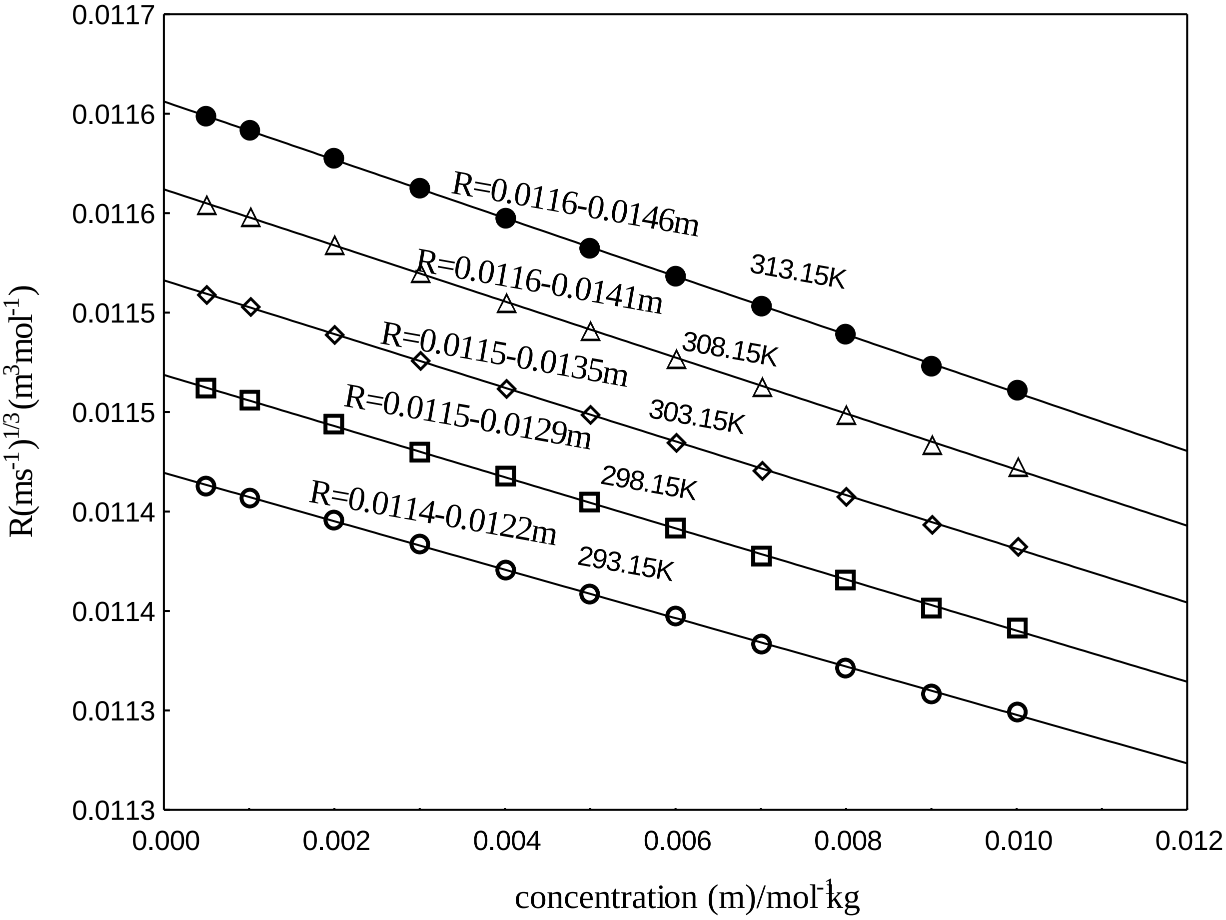

Fig. 5. Variations of Rao's molar sound functions with metabisulfite concentration in pure apple vinegar at different temperatures.

The densities, ultrasonic velocity, specific acoustic impedance, isentropic compressibility, and Rao's molar sound functions of sodium metabisulfite+ apple vinegar at different temperatures are given in Table 1.
Ultrasonic velocity, density, specific acoustic impedance, isentropic compressibility and Rao's molar sound function were plotted as a function of concentration in Figs. 1-5, respectively. The experimental results showed that the values of ρ, u and Z increase in harmony with the increase of the concentration of both studied systems. The values of R and κ_s decreased as the concentration in studied systems increased. For the system studied at a certain concentration, a decrease in κ_s was observed when the temperature raised. Furthermore, at a certain concentration, an increase in u, ρ, r and Z was observed when the temperature increased.

These parameters were correlated with concentrations and the correlation coefficients along with correlation equations and standard deviations, and they were listed in Table 2. From these equations, it is clear that there are excellent linear correlations between acoustic parameters and concentrations.
It was observed that change in concentration of 0.001molal sodium metabisulfite+ apple vinegar cause to the quite change of the values of speeds of sound, density, specific acoustic impedance, isentropic compressibility and Rao’s molar sound function. Acoustical parameters showed a good correlation and they can be used to monitor sodium metabisulfite in apple vinegar.

4.Conclusions

Change in concentration of 0.001molal sodium metabisulfite+ apple vinegar cause to the quite change of the values of ultrasonic parameters. We have show that existing ultrasonic-base instrument can measure ultrasonic properties of sodium metabisulfite+ apple vinegar. These results showed that ultrasonic ultrasonic-base instrument might be a suitable for the measurement of concentration of sodium metabisulfite+ apple.

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RECLAMATION OF SODIC SOILS THROUGH VERMITECHNOLOGY

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Present investigations were carried out during 1998-2000 at Shivri farm of Uttar Pradesh Bhumi Sudhar Nigam, Lucknow, India, to study the application of organic amendments in varied combinations in sodic soils thereby exploring the role of earthworms in soil reclamation. Among the combinations used in the present investigation, amendment [VWTGMEVC] has shown significant results. Sodic soil bioremediation was significant in plots treated with [VWTGMEVC] “vermiwash, tillage, green manure, mulch, earthworms and vermicompost”, suggesting qualitative improvement in the physical, chemical and biological properties of the soil. The average yield of wheat and paddy crop cycle during the two years of trial showed a significantly greater response in plots [VWTGMEVC], compared with the control, chemical and FYM plots. The reduced cost of cultivation, less cost-benefit ratio and higher net income from wheat and paddy cultivation has been recorded through Vermitech pattern compared with the use of chemical fertilisers.

Author Keywords: sodic soils; reclamation; sodicity; vermitech; vermicompost; soil fertilility

Introduction

The role of earthworms in soil formation and soil fertility is well documented and recognized (Edwards et al., 1995; Kale, 1998; Lalitha et al., 2000). An approach towards good soil management, with an emphasis on the role of soil dwellers like earthworms, in soil fertility, is very important in maintaining balance in an ecosystem (Shuster et al., 2000). Large extents of land in India are affected by sodic soils due to major degradation processes like salinization, water logging, chemical impairment and desertification (Dagar and Singh, 1994). The present investigation deals with the reclamation of sodic soil through the use of several organic amendments and highlights the role of earthworms in the process of soil restoration.

Materials and Methods

Experiments were conducted during 1998-2000 at Shivri farm of Uttar Pradesh Bhumi Sudhar Nigam, Lucknow, India, to study the process of reclamation of sodic soil through the application of several organic amendments in varied combinations and thereby to investigate the role of earthworms in soil reclamation.

Cultures of Perionyx excavatus Perrier (epigeic) and Lampito mauritii Kinberg (anecic) varieties of earthworms were set up in cement tanks (pH 9.5-10) and allowed to stabilise in sodic soil and were used in these experiments.Vermicompost and vermiwash were produced by using the process of vermicomposting with the above cultures.Other organic amendments like green manure (Sesbania sp.), farm yard manure (FYM) and mulch (Hay) were also used in experiments. Field experiments were carried out on sodic soil to study the effect of organic amendments on wheat (Triticum aestivum variety Raj 3765), paddy (Oryza sativa variety CSR-30).

The experimental area (1116.3m2) was divided into 30 plots, each of size 6.1m x 6.1m in triplicate for 10 treatments, applying combinations of organic amendments. The combinations of organic amendments set up for wheat and paddy are as follows:

1. [C] Control
2. [CHE] Chemical fertilisers and pesticides
3. [VW] Vermiwash @ 1kl/ha as soil application
4. [VWT] Vermiwash (1kl/ha) + Tillage
5. [VWTG] Vermiwash(1kl/ha) +Tillage + Green manuring.(S. aculeata @ 60 kg/ha)
6. [VWTGM] Vermiwash (1kl/ha) + Tillage + Green manuring (S. aculeata @ 60 kg/ha) + Mulching (4 tonnes/ha)
7. [VWTGME] Vermiwash(1kl/ha) +Tillage + Green manuring (S. aculeata @ 60 kg/ha) + Mulching (4 tonnes/ha) + Earthworm inoculation (P. excavatus and L. mauritii in the ratio 1:2)
8. [VWTGMEVC] Vermiwash (1kl/ha)+Tillage + Green manuring (S. aculeata @ 60 kg/ha) + Mulching @ 6 tonnes/ha + Earthworm inoculation (P. excavatus and L. mauritii in the ratio 1:2) + Vermicompost @ 6 tonnes/ha
9. [VCVWB] Vermicompost @ 6 tonnes/ha + Vermiwash as foliar spray and botanical extract for pest control
10. [FYM] Farm yard manure @ 6 tonnes/ha

Wheat and paddy were harvested after 90 days. Grain yield was recorded during the period of study. Epigeic and anecic earthworms in the ratio 1:2 per hectare were introduced in the channel of size 6m x 0.5m (mulched with paddy straw) in the centre of the plots after tillage and green manuring for sodic soil bioremediation. Earthworm numbers were recorded at the end of the experiments by handsorting (Stöckli, 1928). Soil samples were collected and were subjected to physico-chemical analysis (pH, electrical conductivity, organic carbon, total Kjeldahl nitrogen, potassium, sodium and calcium) (Jackson, 1958).Exchangeable sodium percentage (ESP) or sodicity was also calculated (Levy, 2000).Total cost of sodic soil reclamation and subsequent crop cycles (wheat, paddy and vegetables) were recorded in Indian Rupees (1US$= 48.41 Rupees and 1£= 75.11 Rupees as on 1st Dec 2002) and compared with the conventional method of reclamation along with crops cultivated by farmers during the experimental period.

Results and Discussion

In the experimental sites, at an average, the pH of sodic soil was 9.79, electrical conductivity 0.53 dSm-1, organic carbon 0.24 %, available nitrogen 537.6 kg/ha, available phosphate 9.0 kg/ha, available potassium 291.2 kg/ha and sodicity (ESP) 77.66, showing the poor fertility status of the soil indicating high level of sodicity that arise from anthropogenic processes like improper land management practices, deforestation and inadequate drainage (Rengasamy and Olssen, 1991; Fitzpatrick et al., 1994).

Among the various combinations used in the present investigation, the amendment [VWTGMEVC] has indicated maximum reduction in pH (Table 1). The application of green manure therefore enhances the reclamation action of organic manures like vermicompost by improving the physico-chemical properties of soil and by markedly decreasing soil pH. These observations correlate well with earlier studies (Patcharapreecha et al., 1990), on the effects of amelioration treatments of saline soils where application of compost was the most effective followed by mulching compared to that of gypsum in reclaiming saline soils. Amending soil with vermicompost showed alteration in pH as also reported earlier by Stratton et al., (1995). Introduction of earthworms in sodic soil resulted in the production of humic acid during decomposition, thereby reducing soil alkalinity in terms of pH; as was also observed by Patcharapreecha et al., (1990).

There was maximum increase in organic matter and organic carbon percentage in plots treated with [VWTGMEVC] (Table 1). Increased plant litter incorporation, improved aggregation, better aeration and water relationships and the development of mull characteristics were observed following the establishment of earthworms in sodic soils.

Available nitrogen was maximum in plots treated with [VWTGMEVC] (Table 1) when compared to the plots especially with amendment [CHE] and control [C]. Several workers have confirmed that adequate quantities of nitrogen was supplied by compost applications (Ozores-Hampton, et al., 1994). There was a significant reduction of sodicity (ESP) in plots amended with [VWTGMEVC] (Table 8) when compared to plots with amendment [CHE] and control [C]. The present investigation confirms that green manure, along with vermicompost application, decreases ESP of sodic soils (Table 1).

The application of green manure therefore enhances the reclamation action of organic manures like vermicompost by improving the physico-chemical properties of soil and by markedly decreasing soil pH and ESP and increasing carbon dioxide, calcium and magnesium; these conclusions correlate well with earlier studies (Patcharapreecha et al., 1990). The effectiveness of vermicompost in sodic soil reclamation is due to the production of carbondioxide and humic acids, a drop in redox potential and the replacement of exchangeable Na+ ions by Ca+2 ions leaching out of the root zone; thus reducing the ESP (Dagar, 1995).

The introduction of earthworms in sodic soils through a unique buffering mechanism along with mulch as organic cover resulted in a natural colonization and slow establishment of the earthworm population (Table 2).

Table 1

Soil Chemical Analysis

Amendments	Decrease in pH	Decrease in EC	Increase in OC %	Increase in Av. N	Decrease in Sodicity (ESP)
[C]	0.30	0.07	-0.01	002.13	07.08
[CHE]	0.40	0.07	-0.34	-462.93	09.67
[VW]	0.40	0.19	0.28	227.17	50.50
[VWT]	0.47	0.34	0.24	613.90	53.85
[VWTG]	0.50	0.35	0.23	552.57	54.98
[VWTGM]	0.63	0.33	0.22	492.80	59.21
[VWTGME]	0.70	0.37	0.33	739.20	54.64
[VWTGMEVC]	0.80	0.40	0.44	985.30	64.51
[VCVWB]	0.67	0.41	0.27	604.80	46.44
[FYM]	0.63	0.25	0.11	637.87	23.22

(- Indicate decrease)

Table 2

Earthworm numbers per square metre (Mean ± SD) in sodic soil bio-remediation plots (Number of earthworms inoculated: *L. mauritii* : 42 and *P. excavatus* : 21)

S.NO	Amendment	Number of earthworms per square metre	
		L. mauritii	*P. excavatus*
1	[VWTGME]	91.70 ± 16.26	44.80 ± 20.51
2	[VWTGMEVC]	136.00 ± 29.01	64.96 ± 12.94

Table 3

T. aestivum – Grain yield

(Mean ± SD)

	Grain yield (tonnes/ha)	
	Trial 1	Trial 2
[C]	0.79 ± 0.07	1.09 ± 0.33
[CHE]	1.89 ± 0.47	1.27 ± 0.15
\[VW]	0.94 ± 0.02	1.28 ± 0.01
[VWT]	1.04 ± 0.22	1.28 ± 0.01
VWTG]	1.07 ± 0.19	1.28 ± 0.02
[VWTGM]	1.33 ± 0.01	1.29 ± 0.01
[VWTGME]	1.47 ± 0.01	1.55 ± 0.29
[VWTGMEVC]	1.80 ± 0.29	1.56 ± 0.30
[VCVWB]	1.76 ± 0.39	1.20 ± 0.18
[FYM]	1.07 ±0.05	1.31 ± 0.48

Table 4

O. sativa – Grain yield

(Mean ± SD)

	Grain yield (tonnes/ha)	
	Trial 1	Trial 2
[C]	1.12± 0.07	1.39 ± 0.31
[CHE]	1.49 ± 0.17	1.74 ± 0.003
[VW]	2.16 ± 0.09	2.39 ± 0.09
[VWT]	2.22± 0.29	2.45 ± 0.34
[VWTG]	2.34± 0.08	2.52± 0.51
[VWTGM]	2.39 ± 0.53	2.72 ± 0.07
[VWTGME]	2.44 ± 0.12	2.77± 0.29
[VWTGMEVC]	2.54 ± 0.32	2.84 ± 0.70
[VCVWB]	1.89 ± 0.27	1.90 ± 0.34
[FYM]	1.31 ± 0.05	1.67 ± 0.01

Table 5

Economics of Sodic soil bio-remediation through Vermitech per hectare in comparison with the conventional method of reclamation (Indian Rupees)

Description of work	Vermitech (Organic)	Conventional (Chemical)
Ridge (Bund) preparation	990	990
Irrigation channel	264	264
Field drains	-	100
Link drains	-	759
Leveling and reclamation amendments	627	627
Water and electricity	1190	1190
Organic amendment package [VWTGMEVC]	736	-
Gypsum @ 10 tonnes/ha (Rs 192/tonne)	-	1920
Total cost	3,807	5,850

Table 6

Economics of Wheat (*T. aestivum*) cultivation (Indian Rupees)

S.NO	Details	Vermitech (Organic)	Conventional (Chemical)
I	**Selling price of wheat per kg***	8.00	8.00
II	Average yield (kg/ha)	1681.50	1580.50
III	Gross income /ha (I x II)	13452.00	12644.00
IV	Cost of production	8876.00	9733.00
V	Cost of production/kg (IV / II)	5.28	6.16
VI	Net income/ha (III – IV)	4576.00	2911.00
VII	Cost benefit ratio (III / IV)	1:1.51	1:1.30

* Selling price for this variety taken as Rs 8/kg for both. This wheat variety sells at Rs 8/kg in UP. Organically grown crops, however, fetch a better price in the market.

Table 7

Economics of Paddy (*O. sativa*) cultivation (Indian Rupees)

S.NO	Details	Vermitech (Organic)	Conventional (Chemical)
I	**Selling price of paddy per kg***	10.00	10.00
II	Average yield (kg/ha)	1770.50	1617.00
III	Gross income /ha (I x II)	17705.00	16170.00
IV	Cost of production	11600.00	12735.00
V	Cost of production/kg (IV / II)	6.55	7.87
VI	Net income/ha (III – IV)	6105.00	3435.00
VII	Cost benefit ratio (III / IV)	1:1.53	1:1.27

* Selling price for this variety taken as Rs 10/kg for both. This rice variety sells at Rs 10/kg in UP. Organically grown crops, however, fetch a better price in the market.

Bioremediation of sodic soil was significant in plots treated with [VWTGMEVC] “vermiwash, tillage, green manure, mulch, earthworms and vermicompost” suggesting holistic application of organic inputs qualitatively improve the physical, chemical and biological properties of the soil (Table 1).

The yield of wheat and paddy in the two trials was recorded to be significantly higher in plots subject to tillage and earthworm inoculation and treated with organic amendments such as vermiwash, green manure, mulch and vermicompost [VWTGMEVC], compared with the control, chemicals and FYM plots (Table 3 and 4). Vermicompost application in the wheat-paddy cropping system has been reported to increase crop yield (Sharma and Mittra, 1991; Ismail, 1997), which correlates with the present study where higher yield was recorded with the use of organic amendments compared with chemical fertilisers. This is because nutrients present in vermicompost are readily available to the plants (Rajkhowa et al., 2000). Addition of mulch and establishment of earthworm population leads to easy transfer of nutrients and their availability to the plants (Robinson et al., 1992). Increase in crop production is due to improvement in the physical, chemical and microbiological characteristics of soil by the combined benefits of organic amendments (Selby et al., 1989). Many workers have demonstrated that earthworms inoculated in the soil increased plant growth and yield of crops (Lavelle, 1992).

The cost of sodic soil bioremediation using organic amendments was considerably less compared with the conventional method of reclamation by the use of gypsum; this is attributed to reduced cost of inputs (organic amendments) as these are locally available (Table 5).

The reduced cost of cultivation, less cost-benefit ratio and higher net income from wheat and paddy cultivation through Vermitech compared with the use of chemical fertilisers (Tables 6 and 7) correlates with earlier work on the economics of crops like peanut (Archis hypogaea) and brinjal (Solanum melongena) by organic methods (Ismail, 1997). Organic farming has proved to be environment friendly, sustainable and cost effective (Reganold et al., 2001).

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USING OF THE LIGNOSULFONATES: FERTILIZERS

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Polymers have been used in the processes for biotechnological production, isolation from organisms and modification, material properties and technical applications in various areas such as, for example, in daily life products, medicine, pharmacy, food industry, agriculture, textiles, chemical industry and packaging industry. Polymers are consisted of aromatic constituents occurring in plants and natural environments or as fossil resources. Polymers included are: lignin, melanin, sporopollenin, soil humic substances, etc. Lignin Holds Keys to Plant’s and environment’s Future. Production technology and use of a new organic fertilizer on lignin basis in agriculture is important. With lignin new technologies solve 4 problems at once: 1) it increases industrial hydrolysis processes non-waste coefficient; 2) it provides cleaning of the dump territories of lignin pollutants; 3) it decreases the number of nature pollution sources (livestock and poultry breeding complexes, industrial hydrolysis processes); 4) it increases soil fertility. Lignin based products - crude, slightly modified and specialty lignosulfonates - are used in many chelation, binder or adhesive applications. Lignosulfonates are complex polymeric materials obtained as co-products of wood pulping. This article will be knowledge about binding and chelation and, specifically, their application in fertilizers.

General

Biopolymers represent the most abundant organic compounds in the biosphere and constitute the largest fraction of cells. Seven main classes of biopolymers are distinguished according to their chemical structures. This encyclopedia provides a throughout overview of the occurrence and metabolism of biopolymers. In addition, processes for biotechnological production, isolation from organisms and modification, material properties and technical applications in various areas such as, for example, in daily life products, medicine, pharmacy, food industry, agriculture, textiles, chemical industry and packaging industry are provided. The future perspectives of biopolymers are outlined.

Scientists say lignin, the ``glue" that binds tissues and provides structural support, is what allowed plants to colonize on land some 400 million years ago. With lignin as a protective frame, plants could take up water and nutrients and grow to great heights.
Lignin's crucial role in plant evolution has long fascinated researchers, who are now experimenting with ways to alter the lignin content of plants and trees. While the research is basic in nature, the new techniques could eventually produce specialized plants and trees for forestry and agriculture.
Some trees and agricultural crops might benefit from more lignin, which, in addition to providing support, acts as a kind of armor against drought, insects, disease and bacteria that enter through only ask the questions: “We couldn't test our theories and move forward."

TECHNOLOGY OF TRANSFORMATION OF HYDROLYSIS LIGNIN INTO AN INNOVATIVE ORGANIC FERTILIZER

A biotechnological method of transformation of hydrolysis lignin with the use of special microflora in three weeks into an ecologically safe organic fertilizer enriched with main mineral plant nutritional elements has been worked.

An experimental lot has been tested under production conditions, production technology has been worked.

Comparing to the traditional one, this method allows to accelerate obtaining organic fertilizer from industrial wastes, utilize great amounts of industrial wastes, preserve wetlands from peat extraction (the method is protected by a patent of Russia, sphere of use according to Russian Classifier of Economic Activity, Production and Services (OK004-93): 38.63.55 - methods of ground properties melioration; 87.51 - environment and natural resources protection in separate regions; 37 - collection and recycling of wastes in a form suitable for use as a new raw material; 01 – agriculture).

PRODUCTION TECHNOLOGY AND USE OF A NEW ORGANIC FERTILIZER ON LIGNIN BASIS IN AGRICULTURE OF THE NORTH

This technology solves 4 problems at once: 1) it increases industrial hydrolysis processes non-waste coefficient; 2) it provides cleaning of the dump territories of lignin pollutants; 3) it decreases the number of nature pollution sources (livestock and poultry breeding complexes, industrial hydrolysis processes); 4) it increases soil fertility.

The work has been completed. 14-year stationar tests under semi-industrial and industrial conditions were carried out. As a result of these tests the following positive effect of the technology was found: healthy environment, industrial waste decrease, soil fertility increase, disturbed biosphere carbon cycle restoration.

This technology can be used for soils with normal moisturizing regime. The technical conditions are available. Testing of the new organic fertilizers on highly moisturized soils is needed (Sphere of use according to Russian Classifier of Economic Activity, Production and Services (OK004-93): 87.51 - environment and natural resources protection in separate regions; 01 – agriculture).

LIGNOSULFONATES: IMPROVED FERTILIZER APPLICATIONS

Lignosulfonates are complex polymeric materials obtained as co-products of wood pulping. The end use markets for the co-product mixtures are functionally determined by the surface activity, binding, chelation, reactive group and chemical intermediate properties of the mixtures. This article will be limited to binding and chelation and, specifically, their application in fertilizers.

Lignin based products - crude, slightly modified and specialty lignosulfonates - are used in many chelation, binder or adhesive applications. Some of these binder markets use a mixture of lignosulfonate polymers, wood sugars or sugar acids plus polysaccharides; others use specially formulated lignosulfonate systems. The volume used in some of these markets is as much a function of low cost / performance and availability as it is the specific performance characteristics. The chelation markets use lignosulfonate products resulting from complex chemical processing. Molecular size control as well as the degree of sulfonation and carboxylation have led to optimization of properties for chelation.

Some examples of large volume binder use are road binder, animal feed binder, ceramics, brick and foundry cores. Almost any inert powder may be granulated, pelletized or briquetted with lignosulfonate powdered or liquid solids when processed through appropriate equipment. Carbon black pellets in rubber compounding, light weight fly ash aggregates for concrete, coal pellets for utility boiler furnaces, charcoal briquettes and sawdust fireplace logs and briquettes are among the products that use lignosulfonate as the bonding agent. A relatively new potentially large volume application which utilizes the binding and anti-caking properties of lignosulfonates is in the granulation and prilling of fertilizers, specifically urea in the phosphate product family of fertilizers.

UREA

Extensive laboratory and field evaluations by the Tennessee Valley Authority showed specific lignosulfonate systems could replace formaldehyde and/or urea-formaldehyde resins as conditioner for urea granules and prills. This could be done with improved perfomance for granule strength and at a considerable economic advantage. Namely, a 96% fines reduction on attrition at a $1.95/ton urea savings using lignosulfonate to replace formaldehyde or urea-formaldehyde resin. This equates to the following: a plant making slightly over 500,000 tons of urea granules per year would save $1,000,000 with better product quality.

Lignosulfonate systems in urea have been in commercial use for several years. Use is not universal due to initial product quality problems (now solved) and the perceived resistance to color change. Commercial producers and retail users have found the following advantages:

•Lignosulfonate can be added directly to the melt at the same addition rate as formaldehyde and provides anti-caking properties equal to or better than that of formaldehyde or urea-formaldehyde resins.

•Lignosulfonate has been found to provide increased hardness and strength versus formaldehyde resulting in less dusting in-plant and during subsequent handling throughout distribution. In-plant use has yielded less dust to the scrubber system, thereby reducing costs.

•Lignosulfonate provides a manufacturing cost savings of $0.75 to $1.95 per ton of urea at the same addition rate as formaldehyde. This equates to an annual saving of $75,000 to $195,000 per 100,000 tons of urea produced.

•Lignosulfonate requires no capital expense. The product can be used in the same tanks, lines and feed points as formaldehyde or urea-formaldehyde resins.

•Lignosulfonate is classified by the EPA/FDA as a non-toxic liquid. The EPA has classified formaldehyde as a "probable carcinogen" and the OSHA has issued regulations limiting exposure to formaldehyde.

•Stronger granules mean less dust and minimal product loss. This allows for a more uniform distribution to crops with typical application systems.

•Light tan color of urea made with lignosulfonate provides product differentiation between domestic and imported urea.

Slow release urea systems have been developed through graft copolymerization modifications of lignosulfonate. These modifications have allowed a slow release capability of urea granules and prills. The copolymer at only 5% concentration in urea forms a matrix in the granule or prill that slows the solubility of urea in water, especially under dew precipitation conditions. This allows a more uniform availability of nitrogen to the plant.

PHOSPHATES

Extensive trials for lignosulfonate conditioning of phosphate granules have been carried out on many members of the phosphate fertilizer family. Commercial continuous use on diammonium phosphate and selective use on monoammonium phosphate provides the following benefits:

•Lignosulfonate is classified by the EPA/FDA as a non-toxic liquid.

•Lignosulfonate can be introduced in slurry feed or acid before granulator; safe for use and storage in standard carbon steel equipment.

•Where strengths are low, lignosulfonate increases granule strength over 100% resulting in improved handling / anti-caking properties during production, storage and shipping.

•Lignosulfonate gives significant dust reduction during production, lowering cost of operating dust collectors and improving air quality in the plant. There is less chute plugging and general transfer improvement.

•Plant trials have shown lignosulfonate can allow the producer to lower his recycle rate and significantly improve granulation quality and efficiency before screening.

•With the use of lignosulfonate, coating oil often can be eliminated. Lignosulfonate does not harm transfer belts as does oil. Oil environmental concerns are eliminated.

•Addition rate of lignosulfonate is normally 0.5 gal./ton to 0.75gal./ton of phosphate. Treating cost per ton is less than cost of oil.

•Lignosulfonate offers price stability to the phosphate producer when compared to oil. Being a natural polymer derived from wood, it is not priced on crude oil value which is subject to fluctuation and sudden increases.

Use in DiCal, triple super phosphate, etc. also is applicable, in many cases alleviating dust in the plant completely and showing good granule strength improvement. Competitive spraying of environmentally sensitive oil to coat the outside of the granules remains as a traditional dust alleviation treatment. In contrast, environmentally safe lignosulfonates are added to the acid or to the granulator feed and become an integral part of the fertilizer granule, binding it much like it did originally to cellulose so effectively in the tree. Being an integral part of the granule, dust preventative and anti-caking properties are preserved - even on fracturing.

MICRONUTRIENTS

Micronutrients trace metal chelates such as zinc, iron, copper, magnesium and manganese are widely used in the fertilizer industry. Areas where micronutrient fertilization is needed are increasing; however, they are still quite small compared to acreage where major food nutrients of nitrogen, phosphorus and potassium are used extensively. Increases in acre yields in many cases have depleted micronutrient soil supply. When prepared using specialty lignosulfonate chelation products, the micronutrient trace metals are easily applied and readily available to the plant. Because lignins come from plants, micronutrients based on them can be applied to leaves of plants without any damage to the plant (lack of phytotoxicity).

Research on continued improvement of lignosulfonate for use in fertilizer is on-going and includes many other fertilizer products, fertilizer blends and application areas.

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MODELING THE AEROBIC BIO-OXIDATION STAGE OF AN INDUSTRIAL WASTEWATER TREATMENT PLANT USING ANFIS AS A SOFTWARE SENSOR

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Advanced neuro-fuzzy modeling, namely adaptive network based fuzzy inference system (ANFIS), was employed to develop a model in estimating carbon and nitrogen removal in a full-scale industrial biological wastewater treatment plant treating process wastewaters from a sugar factory. Three independent ANFIS models were developed to predict three water quality parameters (COD_{eff}, NH_4^+-N_{eff} and N_{toteff}) in the plant effluent. The models were developed using the correlations among the influent and effluent historical data from the plant. The ANFIS algorithm was employed in Fuzzy Logic Toolbox of Matlab (Mathworks Inc.) to obtain modeling results. The performances of the models were assessed by evaluating the training/validation results via correlation coefficient (R) and root mean square error (RMSE). The models correlated very well with measured data during the validation step. The correlation coefficients obtained for the validation data set of COD_{eff}, NH_4^+-N_{eff} and N_{toteff} output variables were 0.93, 0.99 and 0.98, respectively. The calculated RMSE values were 23.5, 1.7 and 5.7 mg/L for COD_{eff}, NH_4^+-N_{eff} and N_{toteff} validation, respectively. The developed conceptual ANFIS models appear to provide an alternative generic framework for the modeling of aerobic biological processes, and to be capable of training model structure. Furthermore, the results indicated that the ANFIS models are suitable to describe the relationships between wastewater quality parameters. Therefore, this modeling approach can be used as a software sensor to predict wastewater treatment plant performance.

Keywords: Aerobic biological treatment; ANFIS; artificial intelligence; modeling; sugar processing wastewater

Symbols and abbreviations

AI	Artificial Intelligence
ANAMET	Anaerobic Methane Production
ANFIS	Adaptive Network Based Fuzzy Inference System
ANN	Artificial Neural Network
ASM	Activated Sludge Model
ASP	Activated Sludge Process
COD	Chemical oxygen demand
COD_{denit} (mg/L)	COD concentration in denitrification tank
COD_{eff} (mg/L)	Effluent COD concentration
COD_{inf} (mg/L)	Influent COD concentration
FIS	Fuzzy Inference System
GA	Genetic Algorithms
NH_4-N	Ammonia nitrogen
NH_4^+-N_{dn} (mg/L)	NH_4-N concentration in denitrification tank
NH_4^+-N_{eff} (mg/L)	Effluent NH_4-N concentration
NH_4^+-N_{inf} (mg/L)	Influent NH_4-N concentration
NH_4^+-N_{nit} (mg/L)	NH_4-N concentration in nitrification tank
N_{totdn} (mg/L)	TN concentration in denitrification tank
N_{toteff} (mg/L)	Effluent TN concentration
N_{totin} (mg/L)	Influent TN concentration
Q_{excess} (m^3/d)	Excess sludge flow rate
Q_{inf} (m^3/d)	Influent flow rate
$Q_{recycle}$ (m^3/d)	Recycled sludge flow rate
R	Correlation Coefficient
RMSE	Root Mean Square Error
TKN	Total Kjeldahl Nitrogen
TN	Total nitrogen
TSS	Total suspended solids
TSS_{nit} (mg/L)	TSS concentration in nitrificiation tank
VSS	Volatile suspended solids
VSS_{nit} (mg/L)	VSS concentration in nitrification tank
WWTP	Wastewater treatment plant

1. Introduction

Biological processes are usually employed for the removal of organic carbon and nitrogen from wastewaters. In this context the activated sludge process (ASP) is a treatment method most frequently applied in municipal and industrial WWTPs. ASP is inherently dynamic, because of the large variations in the influent wastewater flowrate and concentration of biological compounds. Therefore, mathematical models and computer simulations are essential to describe, predict and control the complicated interactions of the biological processes (Jeppsson, 1996). In the last two decade, some deterministic approaches such as activated sludge models (ASM1, ASM2, ASM3, TUDP) were developed to describe the mass balance of microbiological (biomass) activities in treatment processes (Henze *et al*., 1987; Henze ., 1995; Gujer *et al*., 1999; van Veldhuizen *et al*., 1999; Brdjanovic *et al*., 2000). Assumptions in these mathematical models are mainly based on engineering principals, thus such models may be highly effective for the prediction of carbonaceous and nitrogenous substrate removal in WWTPs (Jeppson, 1996). However, since these models contain large numbers of kinetic and stoichiometric parameters, the accurate description of the system can therefore result in highly complex equations which may not be very useful from a practical and operational point of view (Jeppsson, 1996; Tay and Zhang, 2000).

New identification, prediction and process control methods have been investigated for WWTPs including artificial intelligence (AI), which focus on data interpretation and data mining techniques for problem diagnosis and decision support (Gregersen and Jørgensen, 1999; Cortès *et al*., 2000). AI methods involve the use of artificial neural networks (ANNs), genetic algorithms (GA), fuzzy logic, rule-based systems, knowledge-based systems and their associated applications called ‘hybrid architectures’ such as adaptive network-based-fuzzy inference system (ANFIS). ANFIS, proposed by Jang (1993), is based on the first-order Sugeno fuzzy model (Jang, 1993). The ANN paradigm used is a multilayer feed forward back-propagation network. ANFIS is a technique for automatically tuning Sugeno type inference systems based on training data. It consists of five key components; inputs and outputs, database and preprocessor, a fuzzy system generator, a fuzzy inference system, and an adaptive neural network representing the fuzzy system (Jang, 1993).

The main objective of this work was to evaluate the ANFIS as a valid input-output model in predicting the performance of aerobic biological treatment stage of a full-scale industrial WWTP treating sugar industry wastewater. Three separate ANFIS models were developed for the estimation of effluent COD, NH_4-N and TN, representing organic carbon and nitrogen removal.

2. Methodology

2.1. Wastewater treatment plant

The process wastewater from the sugar factory (Eregli, Turkey) is treated by a ANAMET type plant which consists of sequential anaerobic and aerobic biological treatment units. The anaerobic unit includes completely-mixed hydrolysis and anaerobic tanks and a lamella type sludge separation system. Aerobic stage is based on pre-denitrification principle involving denitrification and nitrification reactors and final sedimentation tank. Regularly monitored on-line and off-line plant data from the 2002-2003 sugar beet campaign period were obtained from the plant and used to develop three separate ANFIS models. The statistical values of wastewater parameters measured during the operation period are presented in Table 1.

Table 1. Wastewater characteristics

Parameter	Minimum	Average	Maximum
Q_{inf} (m^3/d)	484	3290	4856
$Q_{recycle}$ (m^3/d)	30	3578	5663
Q_{excess} (m^3/d)	0	145	600
COD_{inf} (mg/L)	92	202	416
COD_{denit} (mg/L)	48	110	364
COD_{eff} (mg/L)	40	100	300
pH	7.3	7.7	8.2
TSS_{nit} (mg/L)	316	8555	16100
VSS_{nit} (mg/L)	175	3256	8850
NH_4^+-N_{inf} (mg/L)	10	39	147
NH_4^+-N_{dn} (mg/L)	0	12	139
NH_4^+-N_{nit} (mg/L)	0	12	163
NH_4^+-N_{eff} (mg/L)	0	11	131
N_{totin} (mg/L)	16	50	128
N_{toteff} (mg/L)	4	30	177
N_{totdn} (mg/L)	4	28	172

2.2. Model structure and model implementation

MATLAB® software was used to design a Sugeno fuzzy system prototype for each trial from training data. The function “genfis2” was applied to generate a first order Sugeno FIS using subtractive clustering of the data set. Once a fuzzy system prototype is available, the ANFIS algorithm tunes and optimizes the fuzzy system by learning from the training data and finally produces a Sugeno fuzzy system with the same structure as the prototype. *Xbounds* function, which specifies how to map the data in inputs and outputs into a unit hyperbox, was used in all modeling trials. This function contains the minimum and maximum axis values for scaling the data in each dimension.

The total data set was divided into two sets for training and checking/validation. The data of 110 days (≈60%) was used for training and the remaining data of 73 days (≈40%) was used to validate the model. Training and validation data for ANFIS models were selected randomly.

The resulting model was verified by using a validation database provided from the original database. If the resulting fuzzy system performed satisfactorily with respect to the validation data, then the computation was completed. The performance of the resulting model was determined by evaluating measured and estimated results via correlation coefficient (R) and root mean square error (RMSE). Correlation coefficients were calculated based on linear regression analysis (least squares method); RMSEs were calculated by the below equation:

$$RMSE=\sqrt{\frac{\sum_1^N (x_i-y_i)^2}{N}} \tag{1}$$

where, x_i and y_i are the measured and predicted data, respectively (as $COD_{eff,}$ NH_4^+-N_{eff} and N_{toteff}) and N is the number of observations.

3. Results and Discussions

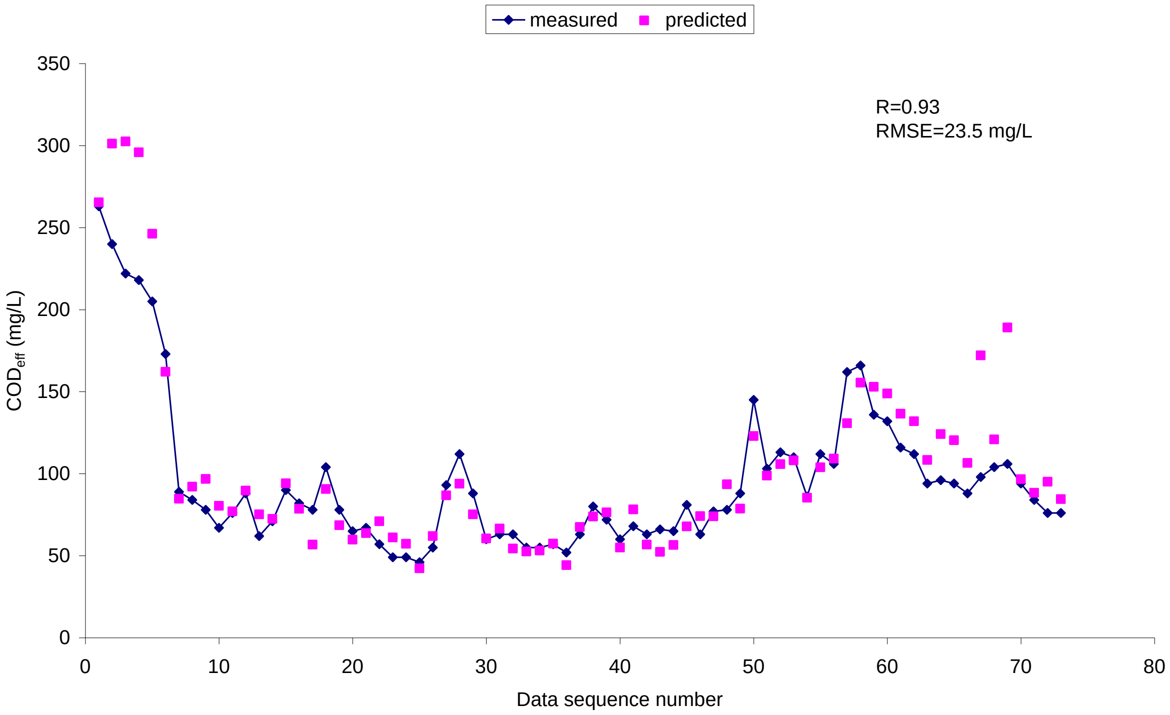
Three independent models were constructed to estimate COD_{eff}, NH_4^+-N_{eff} and N_{toteff}. The model structures and the RMSE and R values are presented in Table 2. Carbon and nitrogen removal is achieved in the treatment plant; thus estimations of carbon and nitrogen removals were targeted in modeling efforts. Selected input variables were trained under many iteration steps (maximum of 500 iterations) for the desired output variable prediction.

After the determination of the optimum training iteration number, the validation process was performed. Validation RMSE values between the estimated and measured data were 23.5 mg/L, 1.7 mg/L, and 5.7 mg/L for COD_{eff}, NH_4-N_{eff} and TN_{toteff} models, respectively. The correlation coefficients (R) ranged between 0.93 and 0.99, which were quite satisfactory given the complex nature of variables in biological wastewater treatment systems.

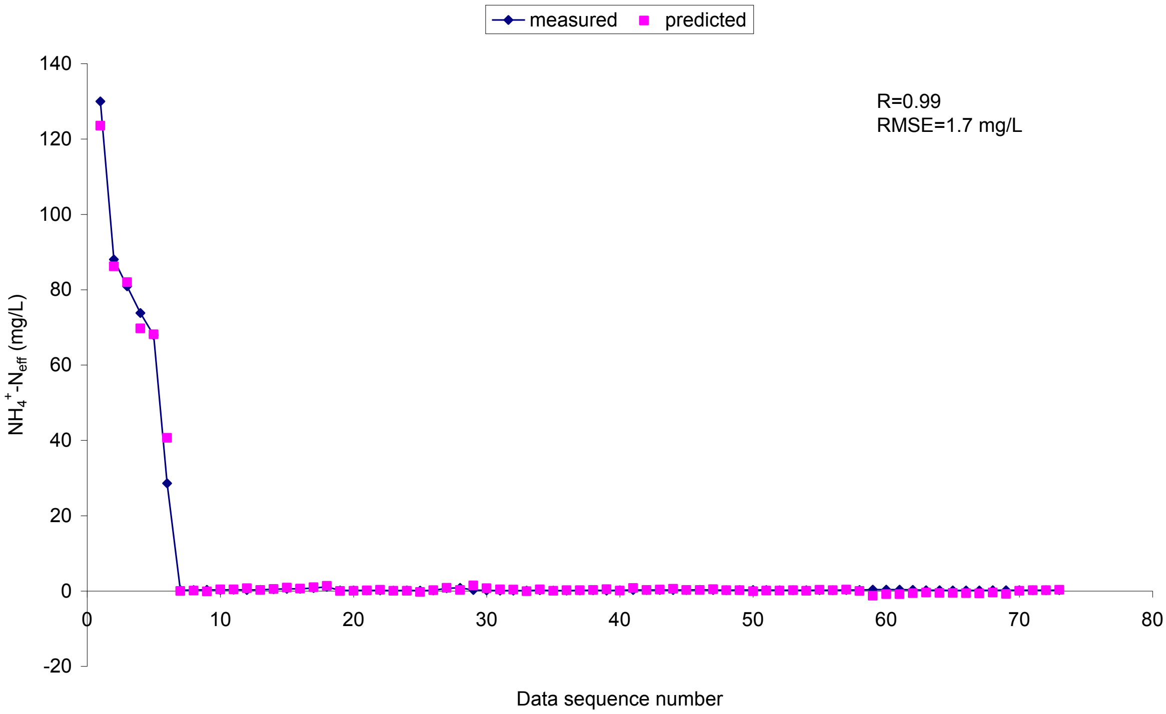
Table 2. Performance of the ANFIS models with the selected input data matrix

Model Output	Model Inputs	Training Results RMSE	R	Validation Results RMSE	R
COD_{eff}	Q_{inf} COD_{inf} COD_{denit} pH $Q_{recycle}$ Q_{excess} TSS_{nit} VSS_{nit}	5.7 mg/L	0.99	23.5 mg/L	0.93
NH_4^+-N_{eff}	Q_{inf} COD_{inf} COD_{denit} pH $Q_{recycle}$ Q_{excess} N_{totin} NH_4^+-N_{inf} NH_4^+-N_{dn} NH_4^+-N_{nit} N_{totdn}	0.5 mg/L	0.99	1.7 mg/L	0.99
N_{toteff}	Q_{inf} COD_{inf} COD_{denit} pH $Q_{recycle}$ Q_{excess} N_{totin} NH_4^+-N_{inf} NH_4^+-N_{dn} NH_4^+-N_{nit} N_{totdn}	3.7 mg/L	0.99	5.7 mg/L	0.98

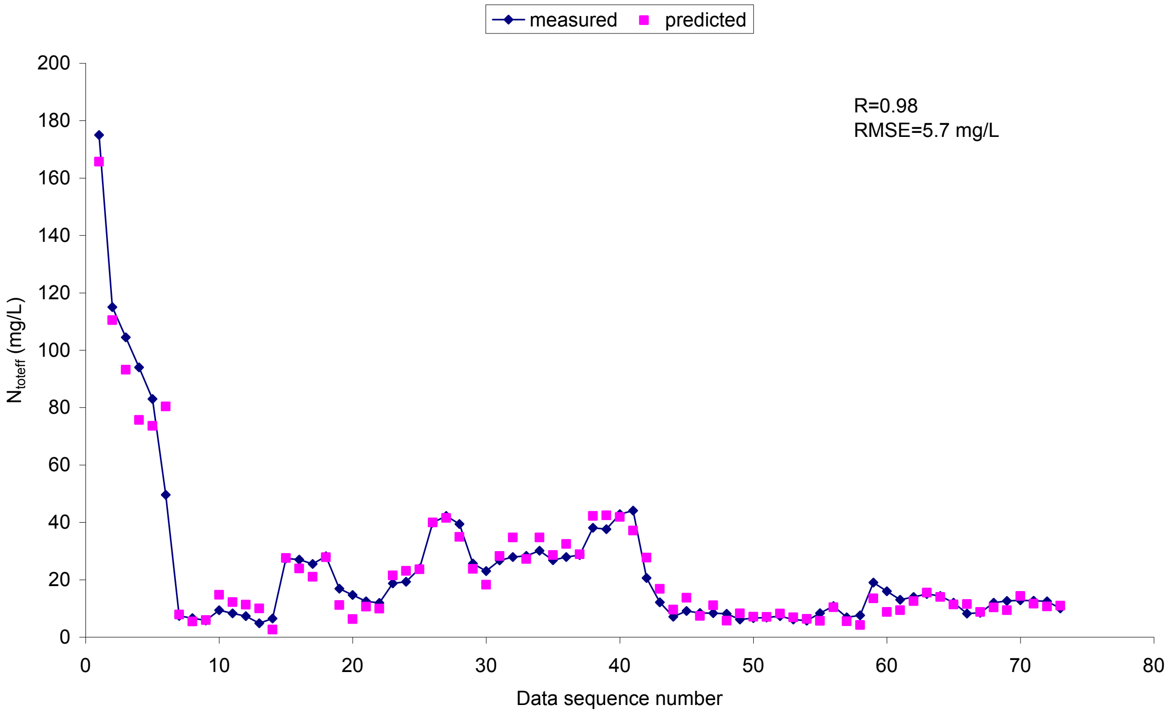
Figure 1 a,b and c present the prediction results of the COD_{eff}, NH_4-N_{eff} and TN_{toteff} models for the validation data sets. As shown in Figure 1, the ANFIS algorithm correlated very well with measured data during the validation step. It is clear that the ANFIS method does capture prediction information successfully for the validation data. However, for the COD simulation, some disparity between the predicted and measured values was noted in the highest concentration region. Results overall indicated that the ANFIS models, although far from perfect, were able to estimate output variables with high correlation coefficients and relatively low root mean square errors. This is particularly important considering the high level of complexity in biological processes and the large quantity of variable information spread in the dataset.



(a)



(b)



(c)

Figure 1. Prediction results of ANFIS models for COD_{eff} (a), NH_4^+-N_{eff} (b) and N_{toteff} (c) (from validation data set)

4. Conclusions

This work evaluated hybrid neuro-fuzzy (ANFIS) modeling method to estimate organic carbon (as COD) and nitrogen removal (as NH_4-N and TN) using the correlations among the past information of input and output variables in a full-scale industrial biological wastewater treatment plant treating process wastewaters from a sugar factory. Model development focused on providing an adaptive, useful and alternative methodology for modeling of carbon and nitrogen removal. The hybrid neuro-fuzzy method appeared to be an alternative framework for the estimation of carbon and nitrogen removal; RMSE and R values of the models were found to be quite satisfactory. Overall, the results indicated that the ANFIS model is suitable to describe the relationship between wastewater quality parameters. Therefore, this modeling approach can be used as a soft sensor to predict wastewater treatment plant performance

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REMOVAL OF COBALT ION FROM AQUEOUS SOLUTIONS BY LIGNOSELLULOSICS MODIFIED WITH PAN

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The aim of this study is to remove the harmful heavy metals for human and ecological life by adsorption method using modified lignocellulosic materials. The polymers using for modification and the lignocellulosic compounds are chosen from the waste materials. Stalk, straw, grass and similar agricultural churns as lignocellulosic compounds and PET, nylon, PP, PAN and other compounds left as contaminant to the environment and used in a wide range in our daily life were used in the modifying process. Thus we can convert this harmful for ecological side and unnecessary materials to a useful raw material and we don’t need to stock and destroy these waste materials any more. On the other hand, the poisonous heavy metals from wastewater were removed by using that modified product in our study. At the same time three different class of contaminant was converted to useful materials.

In this study PAN (polyacrylonitrile) was used for modifying the sunflower stalk. At the daily life PAN has a wide range of use as yarn or fabrics. A method was developed to enhance cobalt ion adsorption of PAN grafted sunflower stalk for aqueous solutions treatment. The PAN grafted copolymer was obtained by free radical initiating process using ceric ammonium nitrate as an initiator. Conversion of nitrile groups of the PAN grafted copolymers into the amidoxime was carried out by treatment with hydroxylamine under alkaline solution. The performance of the modified lignosellulosics against unmodified lignosellulosics has also been carried out. The batch removal of cobalt ion from aqueous solutions under different experimental conditions was used. The effects of initial cobalt concentration, temperature, pH, time and adsorbent dosage have been reported. The batch sorption kinetics and the applicability of the Langmuir and Freundlich adsorption isotherms for the present system have been tested. Polymerization is determined by IR analysis and adsorption is determined by ICP analysis.

Key Words: *Heavy metal, adsorption, lignocellulosics, graft polymerization, PAN*

1. Introduction

In recent times, a great deal of interest has been given to the utilization of agricultural products as adsorbents for the removal of trace amounts of toxic and valuable heavy metals from industrial and municipal wastewater effluents, particularly because of the low cost, high availability of these materials, no need for complicated regeneration process and they are capable of binding to heavy metals by adsorption, chelation and ion exchange. The study of the adsorptive action of metallic ions towards the agricultural products may involve metal interactions or coordination to functional groups present in natural proteins, lipids and carbohydrates positioned on cell walls. Research in the use of agricultural products has included metal binding studies with wheat and rice bran, oat fiber, sugarcane bagasse, sawdust, peanut skins, apple waste, sunflower, peat moss, Medicago sativa (Alfalfa) and walnut waste to mention a few (A. A. Abia 2003).

Lignocellulosics have ion-exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. These are adsorbents for a wide range of solutes, particularly divalent metal cations. Lignocellulosic resources all contain, as a common property, polyphenolic compounds, such as tannin and lignin, which are believed to be the active sites for attachment of heavy metal Lignocellulosic materials are very porous and have a very high free surface volume that allows accessibility of aqueous solutions to the cell all components. One cubic inch of a lignocelluloses material, for example, with a specific gravity of 0.4, has a surface area of 15 square feet., when the lignocellulosic material is ground, the adsorptive surface increases only slightly. Thus, the sorption of heavy metal ions by lignocellulosic materials does not depend on article size. Lignocellulosics are hygroscopic and have an affinity for water. Water is able to permeate the non-crystalline portion of cellulose and all of the hemicellulose and lignin. Thus, through absorption and adsorption, aqueous solution comes into contact with a very large surface area of different cell wall components. (Beom Goo Lee 2004).

The present study may generate useful information for the utilization of native agricultural products such as modified and an modified sunflower stalk for the extraction, of metal ions from wastewater.

In recent years, chemical modification of natural macromolecules has received considerable interest. Polysaccharides of vegetable origin are unique raw materials as they are abundant in nature, widely available in many countries, inexpensive, renewable resources, stable, hydrophilic and modifiable biopolymers. They offer tremendous potential for development of alternate materials. Grafting techniques have received considerable attention; especially regarding those systems in which polysaccharides are used as substrate polymers. An important advantage of graft polymerization is that the grafted polymer chains are held together by chemical bonding, allowing the two polymers to be intimately associated (Anuradha Mishra 2006). The polymer that is grafted is expected to be distributed on the backbone of the substrate polymer and also to impart beneficial effects on its properties. In this study PAN grafted copolymer was used as a cheapest adsorbent matrix preparation and also PAN groups was converted to poly (amidoxime).

Graft polymerization has been a favorite method for surface modification of polymers for a variety of end uses. Adsorption of ions, including toxic heavy metals, is one application that has been explored in detail. The process involves the generation of free radicals on suitable polymeric matrices and then allowing these free radicals to serve as macro initiators for the polymerization of vinyl or acrylic monomers containing complexion agents onto the matrix (Ronald R Navarro 1999).

Removal of cobalt [Co(II)] from aqueous solution is necessary because of frequent appearance of this heavy metal in wastewaters from nuclear power plants and many industries, including mining, metallurgical, electroplating, paints, pigments and electronic industries. Chemical precipitation, electro winning, reverse osmosis, electrodialysis, solvent extraction, ion exchange and adsorption using a variety of sorbents are some of the methods suggested for the removal of heavy metals from wastewaters. Although all these techniques afford moderate to efficient metal removal, ion exchange technique is preferred. Ion exchange process has many advantages over other methods including recovery of metal value, selectivity, sludge free operation, cost-effectiveness and the meeting of strict discharge specifications. Polymeric resins are usually employed for industrial wastewater treatment process. However, they are relatively expensive to produce. Therefore, there is increasing research interest in using alternative low-cost ion exchangers. Recently several investigators have reported the metal binding property of biomass and agricultural byproducts and have been reviewed. All these materials exhibited good adsorptive capacity, but their applications in original forms were found to be limited due to leaching of organic substances such as lignin, pectin, tannin etc. into the solution. Previous research has indicated that graft polymerization on lignocellulosic materials followed by functionalization is a promising technique for modifying physical and chemical properties of the adsorbent and to improve the adsorption property as well as prevent the leaching of organic substances. Graft polymerization on solids may also increase the stability of the adsorbent material, which is an important aspect of the commercial development of biosorbent materials. Many materials have been investigated as polymer support including tea leaves, coconut coir, bagasse pith, cellulose and saw dust for the preparation of sorbents having different functional groups (I: G: Shibi 2004). Recent research has focused on the preparation of amidoxime functionalized adsorbents since they were expected to exhibit a specific binding ability towards highly toxic heavy metals as a consequence of a soft Lewis acid–soft Lewis base (Pearsons_ theory) interaction.

2. Experimental

The sunflower stalk was collected from a village of Konya and break into pieces. These pieces were washed with deionized water and dried. And then, stalk pieces milled and sieved under 100 mash sizes.

PAN fibres were taken from waste fibers of Isparta İpliksan Hand Knitting Yarn Companies.
At the PAN grafting on sunflower stalk experiment; 5 grams of sieved stalk added into 100 ml of dimethylformamide (DMF) and started to mix on the magnetic heater. While it was mixing 1 ml of concentrated acid sulfuric and 5 grams of ceric ammonium nitrate was added. On the other magnetic heater, 5 grams of PAN (polyacrilonitrile) added into 150 ml DMF and 3 ml of concentrated acid sulfuric was added to this mixture. It was heated till the PAN fibers were solved in DMF. And then PAN solvent was added slowly to the mixing stalk. It was refluxed for 6 hour. The reaction yield was filtered and washed with methanol and deionized water and then dried. Structure of the yield is amorphous pieces between 0.5 to 5 mm and these pieces were like plastic before drying. At the converting of nitrile groups to the amidoxime experiments; 1.5 grams of PAN grafted sunflower stalk was added into 150 ml of methanol and started to mix. 0.345 g (0.05 mol) of hydroxylamine hydrochloride and 1 g (0.025 mol) of NaOH was added to the mixture and then refluxed for 4 hour. Mixture was allowed to cool and yield was washed with deionized water and acetone and then left to dry.

At the adsorption experiments; 0.025 grams of unmodified, modified with PAN and modified with PAN and converted to amidoxime adsorbents was added to 25 ml 100 ppm Co solution at the different pH values. Mixture was shaken at 150 rpm for 1 hour at 20 °C. Then adsorbent was filtered and remaining Co amount was determined with ICP analysis.

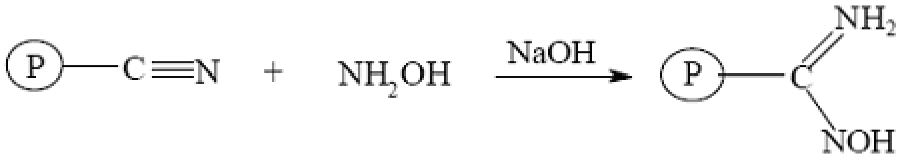
Results and Discussion

1. Polyacrylonitrile grafted copolymer

The PAN grafted sunflower stalk was obtained from waste PAN. In the literature, grafting polymerization starts from monomers. But in this study acrylonitrile chain was used for grafting. PAN was solved in DMF and added to the concentrated sulfuric acid ($H_2SO_{4)}$ for breaking the chain. Ceric ammonium nitrate was added to this solution for obtaining free radicals PAN pieces.

2. PAN to Poly (amidoxime) Reaction

Conversion of nitrile groups of the PAN grafted copolymers into the amidoxime was carried out by treatment with hydroxylamine under alkaline solution. But in this study we used concentrated H_2SO_4 for breaking the chain. So PAN grafted sunflower stalk was too acidic. 0.025 mol of NaOH was not enough to neutralize all HCl of the ($NH_2OH.HCl$) and the remaining acid in the lignocellulose. The last pH of the reaction solvent was 7. Because of that converting of nitrile groups to the amidoxime was occurred in a low amount. Thus the grafting reaction of PAN needs to be in more moderate conditions. Amidoxime reaction occurs as following scheme P is the backbone of the polymer.



3. FT-IR Analysis

Figure 1 shows the IR spectra of sunflower stalk. There are characteristic OH stretching bands at 3042 cm^{-1} and 1640. In addition, C-H stretching bands of cellulose ring shown at 2940 and 1040 cm^{-1}. Figure 2 shows the IR spectra of PAN. The characteristic C≡N stretching bands at 2245 cm^{-1} in Figure 3 is the spectra of PAN grafted sunflower stalk. The little CN stretching band is seen at 2245 cm^{-1}. And also CH_2 band of the PAN backbone at 1453 cm^{-1} shown at the modified copolymer. That means grafting reaction was occurred successfully.

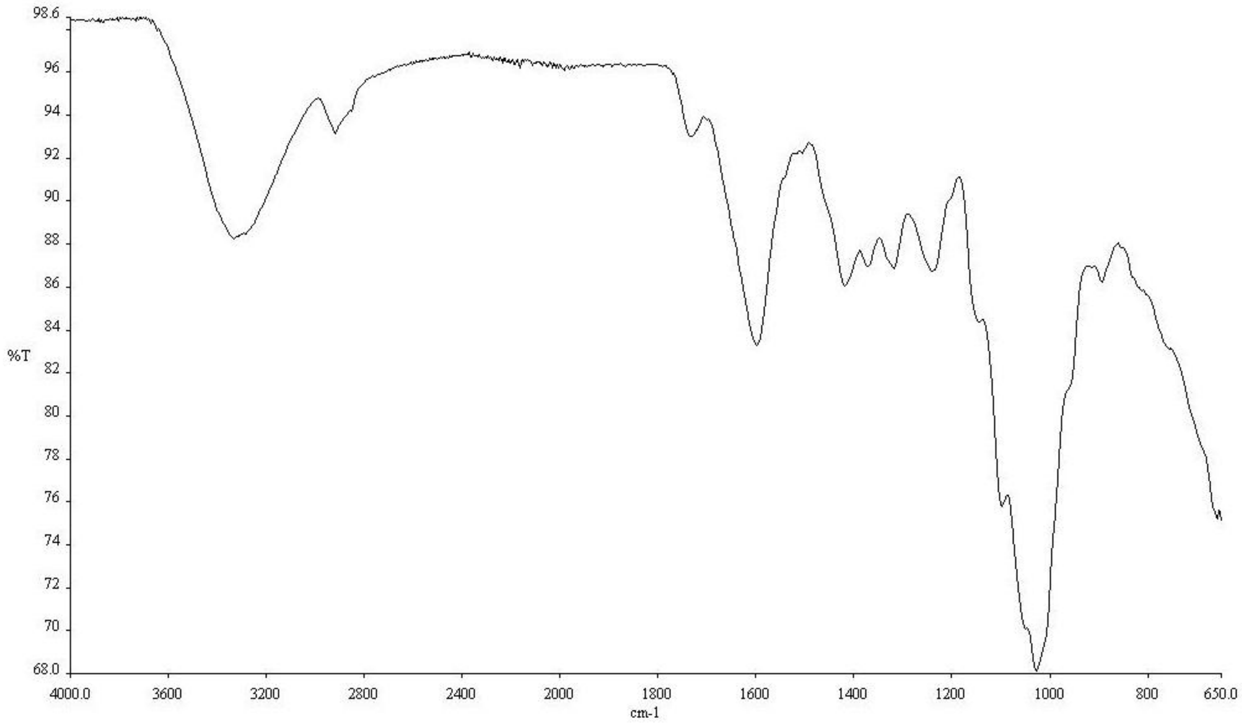


Figure 1 FT-IR spectra of sunflower stalk

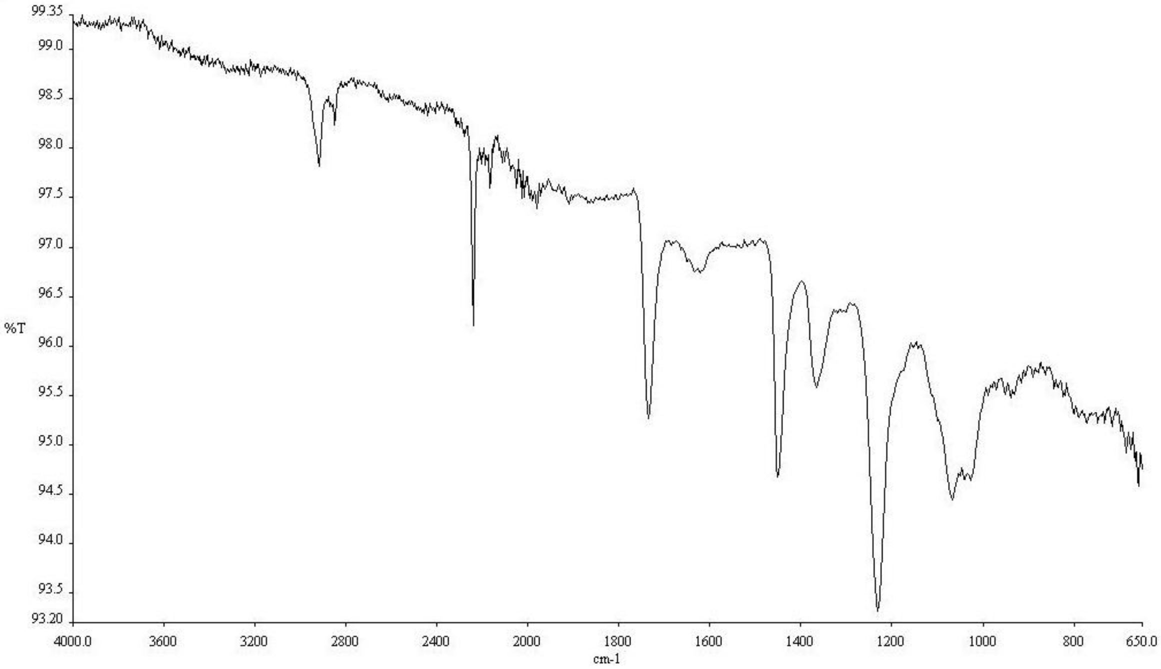


Figure 2 FT-IR spectra of PAN

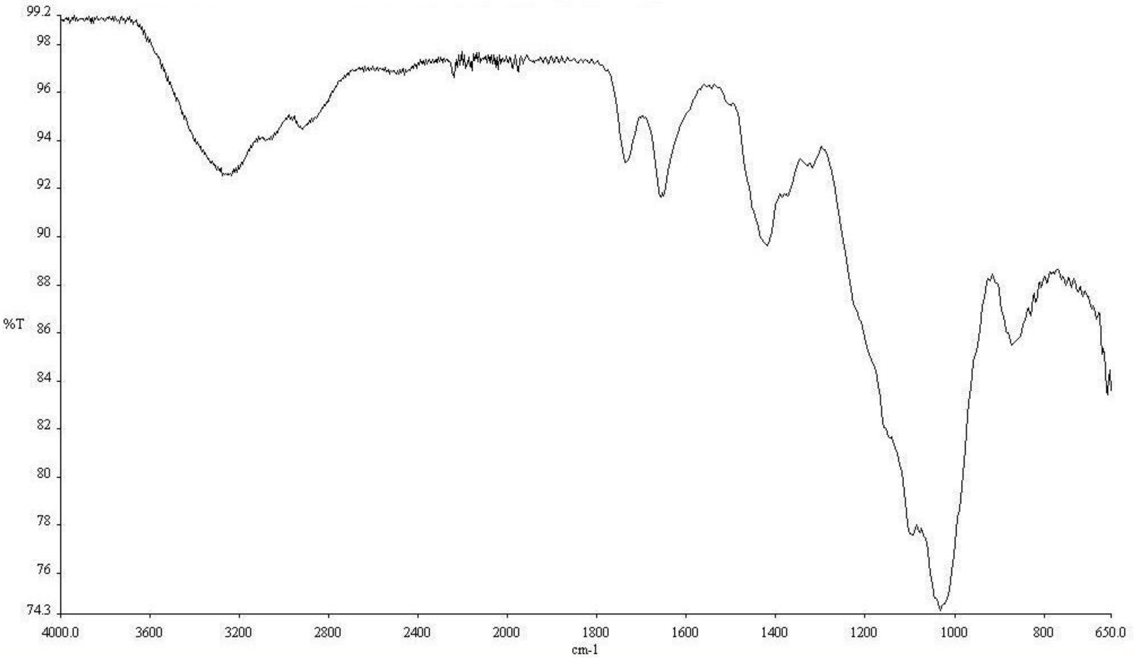


Figure 3. FT–IR spectra of PAN grafted sunflower stalk

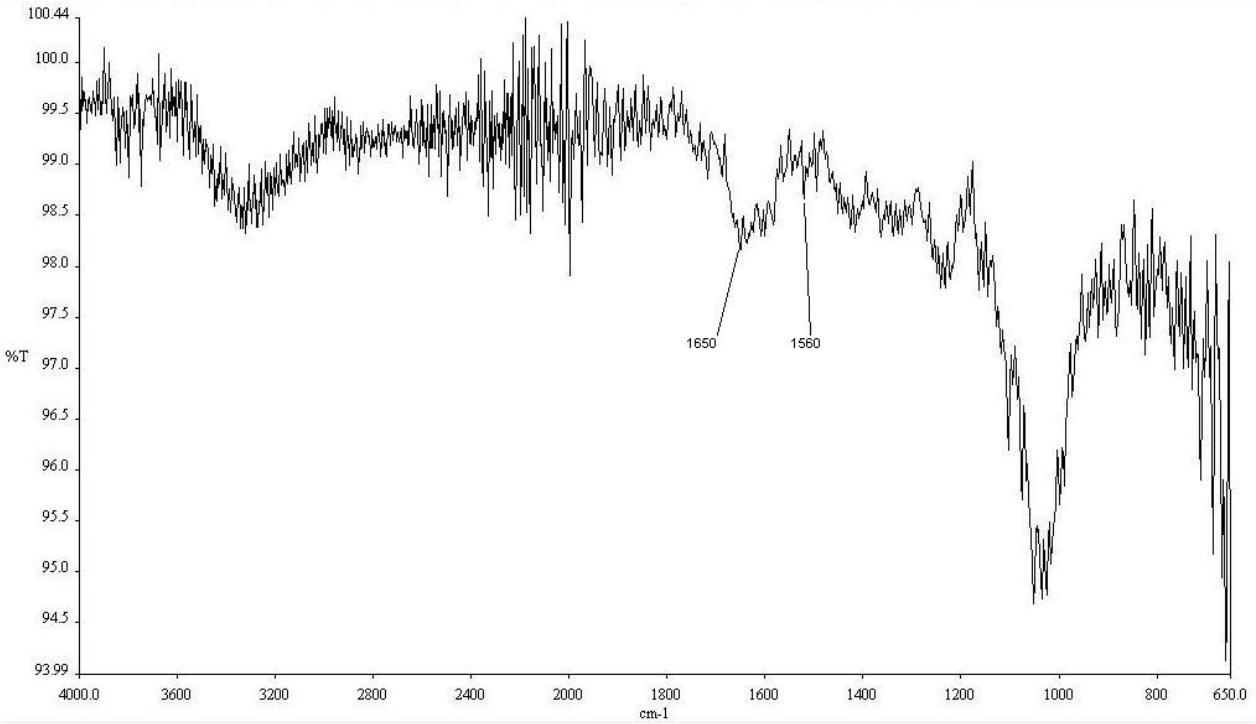


Figure 4 FT-IR spectra of to Poly(amidoxime) grafted sunflower stalk

In figure 4 the new band at 1650 and 1580 cm^{-1} shows the existence of the amidoxime groups.

4. Adsorption Experiments

The binding property of cobalt ion with poly (amidoxime) grafted sunflower stalk was carried out with batch technique for different pH values from 1 to 8. It was found that Co ion adsorption was increased with increasing pH for all kinds of adsorbents. 0.025 mg of adsorbent was added to 25 ml 100 ppm solvent and shaken for 1 hour.

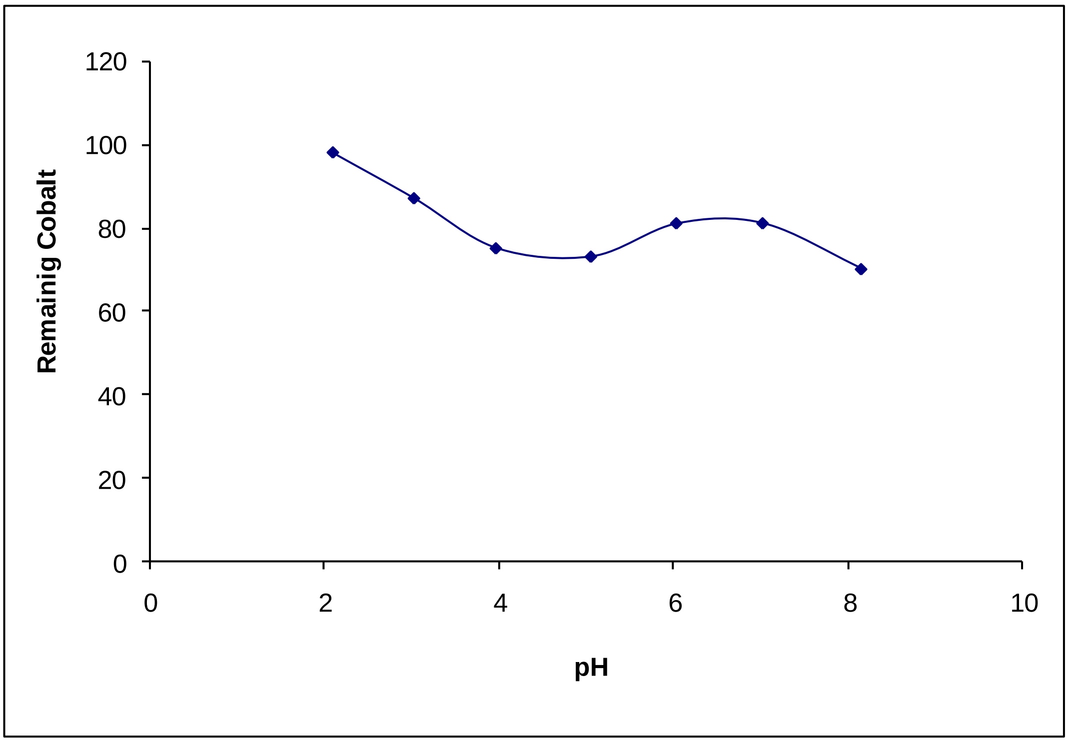


Figure 5: Cobalt adsorption of raw sunflower stalk

The results of adsorption experiments of raw stalk shows that raw stalk adsorbs 30 ppm of cobalt at ph 8.1, but above that pH the addition of NaOH cause the formation of blue $Co(OH)_2$ precipitate and then by heating the color turns to pink. So increasing of adsorption capacity after pH 8 result of precipitation.

Figure 6 shows the adsorption capacity of the PAN grafted sunflower stalk. The adsorption capacity decreases with acidic treatment as it seen from Figure 6. we told before, we used concentrated sulfuric acid at the grafting reaction. After this reaction surface of the adsorbent became so cationic.

Figure 7 shows the adsorption capacity of poly (amidoxime) grafted sunflower stalk. Above pH 5.5 modified lignocellulosic material adsorbs 35 ppm of cobalt. That means modifying sunflower stalk with PAN and amidoxime increases the cobalt adsorption capacity. Adsorption capacity can be increased by increasing the conversion of CN groups to the amidoxime. A Perkin-Elmer 5300 DV ICP-OES was used for analyses.

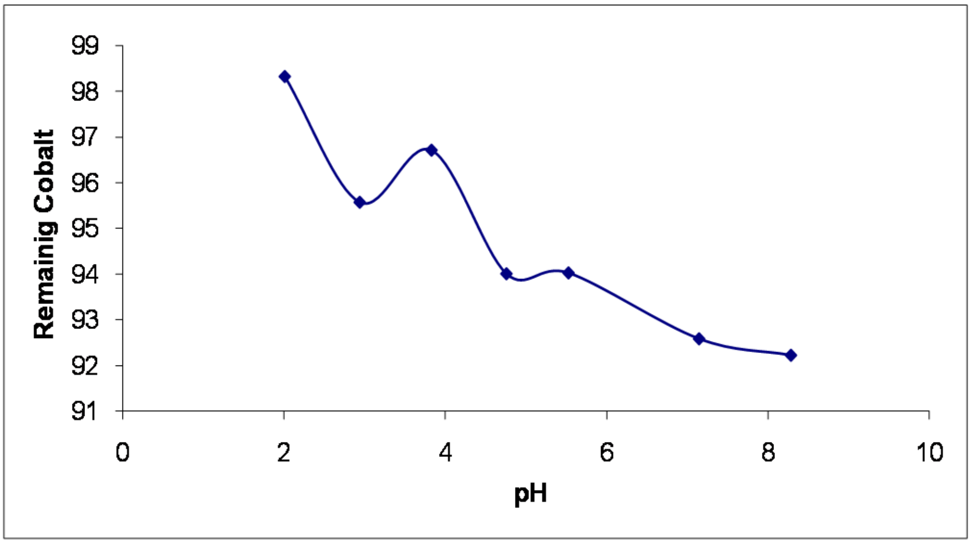


Figure 6 Cobalt adsorption of PAN grafted sunflower stalk

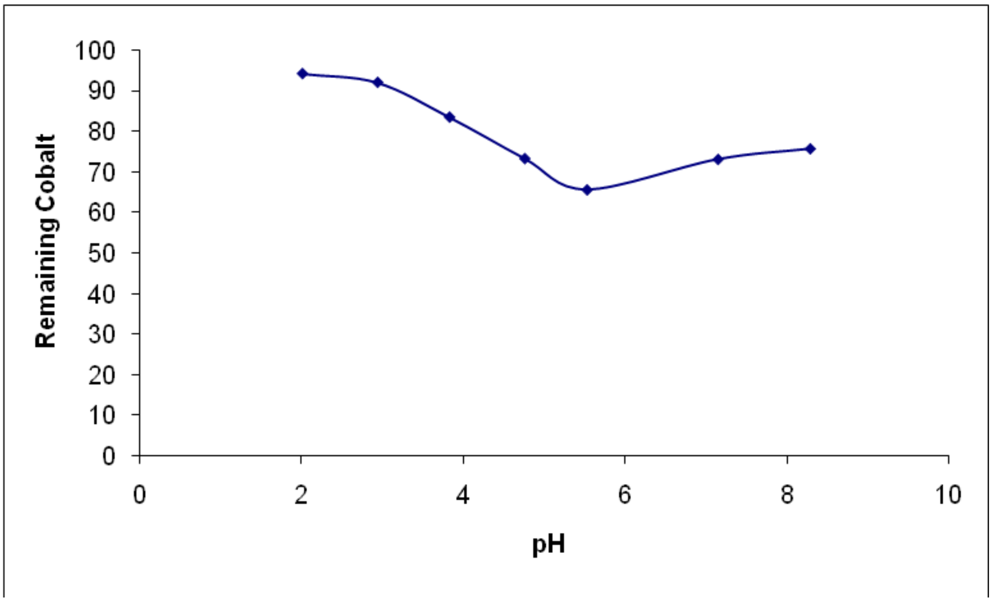


Figure 7. Cobalt adsorption of poly(amidoxime) grafted sunflower stalk

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AN STUDY ON APPLICATION OF DIFFERENT DISOLVED OXYGEN (DO) VARIATIONS IN SEQUENCING BATCH REACTOR

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The different disolved oxygen (DO) variations in sequencing batch reactor (SBR) were studied. The oxidation of COD and ammonium and the formed nitrite and nitrate concentrations and the air quantities given to reactors were evaluated. The results shows that higher simultaneous nitrification and denitrification was obtained and less air was given to reactor (air on in DO: 0.5 mg/l; air off in DO: 1.0 mg/l). Therefore, the intermittent aeration instead of the continuous aeration is suggested.
Keywords: *SBR, DO, oxidation, cost*

1. INTRODUCTION

The activated sludge processs accommodate to many different microorganisms. The microorganisms are called according to its DO affinities and tasks. Generally, DO should be maintained above 2 mg/L for the oxidation of carbon and nitrogen compounds by microorganisms. High DO have advantages such as the prevent of filamentous bacteria growth, higher biomass concentration in the aeration tank, better sludge settling, higher oxygen transfer efficiency and more stable operation [1] But, in recent years, it was found that microorganisms can be oxide both carbon and nitrogen in low DO concentrations. The nitrogen removal in low DO concentration occurred with new phenomenon such as sludge granulation, short-cut nitrification, simultaneous nitrification and denitrification and denitrification by autotrophic bacteria [2].

The sequence batch reactor is composed of an reactor. The SBR has five basic operating periods: fill, reaction, setle, decant and idle. The steps in the react cycle are adjusted to provide anaerobic, anoxic and aerobic phase in certain number and sequence.

The nitrogen removal in advanced wastewater treatment process is obtained with nitrification and denitrification sequence. The denitrification reactor is established to head of nitrification reactor due to carbon requirement. Nitrate formed in nitrification reactor is recycled to denitrification reactor. The high recycle ratio is an disadvantage for advanced treatment processes

Simultaneous carbon removal, nitrification and denitrification under low DO conditions can be occur into the same reactor. Hu et al. [2] found that carbon and ammonium oxidation occured under low DO conditions (about 0.5 mg/l). The operating of wastewater treatment facilities at low DO have advantages such as energy saving and a lower operating cost [3].

In this study, COD and ammonium oxidation and nitrite and nitrate concentrations were evaluated under different DO variations. The most favourable DO variation was determineted by taking into consideration the given air quantity as well.

2. MATERIAL AND METHODS

Experimental setup

The five SBR, which have working volume of 2 l, was used in this study. The aeration was made with diffusers established to bottom of reactors. Simultaneous, the reactors was mixed with an mixer which has an rotating speed of 20 rpm. The experimental setup was given in Figure 1. Without pH control, the temperature was controlled at 25±2^{o}C.

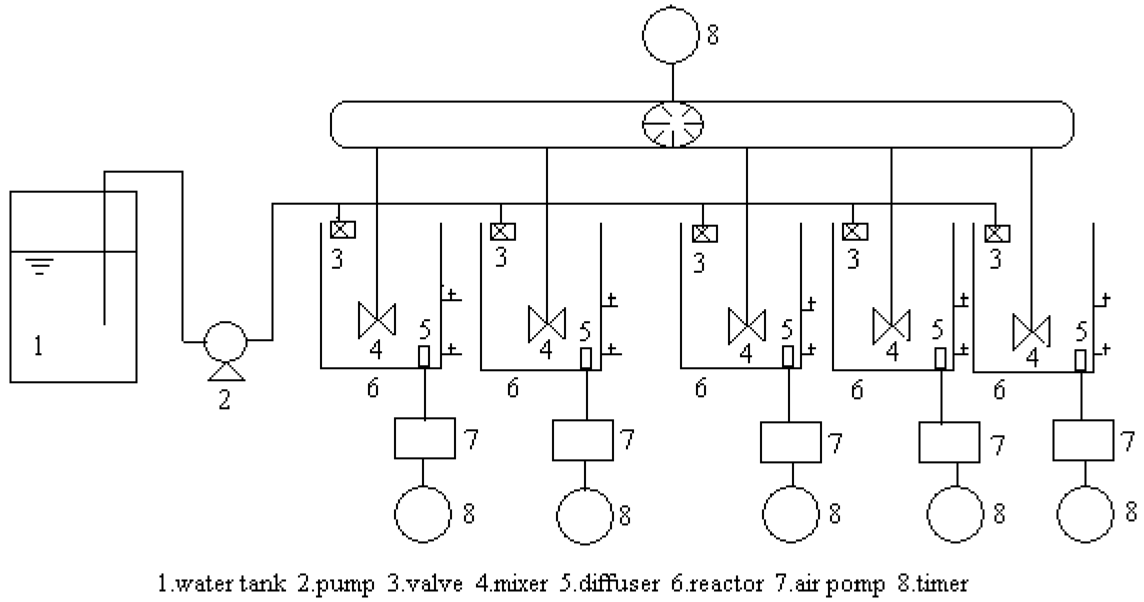

Figure 1. Schematic diagram of the experimental setup.

An cycle in the reactors is composed of 8 hours, including 15 min filling, 405 min aeration, 30 min sedimentation and 30 min draw and idle. The reactors were fed with domestic wastewater of 1 l at the beginning of cycle. The volumetric exchange ratio was 1/2.

Wastewater and Sludge

In this study, Domestic wastewater, which taken from Elazığ Wastewater Treatment Plant, was used. The reactors was seeded with sludge taken from Malatya Advanced Wastewater Treatment Plant. MLVSS concentration in the reactors was maintained at 2000±100 mg/l. The characterization of domestic wastewater was given Table 1.

Table 1. The characterization of domestic wastewater

Composition	Concentration (mg/l)
COD	520
TKN	48
NH_4-N	35
TP	16
PO_4-P	8
NO_3-N	0.90

Analytical Methods

COD, MLVSS concentrations was measured according to Standard methods [4]. DO was monitored by DO meter (WTW OXI 330). Ammonium, nitrite and nitrate concentration was measured by Standard Kit (Merck Specquorant).

Experimental approach

The experimental approachs applied in this study was given in Table 2. In Run 1, the reactor was continuosly aerated and DO concentration was kept constant about 2 mg/l. The reactor was intermittently aerated and the air flux was started at about 0.5 mg/l of DO concentration while air flux was ceased at about 2, 1.5 and 1.0 mg/l of DO concentration in Run 2, 3 and 4, respectively. In Run 5, the reactor was continuosly aerated and DO concentration was kept constant about 0.5 mg/l.

Table 2. The experimental approachs applied in this study.

Runs	Aeration
1	DO= 2 mg/l air on
2	DO= 2 mg/l air off DO= 0.5 mg/l air on
3	DO= 1.5 mg/l air off DO= 0.5 mg/l air on
4	DO= 1.0 mg/l air off DO= 0.5 mg/l air on
5	DO= 0.5 mg/l air on

3. RESULTS AND DISCUSSION

The effect of different aeration variations on simultaneous nitrification and denitrification efficiency was investigated by testing the continuous and intermittent aeration. Fig. 2, 3, 4, 5 and 6 show variations of COD, NH_4-N, NO_2-N, NO_3-N and DO concentrations in Run 1, 2, 3, 4 and 5, respectively. COD oxidation was completed in the whole DO variations. The effluent COD concentrations was obtained as almost the same during the study. The decreasing of COD in the first hour of cycle hour was found by higher because of readily biodegradable carbon in domestic wastewater. In this study, domestic wastewater instead of synthetic wastewater consisted of the readily biodegradable organics was used. Because, Orhon et al. [5] suggested that biological treatment systems are not controlled by the depletion of the readily biodegradable organics, but by hydrolysis of slowly biodegradable organics.

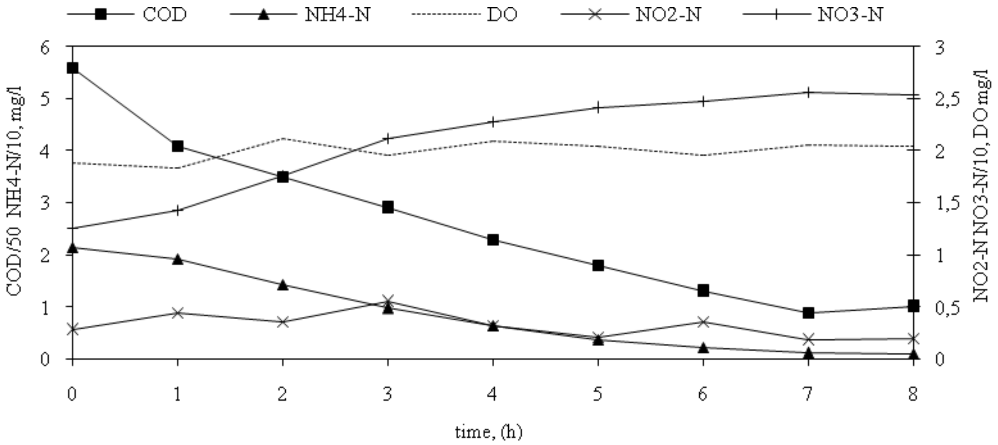

Figure 2. Variations of COD and nitrogen composition in Run 1.

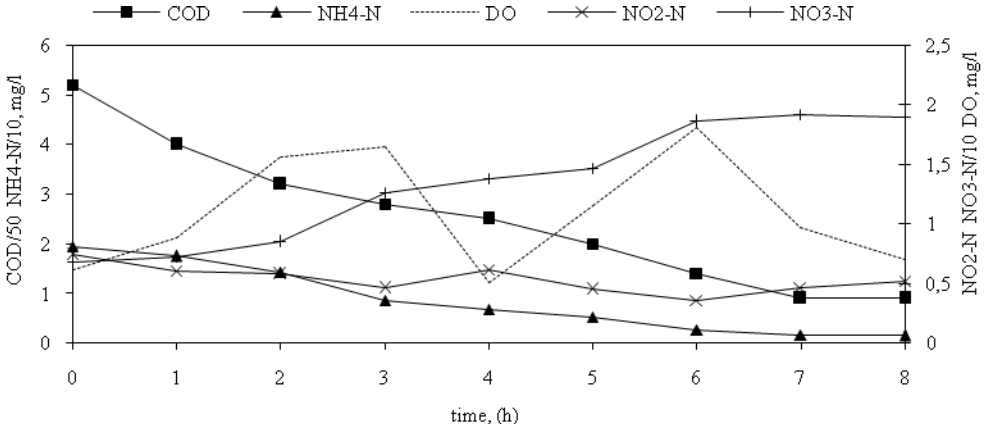

Figure 3. Variations of COD and nitrogen composition in Run 2.

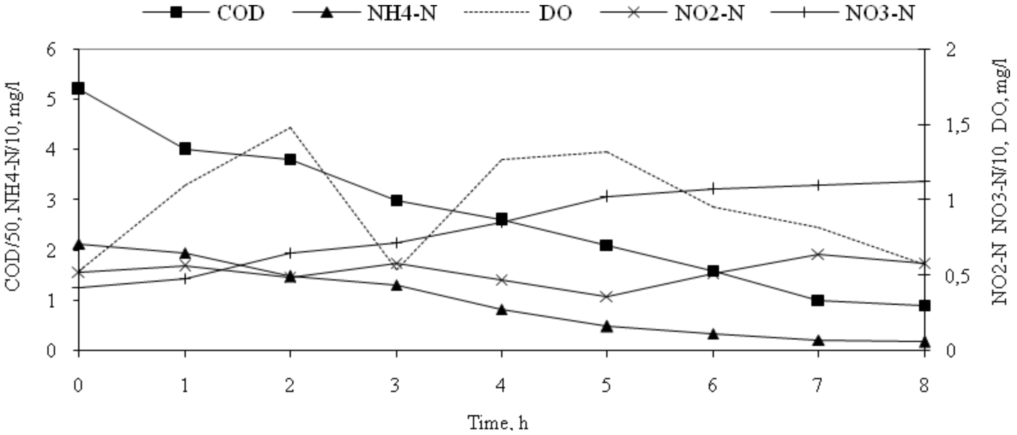

Figure 4. Variations of COD and nitrogen composition in Run 3.

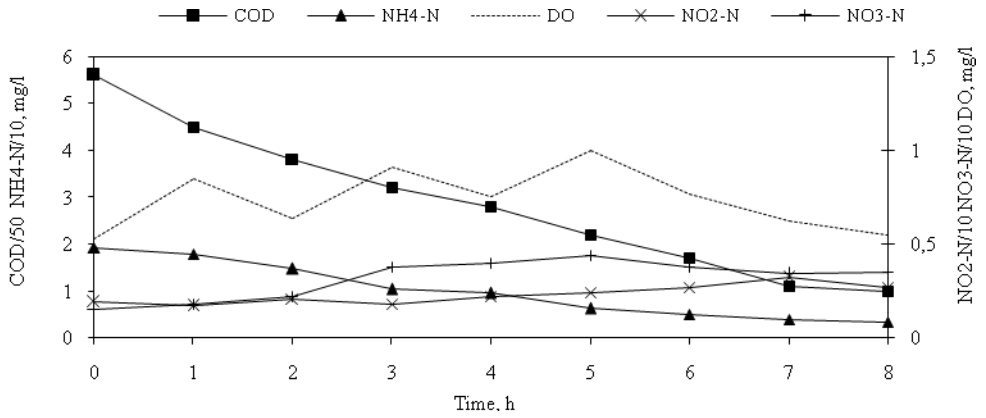

Figure 5. Variations of COD and nitrogen composition in Run 4.

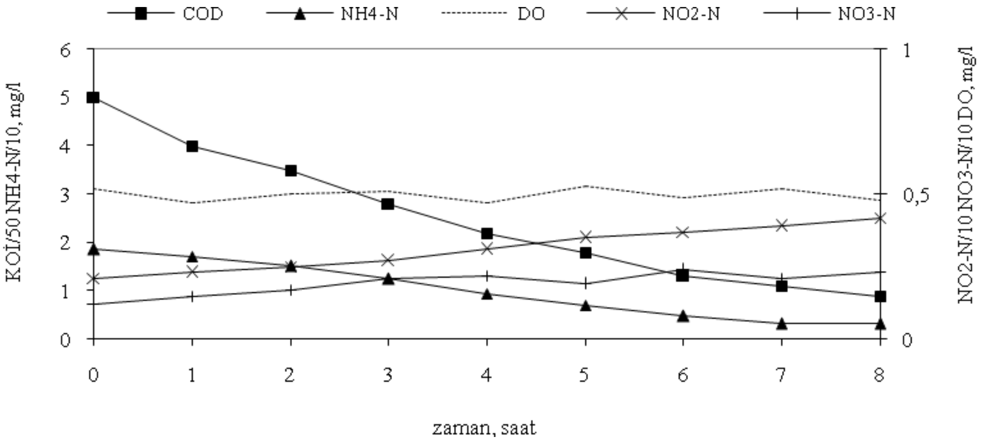

Figure 6. Variations of COD and nitrogen composition in Run 5.

The results show that effluent ammonium concentration increased in Run 4 and Run 5. This result was consistent with that obtained by Wang and Yang et al. [6] who reported that for ammonium oxidation, it is required to maintain the DO in the range of 1.0-1.5 mg/l.

A DO value of around 0.2 mg/l is required for simultaneous nitrification and denitrification [3]. In this study, except for Run 1 and 2, simultaneous nitrification and denitrification was observed. These results show that simultaneous nitrification and denitrification took place in DO concentration (< 2 mg/l). The highest nitrogen removal by simultaneous nitrification and denitrification was obtained as 50 % in Run 4.

The oxygen saturation coefficient of Monod kinetics for nitratation is known to be 1.1 mg/l [6]. In this study, nitrite concentration increased in Run 4 and 5. This case is likely due to inhibition of nitrite oxidizing bacteria.

Table 3 shows the airflow, aeration time and total air quantity in Runs. The results shows that the total air quantity was obtained as lower in Run 4. Subsequently, the quantity of used energy was also lower in Run 4.

Table 3. The airflow, aeration time and total given air quantity in Runs.

Run	airflow, L/h	Aeration time, h	Total air quantity, L
1	100	7.0	700
2	100	4.2	420
3	100	3.8	380
4	100	3.0	300
5	50	7.0	350

CONCLUSIONS

DO parameter has an important role in activated sludge procesess. The intermittent aeration made between DO concentrations of 0.5 and 1.0 mg/l is more favourable due to both higher simultaneous nitrification-denitrification and less aeration cost.

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MICROALGAE REMOVAL FROM SYNTHETIC WASTEWATER BY TILAPIA (*OREOCHROMIS NILOTICUS* AND *OREOCHROMIS AUREUS*)

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In present study, laboratory scale batch aquaculture systems were used to demonsrate the microalgae removal performance of *Oreochromis niloticus* and *Oreochromis aureus* (Tilapia). Microalgae-rich water dominated by green algae (i.e., *Chlorella*, *Scenedesmus*, and *Monoraphidium*) was used to determine removal rates. Different numbers of tilapias were used in each of the six glass aquaria for ten days experimental period. The cell counts of microalgae removed by tilapias indicated significant reduction in microalgae. Results showed that both fish species provided good algae removal via feeding on algae. Removal rates for microalgae were greater than 99 %. Removal efficency increased while the numbers of fish were incresed in the aquaria. Results indicated that COD, BOD_5 concentrations were reduced due to the removal of algae by fish.

Keywords: *Batch systems, algae removal, synthetic wastewater, Tilapia*

Introduction

The discharge of untreated wastewater into surface waters adversely impacts the ecosystem within the aquatic environment causing economic loss and threatening human health. Biological treatment methods have been widely used to control water pollution and reuse wastewater. According to some researchers on pond treatment processes, ponds are low-cost treatment units with minimum technology requirements. Therefore they have been widely adopted in the treatment of domestic and industrial wastewater worldwide during the past few decades [1-2]. Wastewater treatment ponds are efficient systems for removal of many substances and have some advantages. Polishing ponds are often the last stage of sewage treatment prior to discharge into water ways [3]. However, microalgae naturally growing in ponds can be seen as suspended solids in the effluent. If there is not an algae removal process from pond effluents, then the treatment is regarded as unsuccessful. Therefore, additional sedimentation process or removal units for microalgae removal are necessary. Fish can be introduced to waste stabilization ponds as removal agents to control suspended solids, microalgae, organic matter and nutrients [4].

In some countries, utilization of sewage for aquaculture has been in practice since the beginning of the twentieth century [3,5]. Use of microalgae as feed for warmwater fish was investigated in some studies [6-13] conducted on small aquaria or tanks and favorable results were reported.

Direct introduction of sewage into a stabilization pond containing fish is risky because of possible deoxygenation of the pond through excessive organic loading and this could lead to fish kill. A two-stage system may be employed to reduce the risk for fish to be subjected to low dissolved oxygen. In these systems, the waste is treated initially in a stabilization pond and the plankton-rich effluent is fed into a fish pond [14]. This two-stage system has been refined further by substituting a high rate stabilization pond for the conventional stabilization pond. The high rate pond, which was developed by Oswald in California [15], converts human waste into phytoplankton in only a few days due to its shallow depth, usually about 0.5 m, and manual or mechanical mixing of the pond. Living plankton that growing in wastewater can be prepared as dried feed for some fish such as *Cyprinus carpio* and *Tilapia* [7].

On the other hand, ease of cultivation, resistance to poor water quality and diseases, tolerance to a wide range of environmental conditions, ability to convert efficiently organic domestic and agricultural wastes into high quality protein, high growth rates and an amenability to intensification are some of the basic characteristics of *Tilapia* which make them an ideal alternative for fish culture [16]. Nile tilapia is an attractive species for aquaculture with its rapid growth, high production rate, low feeding trophic level and low production costs [17].
Although there are many studies on algae removal processes from stabilization pond effluents with chemical methods, data on microalgae removal from synthetic wastewater by using fish (*Oreochromis niloticus* and *Oreochromis aureus*) are limited. The aim of this study was to test the algae removal performances of the *Tilapia* from synthetic wastewater and observe the pollutant parameter in the water clarified by the *O. niloticus* and *O. aureus*. This method may be used for further investigation of algae removal by the fish.

Materials and Methods

Tilapias (with average weight of 2.184 g and average length of 2.8 cm) were obtained from Fish Ponds of Cukurova University Fisheries Faculty. One hundred tilapia fries were stocked in an 80-L glass aquarium which was initially filled with fresh water. Tilapia fries were fed prior to beginning of the experiments. About 270 L of synthetic wastewater was prepared in a 300-L concrete pond to compose algae-rich water (Fig 1).

Synthetic wastewater used throughout the studies was composed of glucose (240.0 mg/L), yeast extract (60.0 mg/L), NH_4Cl (90.0 mg/L), $MgSO_4.H_2O$ (25.0 mg/L), $FeSO_4.7.H_2O$ (1.0 mg/L), $MnSO_4$. H_2O (1.0 mg/L), $CaCl_2.2H_2O$ (1.0 mg/L), KH_2PO_4 (290.0 mg/L), K_2HPO_4 (785.0 mg/L) [18]. COD and BOD_5 concentrations of synthetic wastewater were 320 and 150 mg/L, respectively.

About 3-L of a mixed algal culture of *C. vulgaris*, *Scenedesmus sp.* and *Monoraphidium* sp. was inoculated into the synthetic wastewater prepared to concrete pond. Mixed algal culture was obtained from Plankton Laboratory of Cukurova University Fisheries Faculty. Algae were allowed to grow for 7 days. Water temperatures were measured and recorded at 6-hours intervals during the 7-days experimental period. Temperature of the water in the pond varied between 17.2ºC and 28.8ºC. After two days the colour of the synthetic wastewaters began to turn green and at the end of the 7-days period the colour

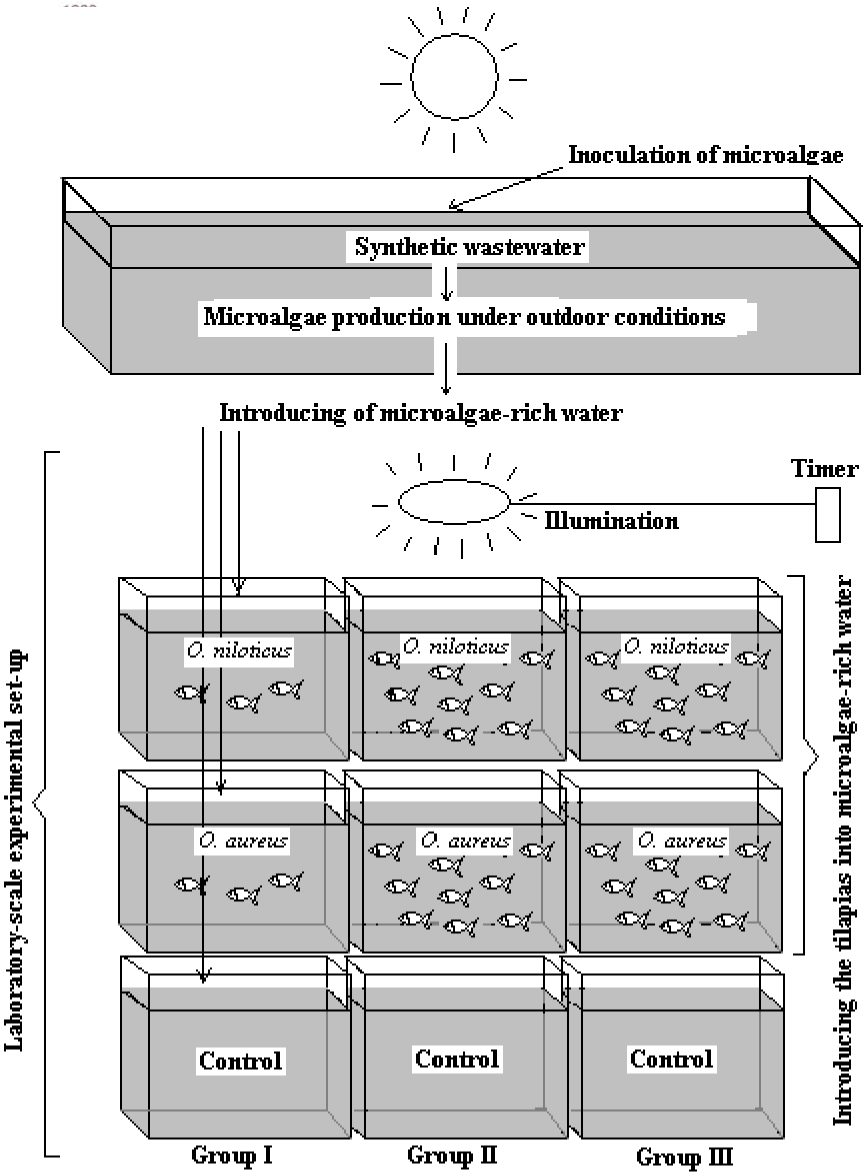

Fig. 1. General scheme of the experimental study

was completely dark green. In the microscopic investigations it was seen that *C. vulgaris* was dominant on *Scenedesmus sp.* and *Monoraphidium sp.*In order to start of laboratory-scale experiments, total of nine 25 L glass aquaria were divided into three groups where within each group was three aquaria. Before introducing the" tilapias, each aquarium was filled with 20 L of algae-rich water and aeration was started continuously.

In each group one aquarium is reserved as control aquarium where the other two aquaria contained *O. niloticus* and *O. aureus* respectively. For groups I and II the operation time was five days whereas ten days operation time was applied for group III. Groups I, II, and III contained 10, 40, and 40 tilapia fries, respectively, except the control aquaria (see Figure 1).

Total numbers of algal cells in the synthetic wastewater was obtained using Improved Neubauer (0.1 mm deep) lam under a light microscope. COD and BOD_5 analyses of algal-rich water in the aquaria were carried out at the beginning and end of the all stages without filtration using Standard Methods [19]. NH_4-N^+ and NO_2^- analyses were done using Nanocolor standard test kit and spectrophotometer (model 100D). pH was measured with Milwaukee brand manual pH-meter. Dissolved oxygen was measured by a YSI model 55 oxygenmeter.

Results and Discussion

In all groups, dissolved oxygen level never fell below 3.0 mg/L. In groups II and III, algae were removed effectively in such that it could be seen with naked eyes fairly easily in two days. But in group I, algae removal efficiency was very low and dark-green colour of algae-rich water was seen even at the end of the 5th day. The numbers of algae and other parameters were shown in Tables 1-3 below.

Table 1. First stage:5-days operation time and 10-fish experimental data

Aquariums	Number of Algae	(cell/ml)	COD(mg/l)		BOD_5(mg/l)		pH	
	1st day	5th day	1st day	5th day	1st day	5th day	1st day	5th day
O.niloticus	$6,02.10^5$	$4,13.10^5$	426	412	240	232	7.1	7.7
O. aureus	$6,02.10^5$	$3,90.10^5$	426	409	240	225	7.1	7.8
Control	$6,02.10^5$	$4,38.10^5$	426	410	240	235	7.1	7.3

Table 2. Second stage:5-days operation time and 40-fish experimental data

Aquariums	Number of Algae	(cell/ml)	COD(mg/l)		BOD_5(mg/l)		pH	
	1st day	5th day	1st day	5th day	1st day	5th day	1st day	5th day
O.niloticus	$9,7.10^4$	$1,4.10^3$	255	102	175	55	7.2	8.1
O. aureus	$9,7.10^4$	$1,8.10^3$	255	105	175	57	7.2	8.1
Control	$9,7.10^4$	$9,1.10^4$	255	250	175	172	7.2	8.4

Table 3. The last stage:10 days operation time and 40-fish experimental data

Aquariums	Number of Algae	(cell/ml)	COD(mg/l)		BOD_5(mg/l)		pH	
	1st day	10th day	1st day	10th day	1st day	10th day	1st day	10th day
O.niloticus	$6,14.10^5$	$2,2.10^2$	435	152	240	85	7.4	8.2
O. aureus	$6,14.10^5$	$3,6.10^2$	435	167	240	90	7.4	8.3
Control	$6,14.10^5$	$3,7.10^3$	435	112	240	65	7.4	8.8

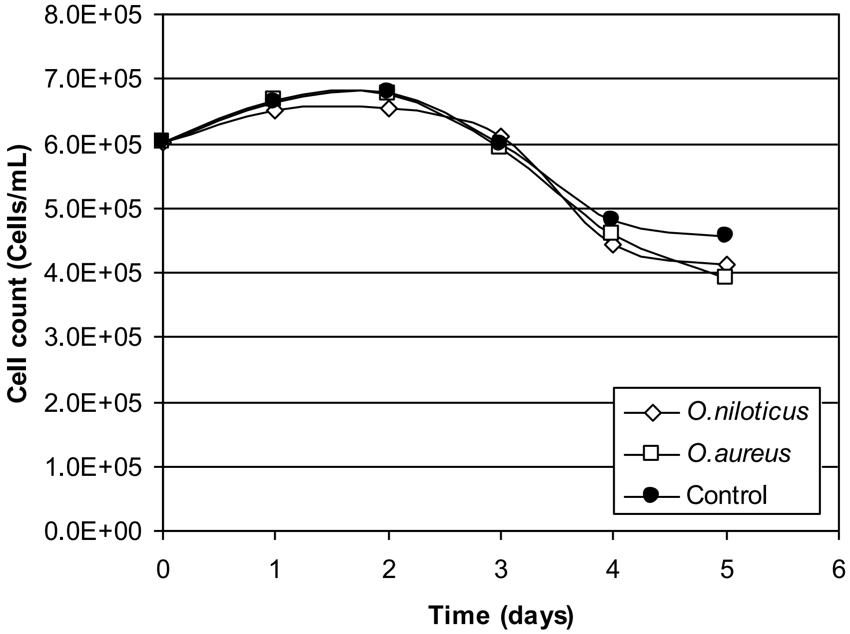

Fig 2. Algae removal at 10-fish population and 5-days operation time (n:*O. niloticus* aquarium, a:*O. aureus* aquarium, C:control aquarium)

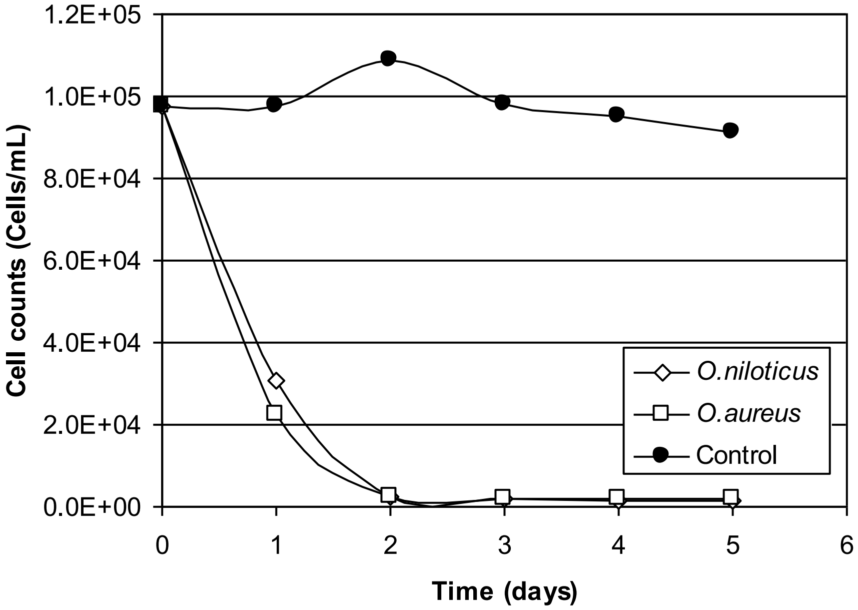

Fig 3. Algae removal at 40-fish population and 5-days operation time (n:*O. niloticus* aquarium, a:*O. aureus* aquarium, C:control aquarium)

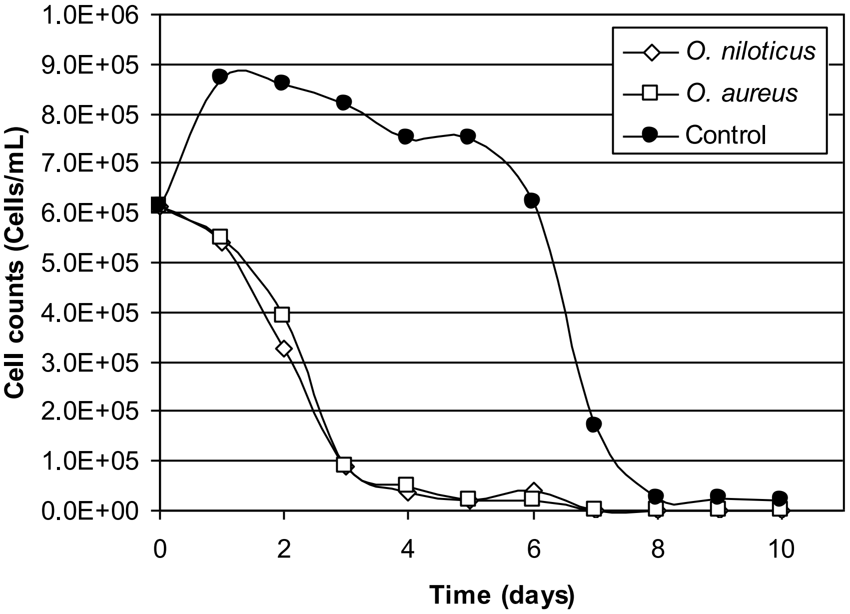

Fig 4. Algae removal at 40-fish population and 10-days operation time (n:*O. niloticus* aquarium, a:*O. aureus* aquarium, C:control aquarium)

Algae removal

Throughout the study, *Chlorella vulgaris* was dominant in the synthetic wastewater. In all aquaria containing fish, there was a substantial decrease in algae population due to favorable feeding by the fish (Tables 1, 2, 3 and Figures 2, 3, 4). But in control aquarium of group III, considerable decrease in algae numbers was observed at the end of 6-7 days (Table 3 and Figure 3). Dark-green colour of the control aquarium of group III gradually disappeared via sedimentation which may depend on nutrient depletion.

Microalgae numbers at the beginning and the end of five days were $6.02.10^5$ – $4.13.10^5$ cells/mL, respectively, in the *Oreochromis niloticus* aquarium of group I with a removal rate was 31.4 %. There was 35.2 % removal rate in the *O. aureus* aquarium in group I and it can be seen that algae removal rate was approx. 98 %. In group II (Table 2) and finally in group III algae removal rate was 99.9 % for both fish species.

Effluent quality

Although an increase of NH_4-N^+ and NO_2^- concentrations was obtained from all groups, COD and BOD_5 concentrations decreased sharply depending on algae removal by the the fish (Table 2, 3) in groups II and III. It can be concluded that the metabolic activation of the fish can be the reason of the increase in NH_4-N^+ and NO_2^- concentrations. Algae removal rate increased when the number of fish was increased in the aquaria. In the aquaria of group I with tilapia, algae removal rate was not very high and the results from the control aquarium were similar. In group I, COD and BOD_5 concentrations did not decrease satisfactorily.

When the number of fish in the aquaria increased, removal rate increased sharply. In group I, COD and BOD_5 removal rates were around 3 %. However, in group II, 60 % COD and 68.5 % BOD_5 removal was obtained and 65 % COD and 64.5 % BOD_5 removal rates were obtained in group III.

The study shows that each species of *Tilapia*, *Oreochromis niloticus* and *Oreochromis aureus* was able to remove microalgae *Chlorella vulgaris* from the synthetic wastewater (*C. vulgaris* was dominant to *Scenedesmus sp*., and *Monoraphidium sp.*). The conditions have been identified as favorable for the growth of microalgae *Chlorella vulgaris*. Although high COD and BOD_5 (255-426 mg COD/L, 175- 240 mg BOD_5/L) concentrations exist in the wastewater depend on microalgae, the results of the study show that algae can be removed with fish even using synthetic wastewater in the laboratory conditions. Moreover, each fish species stayed alive in all groups although there were too much fish (10-40 fry in 25 L). During maximum of 10-days operation time applied in the study, there was not any fish death in the aquaria. pH never increased above 8.3. Maximum NH_4-N^+ concentration was 2.9 mg/L and this concentration did not cause fish death. Moreover, despite the nitrite (NO_2^-) tolerance limits (D_{50}) was reported as 2.1 mg/L in the *Tilapia* culture by Balarin and Haller [16], 2.0 mg/L maximum NO_2^- concentration in the group III did not cause fish death. There are several reports about fish mortalities such that the extent of the algal bloom caused sharp oxygen depletion which killed the fish [20] and increase in ammonia concentration. In this study, oxygenation was supplied with the aid of an air pump. For all groups oxygen concentration never fell below 3 mg/L. As mentioned before, maximum NH_4-N^+ and NO_2^- concentrations were 2.9 and 2.0 mg/l respectively, even 40 fish were used in 25 L synthetic wastewater. There was an intensive algal population in the aquaria ($6.14.10^5$) this intensivity but this did not cause any lethal problem for the fish.

Conclusion

The results of this study show that in the laboratory conditions, removal of microalgae from synthetic wastewater with the *Oreochromis niloticus* and *Oreochromis aureus* is possible. Algae removal with the tilapias can be applied and performed with aeration. Although operation times applied as 5-10 days in the aquaria, considerable number of algae was removed within 2-3 days. Therefore, the ponds that have 2 or 3 days retention time can be constructed for microalgae removal. However the results show that the number of fish is an important factor for algae removal.

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BIOREMEDIATON OF CD(II)-CONTAMINATED KAOLINE BY RHAMNOLIPID BIOSURFACTANT

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In this study, the bioremediation of Cd(II)-contaminated kaoline as a soil component was studied using rhamnolipid biosurfactant. The effects of rhamnolipid concentration, pH and the amount of Cd(II) loaded to kaoline on the recovery of Cd(II) ions from kaoline by rhamnolipid biosurfactant were investigated. When the concentration of rhamnolipid was increased from 12.5 to 100 mM, the Cd(II) recovery efficiency increased with increasing rhamnolipid concentration up to 50-100 mM, and Cd(II) recovery efficiency reached a plateau value of 70.3 -71.5 % of the sorbed Cd(II). To determine the effect of pH on the desorption efficiency of Cd(II), pH was varied between 6.0 and 7.4. Optimum pH was determined as 6.8 and the recovery efficiency was found to be 70.6 % at a 6.3 mmol Cd(II) loading per kg kaoline. As the amount of Cd(II) loaded to kaoline was increased from 1.54 to 11.82 mmol Cd (II)/kg kaoline, the maximum Cd(II) desorption efficiency was 71.9% of the sorbed Cd(II) at 4.42 mmol Cd (II)/kg kaoline, at 80 mM rhamnolipid concentration and pH 6.8.

1. Introduction

Soil contaminated with heavy metals is a salient example of environmental risk. The presence of heavy metals in soils leads to serious problems because they can not be biodegraded: (1) toxicity on biological system and (2) groundwater contamination by leaching process. (Hong et al., 2002). Soil excavation, thermal extraction for volatile metals (e.g. mercury, arsenic, and cadmium as well as their compounds can be evaporated at 800^{o}C), electrokinetics, solidification/stabilization, vitrification, chemical oxidation, soil flushing are traditional remediation technologies developed for heavy metal contaminated soils (Wang and Mulligan, 2004). Due to the great expense of traditional remediation, alternative cost-effective remediation techniques are required. Bioremediation, an alternate novel biotechnology, has potential for the remediation of heavy metal contaminated sites. Biosurfactants generated by bacteria and yeasts could be used potentially for the environmental remediation of heavy metals from soils (Grasmück and Scholz, 2005; Neilson et al., 2003; Peters, 1999). Biosurfactants are interest for use in remediation technologies for several reasons: they are anionic nature, low toxicity, biodegradability and excellent surface active properties and may have unique metal binding capacities and selectivities in comparison to available synthetic surfactants (Herman et al., 1995; Wang and Mulligan, 2004; Miller, 1995). Biosurfactants can enhance the mobility of heavy metals by reducing the interfacial tension between the metals and soil and by forming micelles (Wang and Mulligan, 2004). The biosurfactant used in this study, a rhamnolipid, was from the glycolipid group and was produced by *Pseudomonas aeruginosa.* The type of soil, presence of various components such as clays, feldispats, iron oxides in soil play an important role in the removal of heavy metal ions from soil by rhamnolipid biosurfactant (Frazer, 2000). In this study the recovery (desorption) of Cd(II) ions from kaolin, a component of soil, by rhamnolipid biosurfactant was studied. The objective of this study was to investigate the effects of rhamnolipid concentration, pH, and loaded Cd(II) quantity per unit weight of kaolin on the recovery of Cd(II) ions from kaolin by rhamnolipid biosurfactant.

2. Materials and Methods

2.1. Biosurfactan

The rhamnolipid used (CAS Number: 147858-26-2) was obtained from Jeneil Biosurfactant Co., Llc. with the trademark JBR425. JBR425 is aqueous solutions of rhamnolipids at 25% concentrations. When the biosurfactant is diluted in water to a rhamnolipid concentration up to 50 mg of rhamnolipid per liter (≈0.1 mM), the surface tension is reported to be 29 mN/m. Rhamnolipids are also soluble in most common alcohols. Rhamnolipid aggregate morphology undergoes significant changes in the pH region of 6.0-7.5. At pH 5.5, rhamnolipid begins to visibly precipitate out of solution and it is unstable at extreme pH due to hydrolysis of the glycosidic linkage between sugar and lipid. It is stable to 121^{o}C for at least one hour and at room temperature.

2.2. Bioremediation of Cd(II)-contaminated kaolin using rhamnolipid biosurfactant

To investigate Cd(II) complexation by rhamnolipids from kaolin, firstly kaolin sorbed Cd(II) ions. 1.5 g of kaolin was placed into 40-mL centrifuge tubes. The range of concentrations of prepared metal solutions varied from 0.25 to 5.29 mM. The tubes containing Cd(II) ions and kaolin as an adsorbent were agitated on a shaker at 25^{o}C and 150 rpm for 72 h. After reaching ultimate equilibrium, the tubes were centrifuged, and the supernatant was diluted into 1% HNO_3 for atomic absorption analysis. Sorbed metal ion concentration was calculated from the difference between initial metal ion concentration and metal ion concentration remained in the supernatant after sorption.

The metal-loaded kaolin was suspended in 5 mL solution containing 12.5, 25, 50, 80 and 100 mM rhamnolipid. The centrifuge tubes containing kaolin mixed with rhamnolipid solution were agitated on a shaker at 25^{o}C and 150 rpm for 72 h and then centrifuged at 19000x g for 20 min. The supernatant was analyzed for Cd(II) ion concentration by atomic absorption analysis. The pH of supernatant samples used for atomic absorption analysis was then adjusted using 0.1 mL of concentrated HNO_3 to < 2 to precipitate the rhamnolipid. To remove the rhamnolipid pellets, each sample was centrifuged and then the supernatant was diluted in 1% HNO_3 for atomic absorption analysis. To guarantee that all Cd(II) ions were desorbed from the rhamnolipid pellets, the pellets were treated a second time with 1% HNO_3 and the supernatant was analyzed ones again.

3. Results and Discussion

The first stage of the studies was to load kaolin with Cd(II). As the concentration of Cd(II) ion in solution was increased from 0.25 to 5.29 mM, Cd(II) ions sorption to kaolin decreased from 92.86 to 33.53%. Cd(II) sorption efficiencies of kaolin are shown in Table 1.

Table 1. Cd(II) sorption efficiencies of the kaolin

C_i (mmol/L)	Sorption efficiency (%)
0.24	92.86
0.87	76.02
1.85	58.17
2.66	50.16
3.47	43.35
4.47	37.37
5.29	33.53

In the second stage of the studies, the desorption of Cd(II) ions from kaolin using rhamnolipid biosurfactant was investigated. To determine the effect of pH on the recovery efficiencies of Cd(II) ions, the pH was varied between 6.0 and 7.4. Change of the desorbed Cd(II) concentration with pH is given in Fig.1. At pH 6.8, 0.675 mmol/L Cd(II) was desorbed from the kaolin using rhamnolipid biosurfactant. The best recovery efficiency, 70.6-70.2 % of the sorbed Cd(II), was achieved by adjusting the initial pH value to 6.8-7.0 at 1.15 mM initial Cd(II) ion concentration in solution (6.3 mmol Cd(II) / kg kaolin) and at 80 mM rhamnolipid concentration. Recovery efficiencies of Cd(II) showed more intense increase with increasing pH in the range 6.0-6.8, compared to the decrease in the pH region between 7.0 and 7.4. 55.7 % of the sorbed Cd(II) was recovered from the kaolin at pH 7.4, whereas the desorption efficiency of Cd(II) was only 37.5% of the sorbed Cd(II) at pH 6.0. Different rhamnolipid structures were reported to be strongly dependent on pH (Tan et al., 1994). The type of rhamnolipid structure formed is especially sensitive to pH in the range of 6.0 to 7.0. Rhamnolipid has a pK of 5.6. At a low pH (4.3<pH<5.8), rhamnolipids form liposome-like vesicles. Between pH 6.0 and 6.6, rhamnolipids form either lamella-like structures (6.0<pH<6.5) or lipid aggregates (6.2<pH<6.6), and above pH 6.8, when the rhamnosyl moiety is negatively charged, micelles form (Zhang and Miller, 1992). The most effective structure in the recovery of Cd(II) ions from kaolin was the micelles form of the rhamnolipid, as observed above pH 6.8. Micelles are the smallest basic structure formed, generally less than 5 nm in diameter. Filtration of metal complexes by small kaolin pores has little effect on particles of this size.

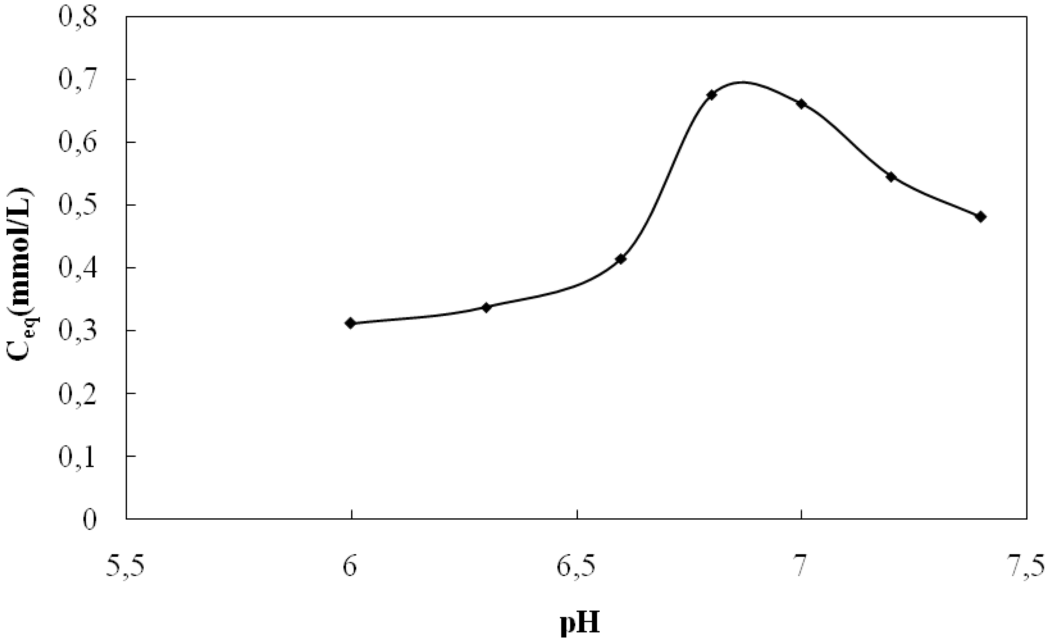

Fig. 1 Effect of pH on recovery of Cd(II) ions by rhamnolipid biosurfactant from kaolin

When the initial Cd(II) ion concentration in solution was held constant at 1.0 mM, the rhamnolipid concentration was varied from 12.5 to 100 mM at pH 6.8 and, at 25°C. As shown in Fig. 2, as rhamnolipid concentration was increased from 12.5 to 100 mM, the recovered Cd(II) concentration increased with increasing rhamnolipid concentration up to 50-100 mM, and the desorbed Cd(II) concentration reached a plateau value of 0.491-0.518 mmol / L at a concentration of 4.8 mmol Cd(II) / kg kaolin. At this plateau value of the desorbed Cd(II) concentration, Cd(II) recovery efficiency was 70.3-71.5 % of the sorbed Cd(II). As higher concentrations of biosurfactants can result in plugging in soil pores by the dispersion of fine materials, or by the formation of viscous emulsions, introduction of excess rhamnolipids into soils containing kaolin should be avoided.

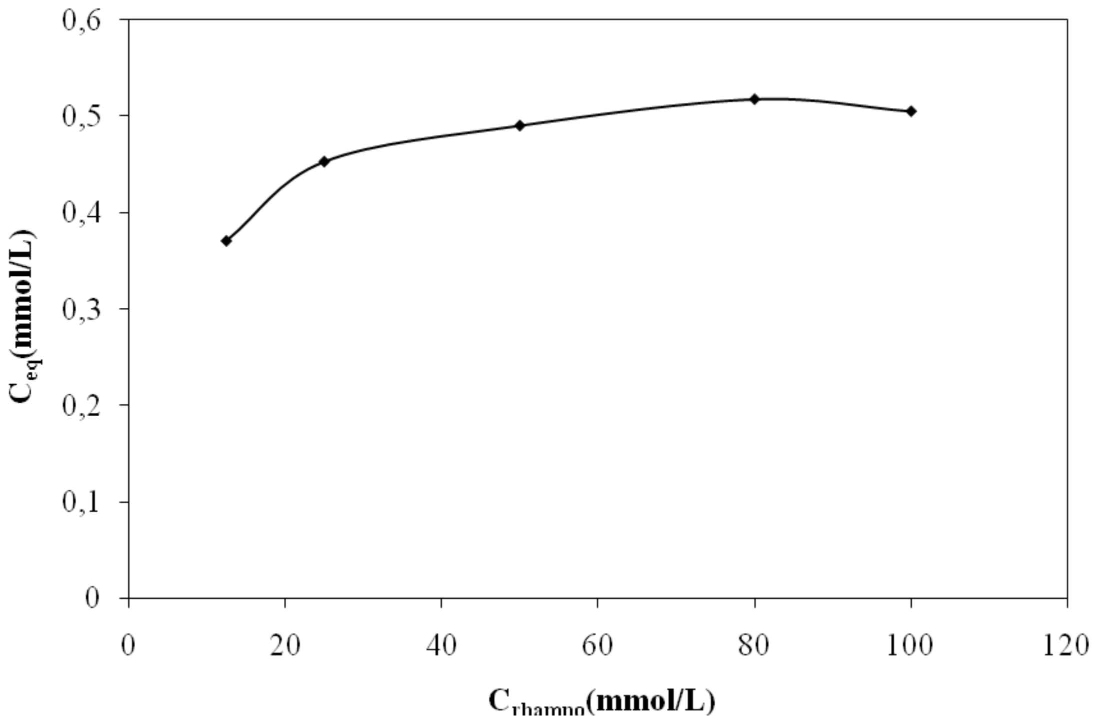

Fig. 2. Effect of rhamnolipid concentration on the recovery of Cd(II) ions by rhamnolipid biosurfactant from kaolin

As the amount of Cd(II) loaded to kaoline was increased from 1.54 to 11.82 mmol Cd (II)/kg kaoline, the amounts of desorbed Cd(II) by 80 mM rhamnolipid solution were determined at pH 6.8. Although the Cd(II) recovery efficiency was the highest (71.9 %) at 4.42 mmol sorbed Cd(II) quantity per unit weight of kaoline (kg), it decreased from 71.9 % to 45.2 % with increasing amount of Cd(II) loaded to kaoline. In Fig. 3, desorption isotherm of Cd(II) from kaoline is presented. Desorption isotherm rising with a moderate slope indicates that desorption of Cd(II) from kaoline was effective, as also confirmed by recovery efficiencies.

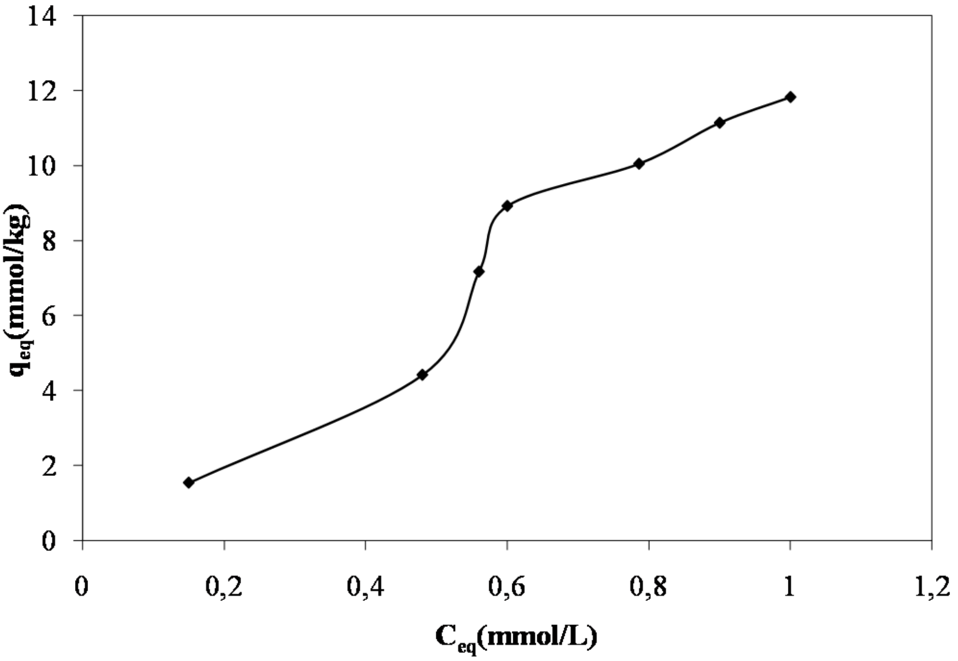

Figure 3. Desorption isotherms of Cd(II) from kaoline

To propose success of the soil-washing process by rhamnolipid biosurfactant on a certain type of soil, the heavy metal recovery capacity of rhamnolipid biosurfactant from components constituting that soil must be known exactly. Soil-washing technology by biosurfactants was reported to sometimes remain ineffective due to several reasons such as inability to treat contaminants in low permeability soils or in soils containing high clay or iron oxide (Frazer, 2000). In this study, rhamnolipid technology as soil-washing process was shown to be applied succesfully in the remediation of Cd(II)- contaminated kaolin, low permeability clayey soil.

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PROPOSAL FOR A SOLID WASTE MANAGEMENT SCHEME FOR THE TURKISH REPUBLIC OF NORTHERN CYPRUS

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The Turkish Republic of Northern Cyprus shows a rapid development in population and urbanization in the recent years. This trend has major negative effects on the environment. One of the urgent problems is the solid waste management. Transport and final disposal of solid waste is becoming a serious problem especially in the summer months. The majority of the municipalities in the country are little towns and villages which have high summer population. They are technically not in the situation to develop and carryout solid waste management strategies. In this work the current situation, solid waste production, existing facilities and projection for the future are discussed.

Keywords: *Turkish Republic of Northern Cyprus, Solid waste management, Composting, Landfill, Sustainability*

1. Introduction

Turkish Republic of Northern Cyprus (TRNC) is one of the Mediterranean countries which show a rapid development in population, urbanization and tourism in the recent years. This situation has major negative effects on the environment. One of them is the solid waste management. Then source separation, collection, transportation and disposal of solid waste produced in the 3355 km^2 of extending land is becoming to be a serious problem throughout the year. The main residential centers and the highways are shown in Figure 1.

The produced municipal and industrial solid wastes are deposited in the environment with minimum any precautions. The majority of the wastes produced in Lefkoşa, the biggest city of the Republic, are transported to Dikmen landfill area and buried there. As only a part of the wastes are sorted and buried in the new constructed sanitary landfill area, great part of the wastes are continued to be deposited in the uncontrolled part of the landfill.

As the solid waste management is an urgent problem, in this work proposal for a management scheme is developed. The management umbrella covers the municipal and health-care wastes. As no waste water treatment sludge is produced, and no data on the industrial wastes exists they are left out of consideration.

In framework of the proposed management scheme the waste will be separated at source (organics, recoverable, non-recoverable) and transported via transfer stations to the central treatment facilities. In these facilities the organics will be composted, recoverable material will be compacted and sold and the remaining non-recoverable waste will be buried in the sanitary landfill of the facility which should be equipped with gas and leachate treatment units.

In this work the population development of the main residential centers as well as the waste production for the coming 20 years are calculated and based on the existing waste management practices a sustainable integrated solid waste management scheme is developed.

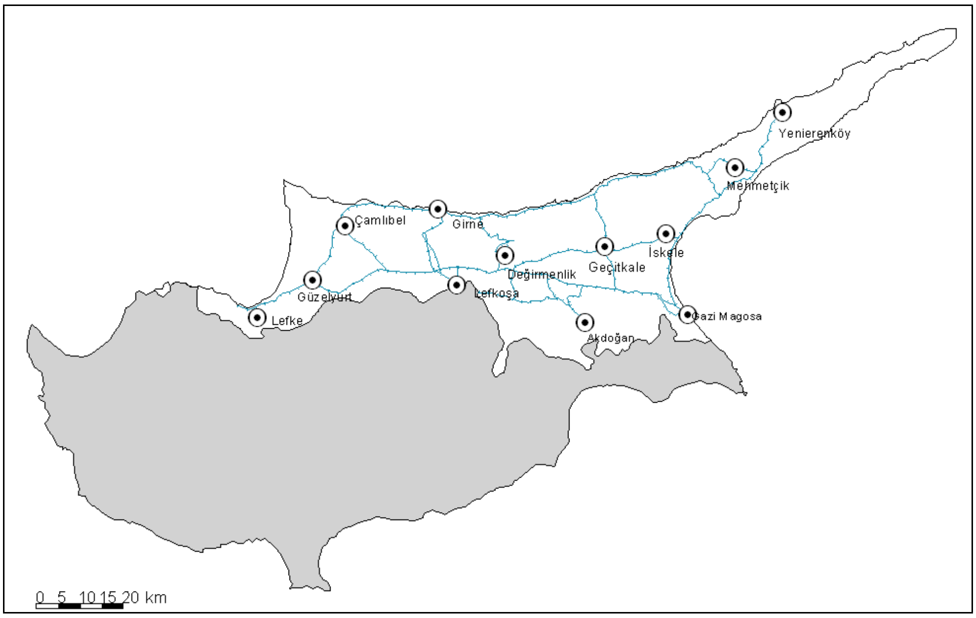

Figure 1. Map of Turkish Republic Northern Cyprus and the main residential areas

2. The Existing Solid Waste Management

2.1 Sources

In this study it is assumed that the residential solid waste comprises the main component of the total waste collected in the country. The medical waste amount is calculated based on the bed capacity and occupancy rates (www.devletim.com).

2.2 Generation rate and density

According to results of the studies conducted by the official institutions in TRNC, the specific waste production in the province is given as 0.9 kg/cap/day (İlktaç and Veysioğlu, 2006). This value is in accordance with the specific waste production rate in Turkey which is given as 1 kg/cap/day (Topkaya, 1999), and 1 - 3.3 kg/cap/day for USA (Tchobanoglous et.al., 1993). The density of solid wastes as delivered in compaction vehicles is given as 500 kg/m^3 (İlktaç and Veysioğlu, 2006), which as comparison, have been found to vary from 178 - 415 kg/m^3 for USA (Tchobanoglous et al., 1993). For the determination of the amount of healthcare wastes it is assumed that the specific waste production (kg/bed/day) is 1,6 kg/bed/day which is determined in studies carried out in health care institutions in Istanbul and Antalya (Kakad, 2003; Topkaya, 2005). The occupancy rate of the institutions varies between 8 – 23 % for the year 2005 (www.devletim.com). It is assumed that this rate will increase to 40 % till year 2025.

2.3 Solid waste composition and production

Solid waste composition in this study is determined by personnel communications with solid waste management firms active in TRNC (Kücükgül, 2006). A comparative study is shown in Table 1 (Tchobanoglous et.al, 1993; Curi, 1994; Topkaya, 1999). It shows minor differences from the main residential areas of Turkey as well as from some industrialized countries. The composition of solid wastes varies with social status as well as geographical conditions but due to lack of statistical information it was not possible to show this detail in this study. In order to calculate the required capacities, the waste generated is sub-divided under three categories as biological (suitable for composting), recoverable and non-recoverable wastes.

Table 1. The variation of the solid waste composition (%)

Component	USA & Canada	Sweden	France	Israel	Japan	İstanbul	Ankara	Antalya	TRNC
Organic*	15	12	24	71	37	43-61	50	40-66	54
Recoverable*	65	76	38	25	31	15-25	23	26	8
Non-recoverable*	20	12	38	4	32	14-42	27	7-33	38

*Organic: Food waste, garden waste etc.
*Recoverable: Paper, Glass, Plastics, and Metal
*Non-recoverable: Construction and demolition waste, Miscellaneous etc.

2.4 Solid waste collection and disposal

In the main residential centers such as Lefkoşa, Girne and Gazimağusa, solid waste collection is accomplished partly by containers and in plastic bags which are collected daily by pressurized solid waste trucks. The waste is transported to the landfill located in Dikmen/Lefkoşa. Some of the waste such as household waste is collected together with green waste and other types of waste produced in the city and transported by open trucks and disposed in the non-sanitary part of the Dikmen landfill area. It is reported that numerous wild dumping places distributed over the country is under operation.

3. Proposed Waste Management Scheme

3.1 Development of the population

In order to develop a proper solid waste management scheme, the population increase must be calculated for the coming decade as precise as possible. This is not an easy task for TRNC as the touristic season population increases to 2-3 times of the winter season population and the recent census data is missing. The population development is calculated based on census data of the years 1996 and 2006. The future expectations are calculated for the years 2010 and 2025. The annual population increase rate is assumed as 1.10 % as given in (İlktaç and Veysioğlu, 2006). The residential centers in TRNC are subdivided to be five regions and 12 districts. In Table 2 and Figure 2 is the population development forecast regarding the main residential centers is shown.

Table 2. Development of the population

	Güzelyurt Region		Girne Region		Lefkoşa Region		İskele Region			Gazimağusa Region		
	Lefke	Güzelyurt	Çamlıbel	Girne	Değirmenlik	Lefkoşa	Yenierenköy	Mehmetçik	İskele	Geçitkale	Akdoğan	G.Mağusa
1996	9287	18236	4365	34350	8323	53972	7363	4899	6917	6554	10923	35398
2010	12121	21227	4365	64467	13252	82296	8453	6132	8785	8734	10923	51312
2012	12586	21692	4365	68393	14059	87308	8623	6330	9086	9104	10923	54120
2014	13069	22168	4365	72558	14915	92625	8796	6534	9398	9491	10923	57082
2016	13570	22653	4365	76977	15823	98266	8973	6745	9720	9894	10923	60206
2018	14091	23150	4365	81665	16787	104250	9153	6963	10053	10313	10923	63501
2020	14631	23657	4365	86638	17809	110599	9357	7187	10398	10751	10923	66977
2022	15793	24176	4365	91914	18894	117335	9525	7419	10754	11207	10923	70642
2024	15775	24706	4365	97512	20045	124480	9716	7658	11123	11683	10923	74508
2026	16381	25247	4365	103450	21265	132061	9912	7905	11505	12179	10923	78586

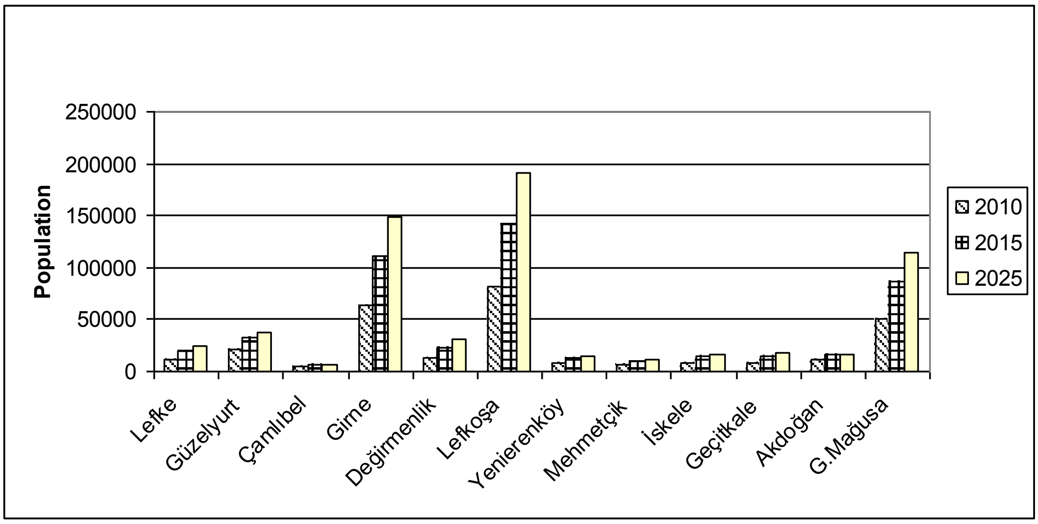

Figure 2. Development of the population of the main residential centers

3.2 Solid waste production and disposal options

Waste produced in the 12 main residential centers is calculated regarding to the population projections calculated above (Table 3).

Table 3. Amount of waste produced in the residential centers

Municipality	2010				2015				2025			
	Organics (t)	Recover. (t)	Non-rec.(t)	Total (t)	Organics (t)	Recover. (t)	Non-rec.(t)	Total (t)	Organics (t)	Recover. (t)	Non-rec.(t)	Total (t)
Lefke	1647,42	244,06	1159,30	3050,78	3521,90	521,76	2478,37	6522,04	4251,24	629,81	2991,61	7872,67
Güzelyurt	3234,88	479,24	2276,40	5990,53	5941,59	880,24	4181,12	11002,94	6621,88	981,02	4659,84	12262,74
Çamlıbel	774,31	114,71	544,88	1433,90	1161,46	172,07	817,32	2150,85	1161,46	172,07	817,32	2150,85
Girne	6093,35	902,72	4287,91	11283,98	19698,54	2918,30	13861,93	36478,78	26473,15	3921,95	18629,25	49024,35
Değirmenlik	1476,42	218,73	1038,96	2734,11	4049,19	599,88	2849,43	7498,51	5441,88	806,20	3829,47	10077,56
Lefkoşa	9574,09	1418,38	6737,32	17729,80	25146,45	3725,40	17695,65	46567,50	33794,66	5006,62	23781,43	62582,70
Yenierenköy	1306,12	193,50	919,12	2418,75	2356,18	349,06	1658,05	4363,30	2602,67	385,58	1831,51	4819,75
Mehmetçik	869,03	128,75	611,54	1609,32	1757,31	260,34	1236,63	3254,29	2059,59	305,12	1449,34	3814,05
İskele	1227,01	181,78	863,45	2272,23	2529,23	374,70	1779,83	4683,75	2993,54	443,49	2106,57	5543,60
Geçitkale	1162,61	172,24	818,14	2152,99	2561,16	379,43	1802,30	4742,88	3152,66	467,06	2218,54	5838,27
Akdoğan	1937,63	287,06	1363,52	3588,21	2906,45	430,58	2045,28	5382,31	2906,45	430,58	2045,28	5382,31
G.Mağusa	6279,25	930,26	4418,73	11628,24	15465,75	2291,22	10883,30	28640,27	20187,16	2990,69	14205,78	37383,63

The main waste producing cities are the Lefkoşa, Girne and Gazimağusa. Regarding to the disposal of the produced waste four scenarios are developed as summarized in Table 4.

Table 4. Waste disposal scenarios

Scenario	Waste collection	Disposal art
I	All the produced waste are collected together (commingled)	Landfill: Lefkoşa
II	Waste produced in the west and east part of the country collected separately (commingled)	West part: Landfill located in Gazimağusa East part: Landfill located in Lefkoşa
III	Source separated waste (Org. + recoverable + non-recoverable)	Main site in Lefkoşa: Separation + Composting + Landfill
IV	Source separated waste (Org. + recoverable + non-recoverable)	West part:Gazimagusa : Separation + Composting + Landfill East part: Lefkoşa: Separation + Composting + Landfill

Scenario I: All of the produced waste are collected together, transported and disposed in the main sanitary landfill located in Lefkoşa

The waste produced in the 12 residential centers is collected commingled and transported to the new sanitary landfill located in Lefkoşa (Figure 3). The volume of waste produced in each center is calculated for the years 2010-2025. The art of transportation is to be decided by the municipalities: The waste can be transported with separate trucks of each community or they could be unloaded in a bigger transfer truck and transported to the end disposal site. In Figure 3 it is assumed that wastes which are transported to Güzelyurt, Girne and Gazimağusa will be unloaded in transfer stations and transported to Lefkoşa with transfer trucks of 58 m^3 capacity. Due to compaction the specific weight of the commingled waste in the trucks and in the landfill will be 500 kg/m^3 and 750 kg/m^3 respectively. The volume of waste (m^3) and necessary landfill space in Lefkoşa landfill are given in Table 5.

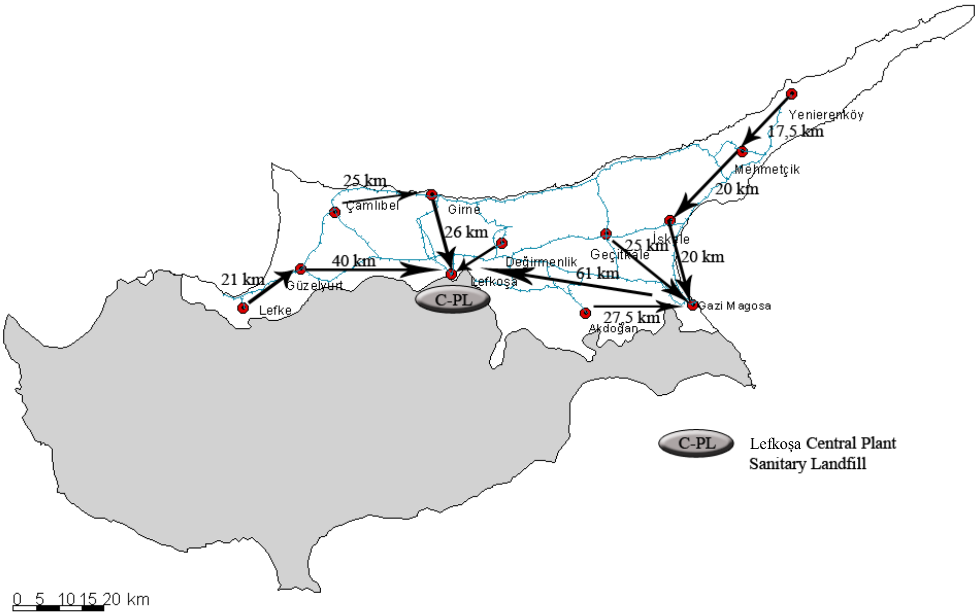

Figure 3. Central landfill in Lefkoşa and waste transport routes (Scenario I)

Scenario II: All of the produced waste are collected together and transported to one of the main sanitary landfills located in Lefkoşa and Gazimağusa

In this scenario it is planned to construct two sanitary landfills in the near vicinity of the two biggest cities of the country: Lefkoşa and Gazimağusa. Waste produced in the 6 municipalities located in the western part of the country will be transported to the new sanitary landfill in Lefkoşa, whereas the waste produced in the remaining 6 municipalities located at the eastern parts of the country will be transported to Gazimağusa (Figure 4). The development of waste production (m^3) and necessary landfill space in Lefkoşa and Gazimağusa are given in Table 5.

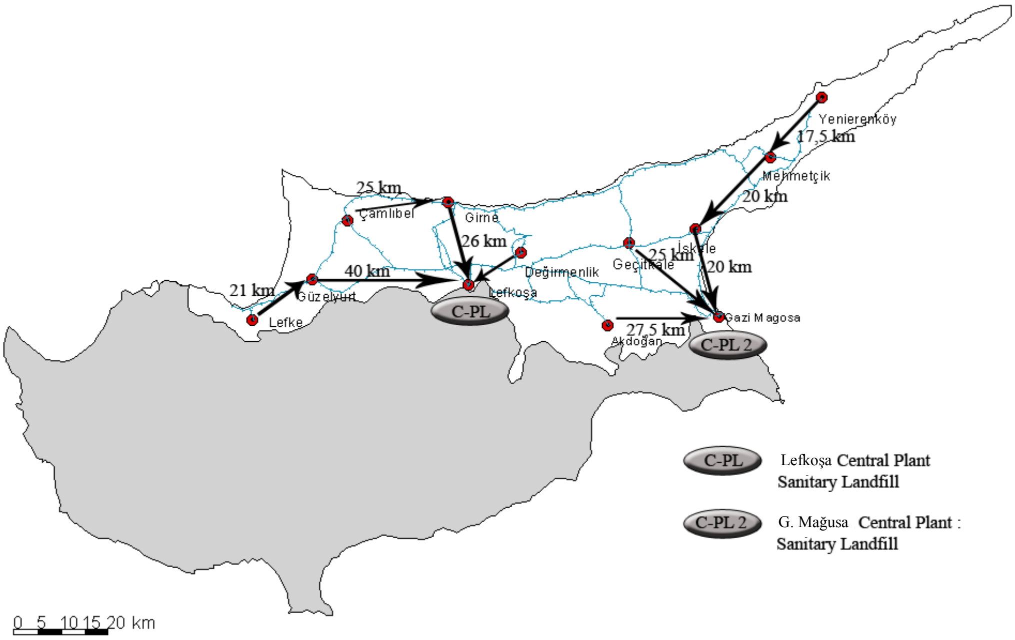

Figure 4.Central landfills in Lefkoşa and Gazimağusa and waste transport routes (Scenario II)

As the art of waste collection and disposal assumed in the first two scenarios are not sustainable, in the following scenarios (III and IV) source separation and separate collection of the wastes, composting of the organics and land filling of the remaining wastes in central sites are the key elements of the new proposed management scheme.

Scenario III: All of the produced waste are separated at source and transported to the main Central Waste Processing Plant in Lefkoşa

In this scenario (Figure 5) it is assumed that the waste produced in each of the residential centers are separated at source and transported to the new Central Waste Processing Plant in Lefkoşa. This plant should be equipped with separation, composting and land filling units. In case of transportation of the waste, the transfer stations located in Güzelyurt, Girne and Gazimağusa will be used. The amount of waste components and necessary landfill space in Lefkoşa is given in Table 5.

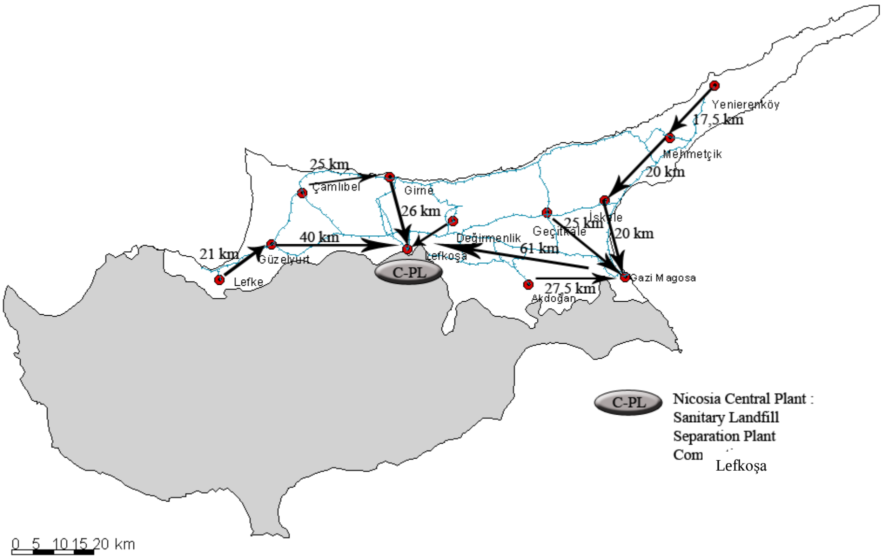

Figure 5. Central Waste Processing Plant in Lefkoşa and waste transport routes (Scenario III)

Scenario IV: Source separated waste produced in the residential centers in west and east part of the country are collected separately and transported to one of the Waste Processing Plants located in Lefkoşa and/or Gazimağusa (Figure 6). The amount of waste components and necessary landfill space in Lefkoşa and Gazimağusa is given in Table 5.

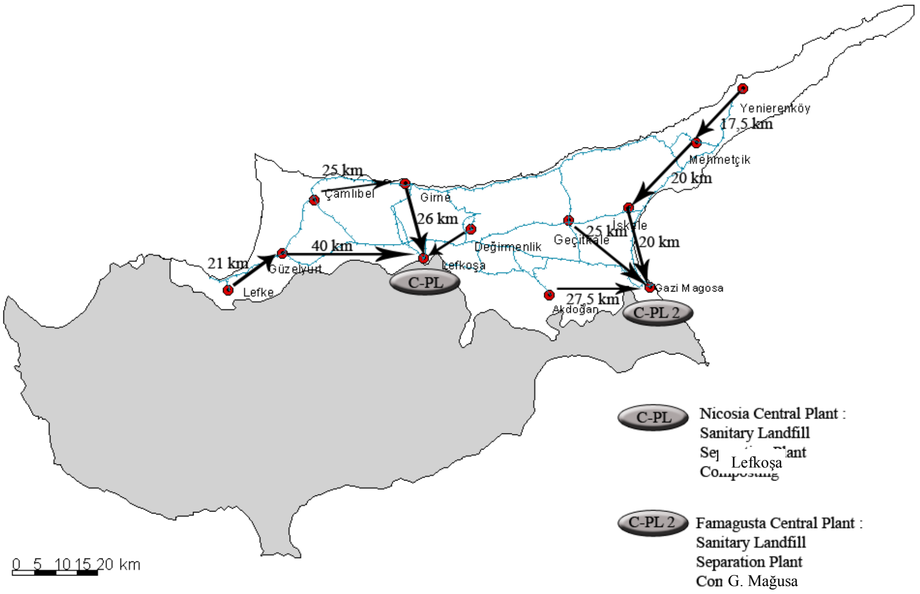

Figure 6. Waste Processing Plants in Lefkoşa and Gazimağusa, and waste transport routes (Scenario IV)

Table 5. Results of the waste management scenarios

Process	**Scenario I**		**Scenario II**		**Scenario III**		**Scenario IV**	
Years	**2010**	**2025***	**2010**	**2025***	**2010**	**2025***	**2010**	**2025***
Landfill Lefkoşa (m3)	127 925	2 207 718	86 607	1 494 615	40 052	691 216	27 115	467 950
Landfill Gazimağusa (m3)			41 320	713 103			12 937	223 266
Composting Lefkoşa (t)					17 269	298 042	11 691	201773
Composting Gazimağusa (t)							5 578	96 268
Recoverable Lefkoşa (t)					7 675	132 465	5 196	86 676
Recoverable Gazimağusa (t)							2 479	42 786

* Cumulative volume (2010 – 2025)

In case the municipalities decide to apply a management scheme according to scenario I, the necessary landfill area will be 127 925 m^3 as seen from Table 5. The waste can be deposited in 3 m high layers with 0,5 m soil daily cover. By applying 10 layers the necessary surface area will be 5000 m^2. For the time till 2025 for every 5 years of period it will be necessary to develop additional landfill area with 20 000 m^2 surface area. On the other hand in case of a decision in favor of Scenario III, only a third of landfill space is to be developed and it will be possible to recover considerable amount of valuable material.

The ultimate decision is to be made by the local authorities. Additional economic feasibility studies which should also take the costs related to the transportation of waste and for the construction of the transfer stations into consideration should be conducted prior to ultimate decision.

In addition to the residential waste the medical waste disposal options are also determined. Infectious and other hazardous waste which should be collected separately in red bags produced in the main health care institutions are calculated as summarized in Table 6. It is assumed that the occupancy rate will be 40 % by the year 2025. One special truck will be sufficient to transport all of the produced “red bag” wastes to the central medical waste disposal site located in the Dikmen landfill in Lefkoşa.

Table 6. Amount of health care waste (www.devletim.com)

Health care institution	Bed capacity	Overnights (2005)	Estimated overnights (2025)	Waste produced in 2025 (t)
Lefkoşa				
Dr.O.Nalbantoglu State Hospital	385	13017	56210	89.9
Chronicle Diseases Hospital	38		5548	8.88
Radiation and Oncology Center	12		1752	2.80
Thalasamia Center	12		1752	2.80
Magusa				
State Hospital	166	5021	23360	37.38
Girne				
Dr.Akçiçek Hospital	54	4490	7884	12.61
Yesilyurt				
Cengiz Topel Hospital	35	1768	5110	8.17
Total	702			162.54

4. Conclusions

For a developing country like TRNC, solid waste management is still an unsolved problem. A solution which includes only (sanitary) landfills without waste separation, recovery, and composting, can not be considered as sustainable management. Besides it is not easy and too expensive to find an appropriate location and to construct a sanitary landfill for each of the residential areas.

It is shown that the feasible solution must include separate collection. To realize this goal, it is advised to collect the waste in two different boxes in houses as organic waste and recoverable material as an initial step, which will also be collected separately by the municipalities. Ultimate separation will be accomplished in the newly proposed central plants. The waste will be transferred to these plants using transfer stations or in separate trucks of the municipalities. Organic waste will be transformed to compost, while the recoverable material can be processed further in the country which will create new working areas. The remaining non-recoverable wastes will be landfilled.

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A STUDY ON RECOVERY AND RECYCLING OF USEFUL MATERIAL IN LEATHER TANNING INDUSTRY

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Tanning industry uses a number of chemicals during the process, only a part of a chemical is consumed and the rest ends up in the effluent as pollutant.

This paper deals with the process development for recycling of these chemicals. Basic chromium sulfate (BCS) is one of the expensive and widely used chemicals in chrome tanning process. We have economically recovered BCS up to99 %, however 1% is left as impurity in effluents. Sodium sulphide is recovered up to 99.5 from the composite wastewater using the very economical method.

This paper also deals with the locally devolved technique of de-liming by the use of CO_2.
This results show that in case of skins, the use of ammonium sulfate can be completely eliminated where as in case of bovine hides the use of ammonium sulfate can be reduced to 20 to 50% (w/w), depending upon the thickness of the pelt (limed hides or skins). These results in proportional reduction of ammonia gas produced along with the reduction in concentration of BOD, COD and sulfate ions by the same amount. Additionally, the system can also produce hot water while cooling the boiler off gases from 280-220 ^{o}C to 105 ^{o}C the quantity of hot water generated depends upon the quantity of boiler off gases being cooled.

Calcium Hydroxide has been recovered up to 68% from leather tannery unhairing wastes by processes which may be adoptable to commercial use. It is also an estimated the cost analysis of total and individual recycling of different Chemicals used in different tanning process.

Introduction

The manufacturing processes of leather tanning requires considerable quantities of water and discharges nearly 30–35 L of water for every kilogram of leather processed.[1] Nearly 90% of the leathers manufactured and currently used contain at least a minor quantity of chromium either as a tanning material or in dyes.

The leather tanning and finishing industry has high water consumption and, respectively, generates great amounts of wastewaters with a very complex composition, large quantities of solids and organic material, nitrogen, salts, in addition to some specific pollutants such as chromium and sulphide. The conventional wastewater treatment, usually applied to the mixture of effluents from all production processes, makes use of solids separation and biological treatment.[2] such approach is a difficult challenge for economical wastewater treatment. To meet water and chemical saving objectives, spent solution recycling was implemented in the unhairing, tanning and pickling processes.[3]

Recycling of unhairing liquors after previous sedimentation of insoluble substances allowed important savings, such as 50% reduction of sulphide, 40% of lime and 60% of process water. The recycling with simply complementing the exhausted chromium solutions reduced chromium loss by 25–35%. Grease and solids pre-separation allowed increasing the amount of the cycles. The conservation measures reduced the water consumption but they failed to reduce substantially the pollution load. Despite of relatively low water quality requirements for processing water, the implementation of water reuse in a high proportion has been difficult because of the high wastewater treatment costs. The search for alternative technologies was stimulated by the acceptance of the waste minimization-elimination strategy. Modifications of processes and techniques of greater exhaustion of the baths have been implemented, which allowed reducing the losses of the used reagents and their concentration in the wastewater.[4]
For example, chromium in the exhausted baths was reduced from 4–8 g/l to 2–5 g/l. Individual treatment of specific effluents was further proposed to avoid dilution of toxic pollutants. Some of them made possible recuperation of materials simultaneously with the reduction of contaminants in the mixed total effluent. Such is the case of chromium removal and recovery by alkaline precipitation, followed by filtration and acidification of obtained $Cr(OH)_3$. In Mijaylova-Nacheva *et al*. (2003) it was demonstrated that chromium can be recovered by almost 98% through precipitation with $Ca(OH)_2$, NaOH or Na_2CO_3 and settling.
Greater efficiencies at lower doses were obtained with $Ca(OH)_2$, with up to 99.88% removal of the Cr^{3+} at doses of 2.3–3.3 g/g Cr^{3+}; sedimentation and compression were more effective for the separation of the precipitate. In addition to removing chrome, the precipitants remove almost 50% of the COD. [5,6]They also can remove TSS, 80% when using hydroxides and 45% when using Na_2CO_3. The use of $Ca(OH)_2$ results in a 30% reduction in water salinity, while NaOH and Na_2CO_3 are unable to affect this parameter. The precipitate separation rate by sedimentation can be almost doubled using laminar modules. Since the effluent from liming process contains sulphides in a high concentration, and, since any mixing of this wastewater with other effluents, related to pH drops, causes a dangerous stripping of H_2S, a pre-treatment of this effluent was suggested to remove sulphides before mixing with the rest of wastewater. One method is the precipitation of sulphides with ferric salts and the separation of precipitate in settlers. This treatment creates great quantities of sludge, which is the reason why the method of catalytic oxidation of sulphides with air oxygen in the presence of manganese catalyst is used more widely.[7] This treatment allows more than 98% sulphide removal with a manganese dose 0.05–0.15 gMn^{2+}/gS^{2-} at 3–4 h of aeration. By applying this method, the sulphide concentration in the total effluent can be reduced 3.5 times. Besides, an additional 6–9% reduction of COD is obtained. After the sulphide oxidation, proteins can be removed and recovered from unhairing waste applying acidification to pH of 3.2–3.9 for protein precipitation, settling and dehydration. This treatment allows 65% protein recovery, more than99% TSS removal and 70–80% COD removal in unhairing effluent. Oil and grease can be removed by simple gravity flotation where 95% removal can be reached in one hour of retention time.8 Previous acidification causes de-emulsification and enhances O&G removal. As the reuse and recovery programs allow lower treatment costs, the possibilities to implement water management strategies with higher or complete recycling are greater. The leather tanning sector in Pakistan is not economically profitable and few tanneries have implemented proper wastewater treatment to meet environmental standards.[8] Only few industries practice recycling of spent solutions.

The lack of comprehensive pollution control systems in the sector has produced serious environmental problems. The objective of this study was to develop an alternative management strategy for the tannery effluents in Pakistan which allows water recycling and valuable material recovery, providing adequate water quality for in-plant processes and also meeting environmental criteria in a cost effective manner.[9]

Under this project various pollution abatement measures have been suggested and implemented in individual tanneries, such as chrome recovery either by direct recycling of spent tanning float or by chrome recovery and reuse method, lime and pickle float recycling of spent tanning float or by chrome recovery and reuse method, lime and pickle float recycling and recycling of relatively clean washed, CO_2 declaiming, dye recycling and reuse of de-liming, dye recycling and reuse of process etc. Majority of these measures are based on the principal of waste minimization at source.

Out of the above discussed cleanser production options, the chrome recovery, lime recycling and reuse of pickle float have been found out most important in chemical and water conservation and reduces significant environmental pollution lad form the tanning industry.

Theses are the objectives of this study are that to determine efficiency of different recycling options: and financial and environmental impacts of selected recycling options, including quality of leather

This study has been conducted as a part of the ICTP programmed in the tanneries of the Punjab. Feats of three processes causing 60 to 70% of the total effluent pollution were selected for recycling as listed below:

1. chrome tanning:
2. Liming; and
3. pickling**.**

Methodology

To study the above-mentioned options, full-scale recycling systems were installed in one tannery under the Pollution control project. Tannery staff was helped to monitor the processes and analyses were conducted in the in-house laboratory mainly. Ten drums were used during this study, and weight processed in each drum was 3,000 kg. All three selected processes were recycled for 10 continuous days.[10,11] Necessary environmental parameters were monitored at the process level and at the final effluent drain, after the primary wastewater treatment plant, both with recycling options for 10 days and for 3 days without recycling at the end. Concentration of unexhausted chemicals in all these recycling options were also analyzed to quantify the amount of fresh chemicals needed to be added in the spent liquor to recycle for the next batch and for the study of financial aspects and pay back period.

Chemical and float

Chemicals and water used in the processes were taken based on the pelt weight of hide. The float taken for tanning and pickle process was 80% and 175% of pelt weight in liming process. The range of chemicals, %age of pelt weight used, and their concentration in float are as given in Table-1

Table-1.Chemical concentration in floats

Sr. No.	Process	Name of Chemical	Chemical (%) of pelt weight	concentration in floats g/l
1	Chromium tanning	Chromium Sulphate	5.0	62.5
2	Pickle	1.Sulphuric acid	2.0	25.0
		2.Sodium chloride	8.0	100.0
		3.Sodium formate	1.5	18.7
3	Liming	1. Sodium sulphate	4.0	22.8
		2.Calcium hydroxide	4.0	22.8

Recycling techniques

The recycling techniques or cleaner options studied are as listed below:

a. Chrome tanning float:

After tanning process the spent float from each drum was pumped in a fiberglass tank and pH was adjusted from 3.8 to 2.8 using sulfuric acid. After Cr2O3 analyses, the spent float was recycled for the next lot coming after pickling process. The fresh powder $Cr_2(SO_4)_3$ used was 70% only and 30% was taken from the recycled float.[12,13]

b. lining float:

Similar to above recycling technique, the spent float from the liming process was collected in the fiberglass tank and analyzed for hydrated lime and sodium sulfide. Spent liming float was recycled back for the next batch and completed the process by adding the required quantity of sodium sulfide and lime.[28]

c. Picking float:

After pickling process, the spent float was pumped in the fiberglass tank and analyzed for sulfuric acid, sodium chloride and sodium formate.Spent pickle float was recycle back for the next batch before tanning. The required exhausted chemicals were added to meet the require recipe.[29]

Results and discussion

Chrome recycling

Chromium metal in the trivalent form is used for leather tanning in the world over. Commercially it is available in the form, basic chromium sulfate (BCS), containing about 26% chromium oxide of 33% basicity. During tanning about 5-7% of pelt weight, BCS is applied. It imparts higher shrinkage temperature, softness, fullness and preservation to the leather. Approximately 63% (135) of 216 tanneries of Punjab are using BCS in tanning and re-chroming process to produce leather of different properties and qualities. The estimated chromium sulfate consumption in these tanneries is 27,657 kg/d. about 7,740 (28%) kg/d BCS is being wasted (survey report 1999 by ICTP). Such huge quantity of this precious chemical is not only an economic loss to the tanners of Punjab but also poses significant environmental impacts on the water bodies. By chrome recycling system the spent chrome can be recycled back for tanning processes, without compromising any leather quality, which is normally 20-30% of the BCS applied. The concentration of chrome in the spent liquor for 10 continuous days is as listed in Table-2

Table No.2 Chrome concentration in spent liquor

Cycle No	BCS in spent liquor (g/l)	BCS Wasted (%)
1	14.06	23.36
2	14.04	23.04
3	15.02	24.32
4	15.04	24.64
5	15.06	24.96
6	15.04	24.64
7	15.06	24.96
8	14.04	23.04
9	15.04	24.64
10	14.02	22.72
Average	15.02	24.03

The discharge of BCS is in the range of 14.2 g/1 to 15.6 g/1. The BCS applied in each batch was 62.5g/1(5%). The difference in effluent concentration is due to small variation of float volume and the chrome exhaustion. The average chrome wastage in this particular tannery is 24%. By direct chrome recycling the saving is about Rs. 453,600 per annum at the production capacity 30,000 kg/d, where as the capital investment of chrome recycling system was about Rs.650,000 (pay back period 1.5 month).[14,15]

The average concentration of different pollution parameters and their load is shown in Table-3, which shows high percentage of TDS, sulfate and chromium in chrome tanning spent liquor. $Cr_2(SO_4)_3$ and sulfuric acid are the main source of these pollutants.[16,17] The concentration of chloride ions is due to sodium chloride used in the pickle bath. Thus recycling of this float has significant effect on the final effluent from the tanning industry.

Table No.3 Average concentration of pollutants

Sr. No.	Parameter	Concentration (mg/l)	Pollution load(Kg/d)	% of total pollution load
1	BOD	1513	37	2
2	COD	4995	120	7
3	TSS	1603	38	2
4	TDS	33580	806	45
5	Sulphate	17498	420	24
6	Chloride	12160	292	16
7	Chromium	1258	61	4

Lime recycling

Liming is a process for the removal of epidermal system and pigmentary matter from the hide .the epidermal system consists mainly of the protein keratin.

A proper liming is necessary for smooth grained, non-cracky leather, processing a tight grain break and high tensile strength. The most commonly used method of depilation is the immersion of the stock in calcium hydroxide and sodium sulphate solution. The amount of lime and sodium sulphate added is about 4% of the pelt weight.

The discharge of liming process is the most polluted stream in the tanning industry. It contributes almost 30 to 40 of the total pollution caused by tanning processes.18,19 Liming effluent contains very high values of BOD, COD, TSS, TDS, alkalinity and sulfide. The recycling of this float would reduce the pollution load substantially and lot of chemical cost saving is possible.20 The concentration of Calcium Hydroxide and Sodium Sulfide in the spent liming liquor is as listed in table 4.

Table 4 . Concentration of Calcium Hydroxide and Sodium Sulfide in the spent liming liquor

Cycle No	Calcium Hydroxide (g/l)	Sodium Sulfide(g/l)
1	6.25	8.50
2	7.10	9.60
3	6.75	10.10
4	6.50	8.95
5	7.20	10.60
6	7.80	10.75
7	7.65	8.30
8	8.10	9.55
9	6.36	10.30
10	6.90	10.75
Average	7.06	9.71

Mean of 10 cycles reveal, 28% saving of Calcium Hydroxide and 39% saving in sodium sulfide. The cost saving is Rs. 37,632 and Rs. 196,560 per month out of lime and sodium sulfide respectively. The capital investment of lime recycling system is about Rs. 700,000 and pay back period is less than three months.
The average concentration of different pollution parameters and their load during the 10 days monitoring is as shown in Table-5.

Table No.5 average concentration of different pollution parameters in liming spent liquor

The above table shows high % of BOD, COD and TDS pollution load. Comparatively low TSS values are due to sieving of spent liquor by the fine screens. The concentration of sulfide is 3,996 mg/1, where as NEQS limit is only 1.0 mg/1 in the final effluent.21 By recycling of the lime spent liquor would ultimately lower the pollution load at the final drain significantly. Without lime recycling the high sulfide concentration requires very high investment for treatment.[22]

Sr. No.	Parameter	Concentration mg/l	Pollution load kg/d	% of total pollution load
1	BOD	20111	1056	18.4
2	COD	43693	2294	40
3	TSS	10891	572	10
4	TDS	30591	1660	28
5	Sulphate	3969	210	3.6

Pickle recycling

The objective of pickling is to completely remove the lime and acidify the stock in a solution of sodium chloride, sodium formate and sulfuric acid for about 4-6 hrs until a pH of 2.5 to 3.5 is achieved. This acidic pH before chrome tanning reduces the astringency of the chrome-tanning agents.

In general after the completion of pickling, basic chromium sulfate is added in the same bath to start the chrome tanning process. So all the load is carried over to the tanning process. But to recycle the chrome-tanning float, one have to drain out the spent pickle float. Which contains high concentration of unexhausted chloride ions and sodium formate and sulfates. The recycling of pickle float would help reduce the pollution load and save the unexhausted chemicals also. The concentration of different chemicals present in the spent pickle float is as given in Table-6.

Table No. 6 The concentration of different chemicals present in the spent pickle float

Cycle No.	Sodium chloride (g/l)	Sodium Formate (g/l)	Sulfuric acid (g/l)
1	40.30	8.00	8.00
2	29.24	9.50	8.33
3	40.30	9.25	7.84
4	41.75	8.75	7.84
5	41.54	8.50	8.50
6	40.70	8.50	8.33
7	41.13	9.00	7.68
8	41.37	8.25	7.35
9	41.60	9.25	8.00
10	39.50	9.75	8.00
Average	40.74	8.87	7.98

The quantity of sodium chloride saved for the next pickling process is 41%, sulfuric acid 28% and sodium formate was about 43%. Total chemical saving is about Rs. 216,000 per month, at Production capacity of 30,000 kg per day. Investment cost for the pickle recycling system is Rs. 500,000 and pay back period is 2.5 months only.[23] The average concentration of different pollution parameters and their load during the 10 days monitoring is as shown in Table-7

Table No.7 average concentration of different pollution parameters in pickle spent liquor

Sr. No.	Parameter	Concentration (mg/l)	Pollution load(Kg/d)	% of total pollution load
1	BOD	1611	38.66	1.50
2	COD	5269	126.30	4.80
3	TSS	2744	65.80	2.50
4	TDS	54055	1297	50.00
5	Sulphate	21489	515.6	20.00
6	Chloride	23381	561	21.50

Above table shows high concentration of TDS, chloride and sulfate in the pickle-spent liquor. High TDS and chloride ions concentration is due to addition of sodium chloride and sulfates are due to sulfuric acid in the pickle bath. The recycling of this present liquor would ultimately reduce the concentration of these pollutants in the final effluent.

Effluent Pollution Load

During the recycling period, 10 days and following 3 days , without recycling, the effluent at final drain was monitored regularly and composite sample were prepared and analyzed daily after the primary treatment plant. The average flow rat was about 674.8 m^3/d, during recycling period and 785m^3 /d without recycling. The comparison of pollution load of different pollution load of different pollution parameter with and without recycling is as given in Table-8.

Parameters	Without Recycling		With Recycling		% Pollution Load Reduction with Recycling	Saving Pollution charges per Month Rs.
	mg/l	Kg/day	mg/l	Kg/day		
Chromium	87	68.3	12	8.1	88	3009
Sulfide	174	136.6	18	12.1	91	6224
Sulfate	1625	1275.6	520	350.9	73	46236
Chloride	3640	2857.4	1980	1336.1	53	76065
TSS	1350	1059.8	375	253.1	76	40332
TDS	7700	604.55	4250	2867.9	53	158830
COD	2750	2158.8	1050	708.5	67	72512
BOD	785	616.2	310	209.2	66	20351
Total		14217.2		5745.9		423559

TableNo.8 Cost Analysis of effluent with and without recycling of Chemicals used in tanning process

Table-8 shows that all these recycling options are very much effective in pollution load reduction along with water conservation. The pollution load reduction of different parameters is in the range of 53 to 91% . Sulfide and chromium reduction is in the range of 88 to 91%. The chromium concentration in the effluent using recycling system is 12 mg /1 and sulfide is 18mg/1. This concentration is due to re-chroming, washing and fleshing.[25]

BOD load reduction is about 407 kg/d (66%), with recycling system. Other than chemical saving, it substantially reduces the capital investment of wastewater treatment plant and operation and maintenance cost also. The capital investment cost of wastewater treatment plant is bout Rs., 28,000/kg of BOD load, at this level of pollution load. With the recycling options the industrialist save Rs. 423,559 per month and Rs. 42,356 per month during the first year, based on 10% charge only.[24]

Moreover the leather produced form all these recycling options passed all quality tests and rather trend of improvement in leather quality has been observed.

Conclusion and Recommendations

It is concluded that here recycling of chrome lime and pickle are very much effective in reducing the pollution load at the final drain and are equally effective source of chemical land water conservation. All these options are financially feasible without any compromising leather quality.

Chrome recycling system results in, 24% basic chromium sulfate cost saving. Where as with recycling, tis concentration lowered down form 87 mg/1 to only 12mg/1 and chromium load reduction was about 60 kg/d. which sis still higher than the NEQS limit of 1.0 mg/1 and needs further treatment of comply with this standard. Which is possible by separate treatment of chrome contaminated stream. Sulfate reduction is quite significant, which is about 925 kg /d (73%) and final effluent comply NEQS limit of 600mg/1

Lime recycling saves 28% Calcium Hydroxide and 39% Sodium Sulfide. Lime recycling spent liquor contains very high BOD, COD and TSS. Its recycling imparts significant impact on the effluent pollution load. Overall reduction of BOD, COD and TSS by recycling of all above discussed options is 407 kg/d, 1,450 kg/d and 807 kg/d respectively, but major impact is due to liming process. Concentration of sulfide ions reduced form 174 mg/1 to 18mg /1 in recycled effluent.

In pickle recycling system the unexhausted chemicals are sodium chloride 41%, sulfuric acid 28% and sodium formate 43%. Chloride ions reduction is about 1,521 kg/d. The remaining chloride ion concentration in the final effluent with pickle recycling is 1,336 mg/1, which is mainly due to discharge of soaking float. The NEQS level of 1,000 mg/1 can be achieved by additional salt dedusting of hid, before the soaking. Overall financial anises show that all theses recycling options need Rs. 1.85 million investment and cost saving is about Rs. 0.90 million, the payback period is only 2 months, at production capacity of 30,000kg/d. Saving in pollution charge is about Rs. 5 million per year.

It is recommended to adopt further cleaner production options like, slat dedusting, recycling of de-dusted salt in the pickle processes, CO_2 Deliming and dye recycling for chemical saving and further reduction of pollution load from the final drain.

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COMPARISON OF THE METAL CONCENTRATIONS IN ATLANTIC HORSE MACKEREL, *TRACHURUS TRACHURUS*, FROM COASTAL WATERS OF TURKEY

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The concentrations of cadmium, iron, lead, zinc, copper, manganese, nickel, chromium and cobalt were determined by ICP-AES in muscles and livers of Atlantic horse mackerel, *Trachurus trachurus*, from coastal waters of Turkey. The analyzed fish samples were collected from different locations in the Black, Marmara, Aegean and Mediterranean seas. The concentrations in tissues of the analyzed metals were significantly affected by sampling sites ($p<0.05$). Iron showed the highest levels in both tissues from all locations. Following Fe; Zn showed the second highest levels. In all locations, the metal concentrations in livers were higher than those in muscles. In addition, the differences between the metal concentrations in tissues were statistically significant ($p<0.05$). Metal levels in tissues were compared with national and international permissible limits. Metals concentrations in the edible parts of fish were assessed for human uses.

Keywords*: Metals, Trachurus trachurus, fish, Atlantic Horse Mackerel, Turkey Waters.*

INTRODUCTION

Industrial wastes, geochemical structure and mining of metals create a potential source of heavy metals pollution in the aquatic environment (1-2). Under certain environmental conditions, heavy metals might accumulate up to a toxic concentration and cause ecological damage (3-4). Metals such as iron, copper, zinc and manganese, are essential metals since they play an important role in biological systems, whereas mercury, lead and cadmium are non-essential metals, as they are toxic, even in traces. Heavy metals in aquatic environment can remain in solution or in suspension and precipitate on the bottom or be taken up by organisms. The analysis of metal concentrations in biota samples at the same locations can indicate the transfer of metals through food chains (5). Therefore, numerous studies have been carried out on metal accumulation in different fish and invertebrate species (6-13). On the other hand, fish have been popular targets of heavy metal monitoring programs in marine environments because sampling, sample preparation and chemical analysis are usually simpler, more rapid and less expensive than alternative choices such as water and sediments (14). Our specific objectives were to determine the distribution of analyzed metals in muscles and livers of *Trachurus trachurus* from the coastal waters of Turkey, to evaluate the differences between the metal concentrations in different sites, and to compare the results with national and international permissible concentrations.

MATERIALS AND METHODS

Fish samples were collected from seven different sites in the coastal waters of Turkey from May 2005 to July 2005. These sampling sites are TRB, SNP and BRT in the Black Sea; YLV in the Marmara Sea; NAS and CAS in Aegean Sea, and IB in Mediterranean Sea (Fig. 1). Specimens collected during the sampling period were brought to laboratory on ice. Total length and weight of the samples were measured to the nearest millimeter and gram before dissection. Approximately 1 g sample of muscle and entire liver from each fish were dissected, washed with distilled water, weighed, packed in polyethylene bags and stored at -18 ^{o}C prior to analysis. To prevent metal contamination of the samples by the laboratory equipments, special care was taken and tissues were dissected by plastic knife and all laboratory-ware was soaked in 2 M HNO_3 for 48 h, and rinsed five times with distilled water, and then five times with deionized water prior to use. All tissue samples were transferred into 100 ml Teflon beakers. There after, 10 ml ultrapure concentrated nitric acid was added slowly to the sample. The Teflon beaker was covered with a watch glass, and heated at 200 ^{o}C on a hot plate for 3 h, until the solution evaporate slowly to near dryness. Two milliliters of 1 N HNO_3 was added to the residue and the solution was evaporated again on the hot plate. By repeating the additional digestion twice, all organic materials in each sample were completely digested. After cooling, 2.5 ml of 1 N HNO_3 was added to digested residue and was transferred to 25 ml volumetric flasks, then diluted to level with deionized water. Before analysis, the samples were filtered through a 0.45 μm nitrocellulose membrane filter. Sample blanks were prepared in the laboratory in a similar manner to the field samples (7). Metal contents were expressed as $\mu g\ g^{-1}$ wet weight for tissues.
All samples were analyzed three times for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn by ICP-AES Varian Liberty Series-2. Standard solutions were prepared from stock solutions (Merck, multi element standard). The accuracy and precision of our results were checked by analyzed certified reference material (CRM, Dorm-2). The results showed good agreement between the certified and the analytical values (Table 1), the recovery of elements being partially complete for most of them. The absorption wavelengths for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were 228.8, 238.9, 267.7, 324.8, 259.9, 257.6, 231.6, 220.4, and 213.9 nm, respectively.

Table 1. Concentrations of metals found in Certified Reference Material DORM-2 (dogfish muscle) from the National Research Council, Canada (all data as means ± standard errors, in $\mu g\ g^{-1}$ dry wt)

Value	Cd	Cu	Cr	Pb	Zn	Ni	Mn	Fe	Co
Certified	0.043	2.34	34.7	0.065	26.6	19.4	3.66	142	0.182
SE	0.008	0.16	5.5	0.007	2.3	3.1	0.34	10	0.031
Observed[a]	0.047	2.48	32.9	0.069	24.9	20.8	3.39	137	0.169
SE	0.006	0.19	4.7	0.008	2.2	2.3	0.48	9.0	0.021
Recovery (%)	109	105	95	106	94	107	93	97	93

[a] Each value is the average of ten determinations.

A logarithmic transformation was done on the data to improve normality. To test the differences between the concentrations in tissues of the samples from different sites, one way ANOVA was performed. Post hoc test (Duncan) was applied to determine statistically significant differences following ANOVA. Possibilities less than 0.05 were considered statistically significant ($p<0.05$). All statistical calculations were performed with SPSS 13.0 for Windows.

RESULTS AND DISCUSSION

Table 2 presents the mean lengths and weights of the samples analyzed in this study.

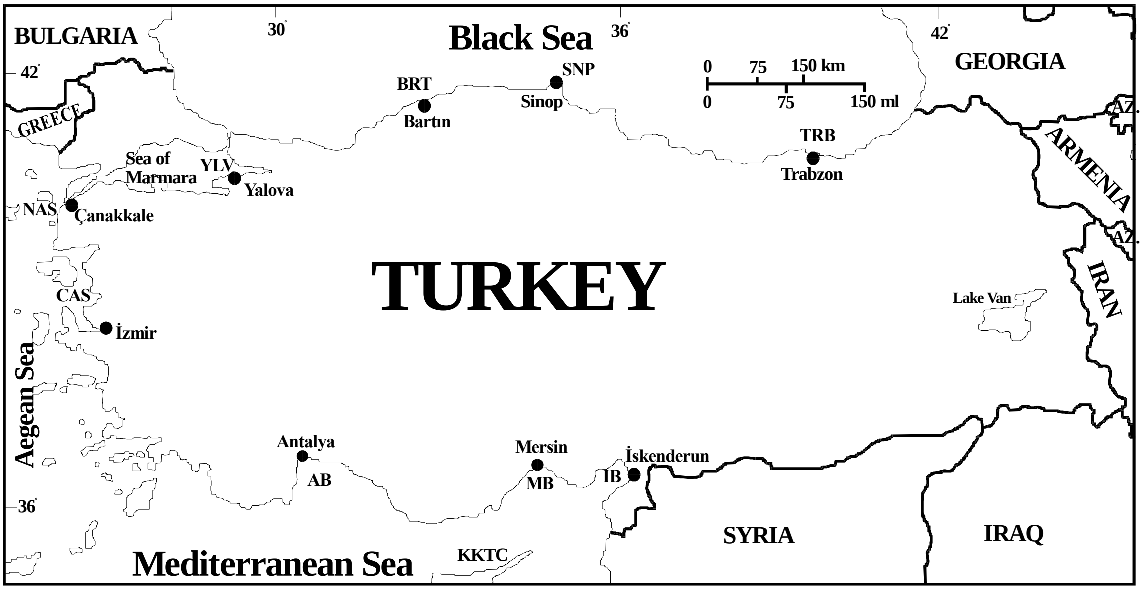

Figure 1. The sampling locations from the coastal waters of Turkey (TRB: Trabzon, SNP: Sinop, BRT: Bartın, YLV: Yalova, NAS: North Aegean Sea, CAS: Central Aegean Sea, IB: İskenderun Bay).

The mean metal concentrations in the tissues of Atlantic Horse Mackerel, Trachurus trachurus from different locations in the coastal waters of Turkey were presented in Table 3. Iron had the highest levels in both tissues, and followed by zinc in all locations. Followed zinc; copper generally showed the third highest levels except nickel in liver from TRB and SNP, and Mn in muscle from BRT. On the other hand, cadmium showed the lowest levels in both tissues from all locations, especially in TRB, YLV and NAS. Followed cadmium; cobalt had the second lowest levels, in agreement with the results of many researchers (5, 9, 12, 15-17).

Table 2. The mean lengths and weights of the samples analyzed in this study.

Sites	N	Length ± SE (cm)	Weight ± SE (g)
TRB	7	13.90±0.28	21.95±0.76
SNP	7	14.38±0.37	26.94±1.01
BRT	9	14.50±0.14	26.26±1.67
YLV	8	14.12±0.36	23.80±1.39
NAS	10	14.34±0.33	22.77±1.24
CAS	8	14.60±0.91	26.24±2.11
IB	9	15.13±0.25	30.83±1.66

In addition, the metal concentrations in livers were higher than those in muscles from all locations, and the differences between the metal levels in tissues were statistically significant ($p<0.05$). This situation is in agreement with the results of many researchers (7-8).

The concentrations in tissues of the analyzed metals were significantly affected by sampling sites, and differences between the metal levels in similar tissues of samples from different locations were statistically significant ($p<0.05$). In muscles, the levels of cadmium and manganese in BRT, cobalt, nickel, zinc and iron in NAS, chrome in TRB, copper in IB, and lead in YLV were higher than those in other locations. Again in muscles, cadmium in TRB, YLV and NAS, and lead in TRB, cobalt and iron in IB, chrome, manganese and nickel in YLV, copper and zinc in CAS had lower levels than those in other locations. In livers, the levels of cadmium, copper, manganese and zinc in BRT, cobalt and iron in CAS, chrome in IB, nickel in SNP and lead in NAS were higher than those in other locations. Again in livers, the levels of cadmium, cobalt, chrome, manganese and nickel in YLV, copper in SNP, iron in BRT, lead and zinc in TRB had lower levels than those in other locations.

Table 4 compiles the data on concentrations of metals in the muscles of Trachurus trachurus from coastal waters of Turkey with other studies, Turkish permissible concentrations (TPCs) and tolerable concentrations in fish according to the Turkish Fisheries Law and Regulations. When our results were compared with other studies, as can be seen, the concentrations of Cd, Co, Cr, Cu, Mn and Zn from Black Sea (TRB, SNP and BRT) were generally lower than those presented by Topçuoğlu et al (5), but the concentrations of Fe, Ni and Pb were in agreement with their results. Similarly, Cd, Cu, Mn and Zn levels were lower than those presented by Tüzen (9), but Fe and Pb were in agreement with his results. The levels of Cd and Pb for CAS were generally in agreement with levels reported for Eastern Aegean by Küçüksezgin et al (11).

Table 3. Mean metal concentrations with standard errors in the tissues of *Trachurus trachurus* from the coastal waters of Turkey and comparison of different sites (µg g^{-1} wet wt)*

Metals	Tissues	Sites						
		TRB	SNP	BRT	YLV	NAS	CAS	IB
Cadmium	Muscle	0.01±0.00^{a}	0.03±0.00^{ab}	0.08±0.01^{c}	<0.01^{a}	<0.01^{a}	0.05±0.02^{b}	0.03±0.00^{ab}
	Liver	0.13±0.05^{b}	0.09±0.02^{b}	0.19±0.03^{b}	0.04±0.01^{a}	0.05±0.01^{a}	0.10.03^{b}	0.11±0.03^{b}
Cobalt	Muscle	0.06±0.01^{b}	0.07±0.01^{b}	0.08±0.01^{b}	0.05±0.01^{b}	0.16±0.03^{a}	0.04±0.01^{b}	0.03±0.01^{b}
	Liver	0.22±0.07^{ab}	0.16±0.03^{ab}	0.41±0.02^{ab}	0.11±0.04^{a}	0.41±0.05^{ab}	0.64±0.22^{b}	0.20±0.07^{ab}
Chrome	Muscle	0.26±0.07^{a}	0.20±0.09^{a}	0.16±0.06^{a}	0.07±0.02^{a}	0.08±0.02^{a}	0.13±0.03^{a}	0.22±0.02^{a}
	Liver	0.88±0.16^{b}	0.46±0.12^{ab}	0.83±0.09^{b}	0.14±0.08^{a}	0.63±0.09^{ab}	0.84±0.14^{b}	1.02±0.32^{b}
Copper	Muscle	0.80±0.19^{abc}	1.17±0.12^{bc}	0.82±0.09^{abc}	0.56±0.15^{ab}	1.03±0.32^{abc}	0.48±0.12^{a}	1.30±0.22^{c}
	Liver	1.39±0.29^{b}	1.31±0.28^{b}	20.5±2.54^{a}	1.33±0.14^{b}	16.7±2.60^{a}	6.13±1.69^{b}	3.73±0.38^{b}
Iron	Muscle	22.4±2.43^{ab}	24.9±5.09^{ab}	28.0±1.59^{ab}	39.4±13.3^{bc}	52.3±2.88^{c}	29.9±5.08^{ab}	19.3±2.32^{a}
	Liver	202±78.4^{ab}	165±42.34^{ab}	76.7±9.89^{a}	102±21.1^{a}	93.1±8.00^{a}	308±89.9^{b}	182±37.9^{ab}
Manganese	Muscle	0.24±0.08^{a}	0.39±0.08^{ab}	0.86±0.05^{c}	0.19±0.09^{a}	0.64±0.16^{bc}	0.21±0.04^{a}	0.30±0.06^{a}
	Liver	0.78±0.19^{a}	1.12±0.10^{ab}	2.11±0.17^{c}	0.46±0.12^{a}	1.29±0.19^{abc}	1.94±0.45^{bc}	0.86±0.14^{a}
Nickel	Muscle	0.75±0.19^{bc}	0.83±0.24^{bc}	0.27±0.02^{ab}	0.06±0.01^{a}	1.03±0.19^{c}	0.46±0.17^{abc}	0.44±0.13^{ab}
	Liver	2.26±0.57^{c}	3.97±0.53^{d}	0.77±0.12^{ab}	0.16±0.04^{a}	1.89±0.33^{bc}	2.58±0.31^{c}	0.92±0.18^{ab}
Lead	Muscle	0.08±0.27^{a}	0.41±0.13^{a}	0.16±0.04^{a}	0.44±0.15^{a}	0.31±0.05^{a}	0.29±0.11^{a}	0.28±0.13^{a}
	Liver	0.56±0.14^{a}	1.01±0.16^{a}	0.59±0.12^{a}	1.28±0.44^{a}	1.79±0.35^{a}	0.93±0.19^{a}	1.08±0.38^{a}
Zinc	Muscle	9.02±1.26^{b}	8.78±0.67^{b}	4.34±0.84^{a}	9.24±0.83^{b}	11.2±1.15^{b}	3.41±0.72^{a}	9.79±1.06^{b}
	Liver	15.8±1.29^{a}	17.5±1.45^{a}	37.9±2.75^{b}	19.5±1.12^{a}	20.6±1.77^{ab}	16.0±2.58^{a}	32.3±7.15^{ab}

*Horizontally, letters *a*, *b* and *c* show differences among sites. Means with the same letter are not statistically significant, p>0.05

Table 4. Comparison of the overall metal concentrations in the muscles of *Trachurus trachurus* from coastal wares of Turkey with other studies in Turkey waters and guidelines.

Sites	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
[a] This study	<0.01-0.08	0.03-0.16	0.07-0.26	0.48-1.30	19.3-52.3	0.19-0.86	0.06-1.03	0.08-0.44	3.41-11.2
[b] İskenderun Bay	0.83-1.34	0.95-2.16	1.31-2.72	1.32-2.20	4.18-13.2	1.27-2.15	1.36-6.53	1.81-3.47	3.03-4.87
[c] Aegean Sea	<0.01-0.05	-	-	-	-	-	-	0.04-0.21	-
[d] Black Sea	<0.02-0.24	<0.05-0.40	<0.06-0.84	1.01-4.54	30.0-57.0	0.69-3.56	<0.01-2.04	<0.05-0.6	25.7-44.2
[e] Black Sea	0.10-0.48	-	-	1.28-2.93	9.52-32.4	1.33-3.76	-	0.22-0.74	9.50-22.94
[f] Guideline	0.1	-	-	20	-	-	-	1.0	50
[g] Guideline	0.05-5.5	-	1.0	10-100	-	-	-	0.5-6.0	30-100

[a] This study, *Trachurus trachurus* (µg g^{-1} wet wt).

[b] Türkmen et al (17), *Saurida undosquamis*, *Sparus aurata* and *Mullus barbatus* (µg g^{-1} dry wt).

[c] Küçüksezgin et al (11), *Mullus barbatus* (µg g^{-1} wet wt).

d Topçuoğlu et al (5), *Engraulis encrasicholus*, *Alosa bulgarica*, *Merlangius euxinus* and *Dicentrarchus labrax* (µg g^{-1} dry wt).

e Tüzen (9), *Alosa caspia*, *Engraulis encrasicholus*, *Trachurus trachurus*, *Sadra sadra* and *Clupea sprattus* (µg g^{-1} dry wt).

[f] TKB (21), Turkish Permissible Concentrations.

[g] Nauen (20), The ranges of maximum permissible concentrations for different countries (FAO), (µg g^{-1} wet wt).

The levels of Cd, Co, Cr, Mn, Ni and Pb for İskenderun Bay were generally lower than those reported by Türkmen et al (17), but Cu, Fe and Zn levels were in agreement with their results. In general, there were differences between the levels of some metals reported in this study and other studies, the reason for these may be differences of species, sampling locations and seasons. Because, it is very difficult to compare the metal concentrations even within the similar tissues of two different species because of different feeding habits, the differences in the aquatic environments concerning the source and level of water pollution (18), growing rates of the species, types of tissues analyzed and some other factors. Thus, the differences between metal accumulations in similar tissues of different species are probable. When our results were compared with guidelines, Cd, Co Pb and Zn levels were lower than those in UN FAO Codex for fish and Turkish Fisheries Law and Regulations (19-20).

CONCLUSION

Present study provides useful information on the distribution of metal concentrations in tissues of Trachurus trachurus from coastal waters of Turkey. Based on the samples analyzed, the values for cadmium, cobalt, chrome, copper, iron, manganese, nickel, lead and zinc measured in the edible parts of fish are not heavily burdened with metals, and the concentrations did not exceed the established quality standards for fish and mussels (19-20). Therefore, it can be concluded that these metals in edible parts of the examined species should pose no health problems for consumers. However, in the future, bioaccumulation of analyzed metals in this study can be a possible risk for the consumption of these species, if the dose of the pollution discharged in these seas increase.

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EFFECT OF TOTAL AMMONIA NITROGEN CONCENTRATION AND PH ON GROWTH RATES OF *LEMNA MINOR*

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The use of lemna sp. in domestic wastewater treatment is receiving growing attention over the last few decades. Lemna-based ponds in combination with anaerobic pre-treatment may be a feasible option for organic matter and nutrient removal. The main form of nitrogen in anaerobic effluent is ammonium. This is the preferred nitrogen source of lemna but at certain levels it may become inhibitory to the plant. Renewal fed batch experiments at laboratory scale were performed to assess the effect of total ammonia ($NH_3 + NH_4^+$) nitrogen and pH on the growth rate of lemna minor. The experiments were performed at three different total ammonia nitrogen concentrations of 20 ppm, 50 ppm, 100 ppm, and four different pH ranges of 5, 7, 8, 9. Twelve treatments replicated three times. Total dry weight of each replicates was calculated at the beginning and end of the study. The inhibition of lemna growth by ammonium was found to be due to a combined effect of ammonium ions (NH_4^+) and ammonia (NH_3), the importance of each one depending on the pH.

Key words: *Ammonia, ammonium, growth inhibition, nitrogen, Lemna minor, toxicity*

INTRODUCTION

Because of their various advantages, duckweed-covered systems are one option for sustainable wastewater treatment (Reddy and Smith, 1987; Brix and Schierup, 1989), for example, high nutrient removal efficiencies due to very high growth rates (Hillman, 1961; Landolt, 1986; Vermaat and Hanif, 1998) and the high nutrient content of duckweed (Culley et al., 1981; Lüönd, 1982). The advantage of duckweed-covered systems here is that nutrients are (partly) recovered rather than lost to the atmosphere, or removed with the effluent Ammonia is one of the major constituents of domestic wastewater and concentrations commonly range from 10 to 50 mg l^{-1} N, but might be as high as 200 mg l^{-1} N in industrial wastewater (Konig et al., 1987) or in domestic wastewater in arid and semi-arid countries (Veenstra et al., 1995). Despite being the preferred nitrogen source by duckweed plants (Porath and Pollock, 1982), it may become one of the parameters inhibiting the growth of duckweed in wastewater (Bitcover and Sieling, 1951; Lüönd, 1982).

Total ammonia actually exists in water as two forms, the ammonium ion (NH_4^+) and un-ionised ammonia (NH_3), with relative concentrations being pH and temperature dependent (Tepe and Boyd, 2002). The un-ionised form is most toxic due the fact that it is uncharged and lipid soluble and thus traverses biological membranes more readily than the charged and hydrated NH_4^+ ions (Boyd and Tucker, 1998). Several studies have been made on the toxicity of ammonia for duckweed (Oron et al., 1985; Wang, 1991; Monselise and Kost, 1993; Clement and Merlin, 1995; Caicedo et al.,2000), but pH was often not controlled which precludes any distinction of the effects of NH_3 and NH_4^+.

In the present study, controlled pH ranges were used carefully to distinguish between the effect of the un-ionised NH_3 and the NH_4^+ ion. The objective was to determine the relationship between total ammonia, pH and relative growth rate of *Lemna minor*.

MATERIAL AND METHODS

Study Area

The study was carried out in the Plankton Research Laboratory at Mustafa Kemal University. Lemna minor samples for the study were colleted from a lake in the campus and brought to the laboratory 15 days prior to start the study. Twelve fluorescent lights, each has 1200 lumen, were used as light source. Plants were placed in 1 liter glass jar and top water used for the study.

Experimental Setup

The effects of total ammonia concentration, pH and type of growth medium on duckweed growth were studied under various experimental conditions (Table 1). These experiments were conducted in 250 ml glass jars with a water depth of 5 cm. Ten healthy duckweed fronds from a stock culture were put in each jars. The fronds were counted every 3 days. The experiment lasted for 14 days. The total dry weight of the duckweed biomass was determined at the start and at the end of the experiments. The medium was replaced every 4 days to compensate for nutrient losses and to reduce algae growth. In addition, the ammonium nitrogen levels were restored to the initial concentration every other day by adding NH4Cl. The pH was measured every day and subsequently adjusted to the initial conditions with NaOH or HCL solutions. The average pH during a particular day was assumed to be the average of the pH measured just before the pH adjustment, and the pH that was set. The average pH for the total incubation period was calculated by taking the average of the daily average pH values, for the three duplicates. The pH range was defined as the range between the maximum and minimum daily average value. Evaporation losses were compensated for every day with tap water. Each treatment had three replicates.

Table 1.

Total ammonia nitrogen (TAN) ($NH_3 + NH_4^+$) were done according to standard procedures by using Shimadzu brand UV-1601PC model spectrophotometer (Boyd and Tucker, 1992). pH were determined with ion selective electrodes pH by Orion model 420A pH meter. The average values for these parameters during each experiment were used to calculate the characteristic NH_3 concentration, by using following equation:

$$Ka = \frac{[H^+]\,[NH_3]}{[NH_4^+]}$$

Where, Ka is the ammonia dissociation constant.

Growth Analysis

Duckweed growth was evaluated on the basis of the relative growth rate (RGR) as given in the following equation:

$$\ln (Nt) = \ln(N_o) + RGR*t$$

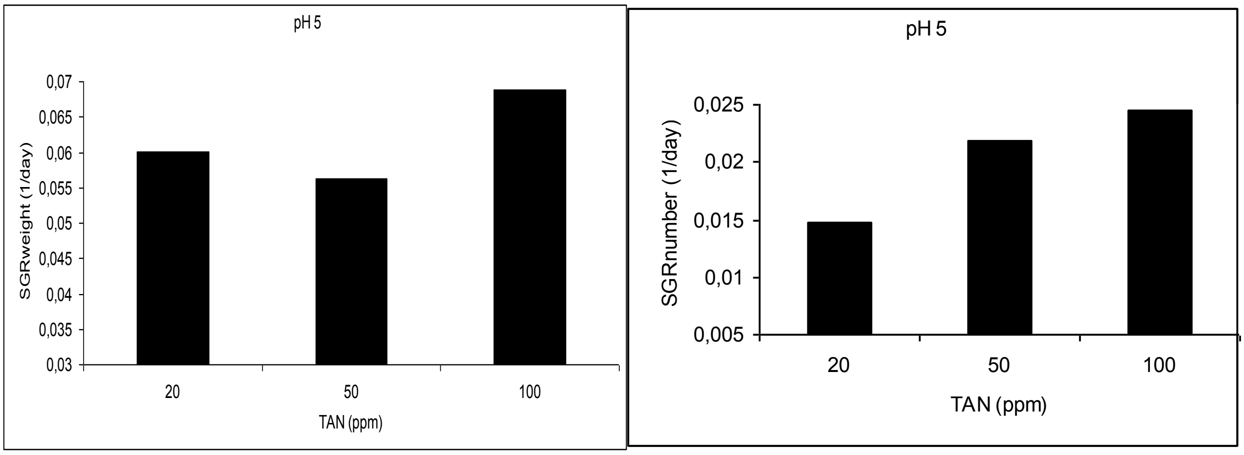
where Nt=number of fronds or dry weight, at time t and N_0=number of fronds or dry weight, at the beginning of the study.

The RGR was determined in two ways: firstly on the basis of the frond numbers at the beginning and end of the experiments, and secondly on the basis of the dry weight biomass at the beginning and end of the experiments. The RGR was calculated by using the equation above. Initial dry weight was determined by drying ten representative samples of 10 healthy fronds at the beginning of the experiments. The dry weight of the plants was measured after drying the plants at 70^oC until constant weight (Vermaat and Hanif, 1998).

RESULTS

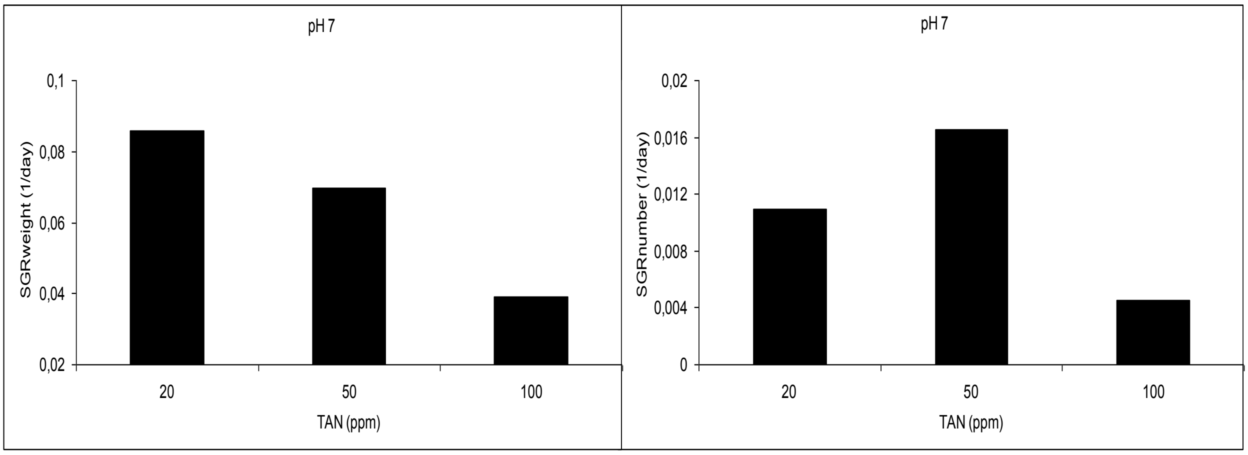
Specific growth rates as dry weight and frond numbers were calculated for the experimental groups of pH 5-$NH_4Cl_{(20\ ppm)}$, pH 5-$NH_4Cl_{(50\ ppm)}$ and pH 5-$NH_4Cl_{(100\ ppm)}$. Specific growth rates as dry weight were calculated as 0.060 for the pH 5-$NH_4Cl_{(20\ ppm)}$, 0.056 for the pH 5-$NH_4Cl_{(50\ ppm)}$ and 0.069 for the pH 5-$NH_4Cl_{(100\ ppm)}$. Specific growth rates as frond numbers were also calculated as 0.018**,** 0.022 and 0.025 for the same groups, respectively (Figure 1).

Figure 1. Specific growth rates as dry weight and frond numbers for the pH 5-$NH_4Cl_{(20\ ppm)}$, pH 5-$NH_4Cl_{(50\ ppm)}$ and pH 5-$NH_4Cl_{(100\ ppm)}$ groups.



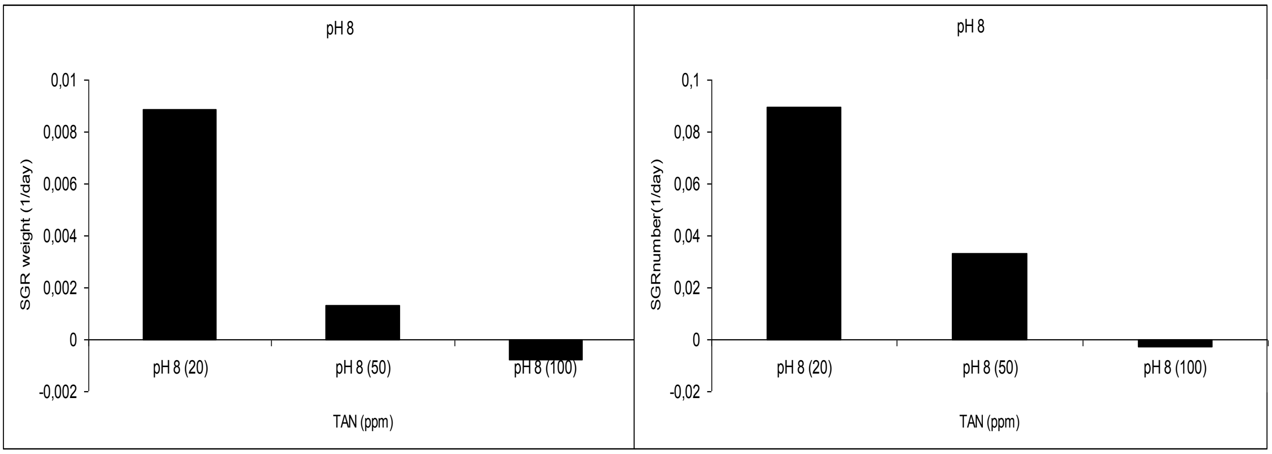
At the end of the experiment, specific growth rates as dry weight and frond numbers were calculated for the experimental groups of pH 7-$NH_4Cl_{(20\ ppm)}$, pH 7-$NH_4Cl_{(50\ ppm)}$ and pH 7-$NH_4Cl_{(100\ ppm)}$. Results of specific growth rates as dry weight were 0.086 for the pH 7-$NH_4Cl_{(20\ ppm)}$, 0.070 for the pH 7-$NH_4Cl_{(50\ ppm)}$ and 0.040 for the pH 7-$NH_4Cl_{(100\ ppm)}$ group. Results of the same groups, calculated as frond numbers, were 0.011**,** 0.017 and 0.005. (Figure 2).

Figure 2. Specific growth rates as dry weight and frond numbers for the pH 7-$NH_4Cl_{(20\ ppm)}$, pH 7-$NH_4Cl_{(50\ ppm)}$ and pH 7-$NH_4Cl_{(100\ ppm)}$ groups.



Specific growth rates were calculated according to dry weights and frond number for the pH 8-$NH_4Cl_{(20\ ppm)}$, pH 8-$NH_4Cl_{(50\ ppm)}$ and pH 8-$NH_4Cl_{(100\ ppm)}$ groups at the end of the experiments. Groups averages calculated as dry weight were , 0.090 for the pH 8-$NH_4Cl_{(20\ ppm)}$, 0.033 for the pH 8-$NH_4Cl_{(50\ ppm)}$ and -0.003 for the pH 8-$NH_4Cl_{(100\ ppm)}$ groups. Specific growth rates of the same groups as frond numbers were 0,009**,** 0,001 and -0,001, respectively (Figure 3).

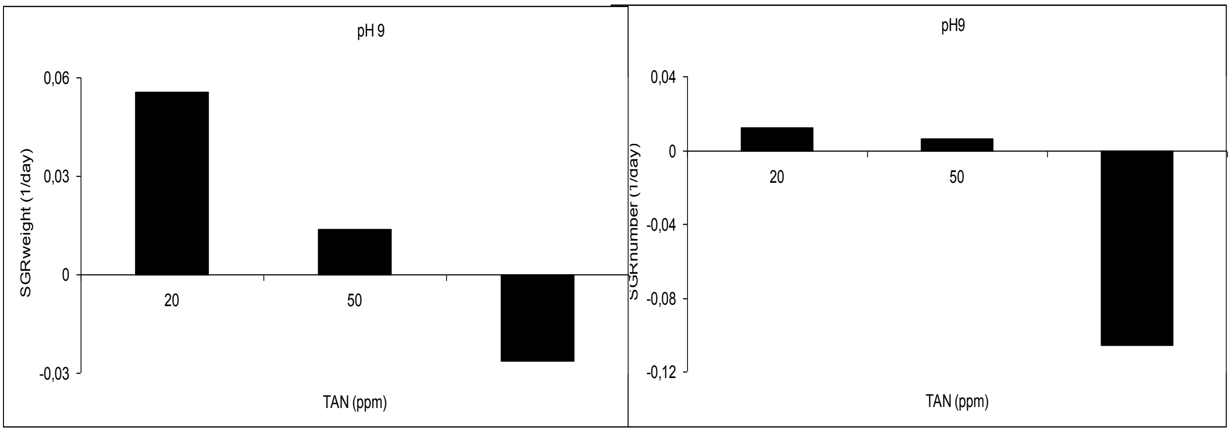
Figure3. Specific growth rates as dry weight and frond numbers for the pH 8-$NH_4Cl_{(20\ ppm)}$, pH 8-$NH_4Cl_{(50\ ppm)}$ and pH 8-$NH_4Cl_{(100\ ppm)}$ groups.



Specific growth rates of the pH 9-$NH_4Cl_{(20\ ppm)}$, pH 9-$NH_4Cl_{(50\ ppm)}$ and pH 9-$NH_4Cl_{(100\ ppm)}$ groups were also calculated based on their dry weights and frond numbers at the end of the experiments. Based on dry weight measurements, the average of the groups were 0.056 for the pH 9-$NH_4Cl_{(20\ ppm)}$, 0.0146 for the pH 9-$NH_4Cl_{(50\ ppm)}$ and 0.026 for the pH 9-$NH_4Cl_{(100\ ppm)}$.

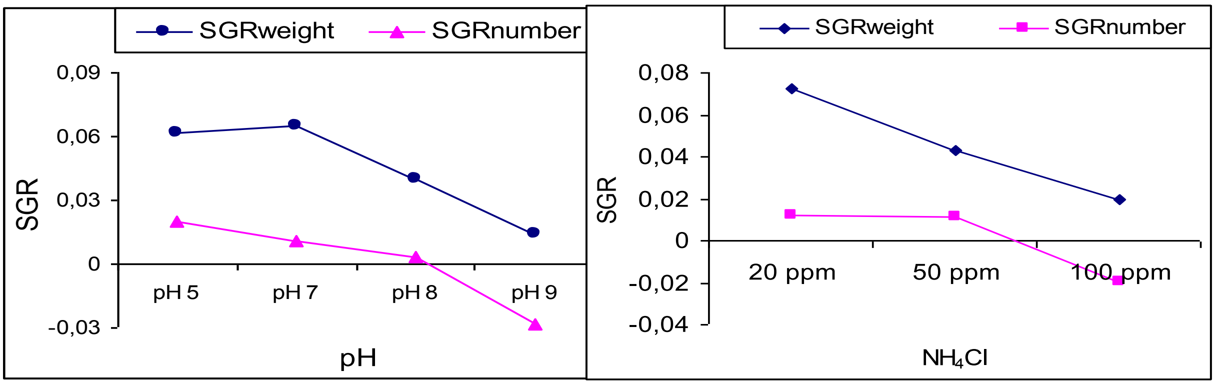
The averages of the same groups were 0,012**,** 0,007 and -0,105, respectively when frond numbers were taken in account. (Figure 4).

Figure 4. Specific growth rates as dry weight and frond numbers for the pH 9-$NH_4Cl_{(20\ ppm)}$, pH 9-$NH_4Cl_{(50\ ppm)}$ ve pH 9-$NH_4Cl_{(100\ ppm)}$ groups.



Specific growth rates of the pH treatments were calculated based on dry weight and frond numbers of the lemna plants. According to calculations, specific growth rates based on dry weights were 0.062 for the pH 5 0.065 for the pH 7, 0.040 for the pH 8 and 0.014 for the pH 9 treatments. Specific growth rates of the same groups based on frond numbers were 0,020, 0,011, 0,003 and -0,029, respectively (Figure 5).

Figure 5. Average specific growth rates based on pH and ammonium chloride (NH_4Cl).



Different doses (20 ppm, 50 ppm, 100 ppm) of ammonium chloride (NH_4Cl) were applied to the treatment groups and specific growth rates by number and weights were calculated. According to these calculations, specific growth rates, calculated by weight were 0.073 for $NH_4Cl_{(20\ pm)}$, 0.043 for $NH_4Cl_{(50\ ppm)}$ and 0.020 for $NH_4Cl_{(100\ ppm)}$ treatment. Specific growth rates of the same treatments calculated by weight were according to frond numbers were 0.012, 0.012 and -0.019, respectively (Figure 5). The plants in all three replicates of 100 ppm NH_4Cl group pH 9 treatment died.

Table 1. Experimental variables for the growth experiments with *Lemna minor*.

pH 5-NH_4Cl (20 ppm)	pH 5-NH_4Cl (50 ppm)	pH 5-NH_4Cl (100 ppm)
pH 7-NH_4Cl (20ppm)	pH 7-NH_4Cl (50 ppm)	pH 7-NH_4Cl (100 ppm)
pH 8-NH_4Cl (20 ppm)	pH 8-NH_4Cl (50 ppm)	pH 8-NH_4Cl (100 ppm)
pH 9-NH_4Cl (20 ppm)	pH 9-NH_4Cl (50 ppm)	pH 9-NH_4Cl (100 ppm)

Each treatment replicated three times.

Table 2. The average temperature and pH values of the groups.

Groups	Temperature (C^o)	pH
pH 5-NH_4Cl (20 ppm)	24	6,4
pH 5-NH_4Cl (50 ppm)	24	6,3
pH 5-NH_4Cl (100 ppm)	24	6,1
pH 7-NH_4Cl (20 ppm)	24	8,4
pH 7-NH_4Cl (50 ppm)	24	8,3
pH 7-NH_4Cl (100 ppm)	24	8
pH 8-NH_4Cl (20 ppm)	23,8	8,8
pH 8-NH_4Cl (50 ppm)	23,6	8,6
pH 8-NH_4Cl (100 ppm)	23,5	8,3
pH 9-NH_4Cl (20 ppm)	23,4	9
pH 9-NH_4Cl (50 ppm)	22,9	8,8
pH 9-NH_4Cl (100 ppm)	23	8,7

The average water temperature was 23.7 C. Temperature and pH in all treatment groups were measured everyday and the average values of each groups were given in table 2.

DISCUSSION

Specific growth rates of pH 5 treatment, calculated by weight and number, pH 5-NH_4Cl (100 ppm) group showed best growth with 0,069 as weight and 0,025 as frond number. Plants of these treatments continued to growth and reproduction until the last day of the experiments, without any showing decay or paleness on their appearance. When results of specific growth rates based on weight from pH 7 treatment investigated, pH 7-$NH_4Cl_{(20\ ppm)}$ group showed the highest with 0.086. Some decay and paleness have seen in the pH 7 at 100 ppm NH_4Cl dosage. Additionally, the maximum average specific growth rate based on frond number have achieved with 0.017 in the pH 7-$NH_4Cl_{(50\ ppm)}$ group. The optimal pH value of lemna reported as about 7 (Bitcover ve Sieling, 1951; Landolt, 1987), this was confirmed by the present study. Several studies have been made on the toxicity of ammonia for duckweed (Oron et al.,1985; Monselise and Kost, 1993; Clement and Merlin, 1995; Caicedo et al.,2000), but pH was often not controlled which precludes any distinction of the effects of NH_3 and NH_4^+. The incubations with pH values in the range where the pH is assumed not to affect directly the duckweed growth (6 - 8) showed that growth inhibition increased with increasing total ammonia concentrations and also with increasing pH values. Several researchers have explained this phenomenon as a result of the simultaneous increase in NH_3 concentration (Azov and Goldman, 1982; Wang, 1991). The minimum growths have seen in pH 9 treatment among the all treatments.

CONCLUSION

Lemna minor plants have showed good growth at all replicates of pH 5 treatment, no matter what the ammonium chloride dosage. Plant tolerance level for ammonium chloride was decreased by increasing pH. The best average specific growth rate based on weight was occurred in pH 7 among pH treatments, and in 20 ppm NH_4Cl added ones among ammonium chloride treatments.

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SEQUENTIAL (ANAEROBIC- AEROBIC) TREATMENT OF CHEESE WHEY

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Feeding cheese making wastewater to upflow packed bed anaerobic reactors (UAPBR) has lasted for 185 days. Organic loads have changed between 2-15 g COD/(l day) for Reactor 1 and 0.3-2.23 g COD/(l day) for Reactor 2. At 4.8 g COD/(l day) organic load and 85 hours retention time, 98.9% total COD removal in two reactors has gained. Following the UAPBR experiments aerobic experiments were conducted in batch reactors and further COD removal and oil-grease removal of up to 76 and 85%, respectively, were achieved.

Keywords: *Sequential treatment, anaerobic processes, cheese whey, upflow anaerobic packed bed reactor*

1. INTRODUCTION

The dairy industry, like most other agro-industries, generates strong wastewaters characterized by high Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) concentrations representing their high organic content [1]. Cheese whey is a protein and lactose rich byproduct of the cheese industry and is cost-effective utilization or disposal has become increasingly important due to more stringent legislative requirements for effluent quality.

Dairy wastewaters are treated using physico-chemical and biological treatment methods. However, since the reagent costs are high and the soluble COD removal is poor in physical-chemical treatment processes, biological procersses are usually preferred [2]. Among biological treatment processes, treatment in ponds, activated sludge plants and anaerobic treatment are commonly employed for dairy wastewater treatment [1]. In contrast the contrary, high energy requirements of aerobic treatment plants are a significant drawback of these processes. COD concentrations of dairy effluents vary significantly; moreover, dairy effluents are warm and strong, enabling them ideal for anaerobic treatment. If for any reason (economic, sanitary, local) whey valorization technologies (such as protein and lactose recovery, spray drying, etc.) or direct utulization of whey for animal feed are not applicable, anaerobic treatment can be a solution to whey disposal [3].

The aim of this study was to determine the best combination of hydraulic retention time and organic loading rate for cheese whey in combined (anaerobic- aerobic) reactors.

2. MATERIALS AND METHODS

2.1. Characterization of wastewaters

The cheese whey which was obtained from a cheese production factory located near the city of Eskisehir, Turkey, used in the Upflow Anaerobic Packed Bed Reactor (UAPBR) experiments. Samples collected were stored at 4 °C during the study. Table 1 shows the typical characteristic parameters of the wastewater samples.

2.2. Anaerobic seed sludge

A mixed mesophilic sludge (suspended solids 60 g l^{-1} and volatile suspended solids 38 g l^{-1}) obtained from anaerobic digesters of the Ankara Municipal Wastewater Treatment Plant, Turkey, was used as the inoculum in the UAPBRs

2.3. Aerobic cultures

Aerobic cultures were obtained from aeration tanks of the activated sludge units of the Eskisehir Municipal Wastewater Treatment Plant, Turkey.

Table 1. Characterization of the wastewater

Parameters	**Wastewater**
pH	4,3
Chemical oxygen demand (mg l^{-1})	90000±500
Suspended solids (mg l^{-1})	6000±100
Total solids (mg l^{-1})	64000±450
Volatile total solids (mg l^{-1})	55000±700
Oil-greases (mg l^{-1})	13000±150
Alcalinity ($CaCO_3$ mg l^{-1})	2600±100
Total phosphorus (mg l^{-1})	200±50
Total kjeldahl nitrogen (mg l^{-1})	57±20
Fe (mg l^{-1})	22±0,4
Ni (mg l^{-1})	81±0.8
Mn (mg l^{-1})	92±0.2
Al (mg l^{-1})	7±0.2
Cu (mg l^{-1})	44±0,4
Ca (mg l^{-1})	50±5
Zn (mg l^{-1})	39±0.6
Mg (mg l^{-1})	45±5
K (mg l^{-1})	100±10

2.4. Analytical methods

pH measurements were obtained with a pH meter (WTW, Inolab Level 2) and a pH probe (BO11207-023, WTW). COD, Total Solids (TS), Suspended Solids (SS), and Volatile Suspended Solids (VSS), alkalinity, Volatile Fatty Acids (VFA), total kjeldahl nitrogen, oil-grease were all measured by following standard methods, 5220B, 2540B, 2540D, 2540E, 2320B, 5560C, 4500-N_{org} B, 5520B, respectively [4].

Total phosphorus, Fe, Ni, Mn, Al, Cu, Ca, Zn, Mg and K were measured by the Merck cell tests and Cecil 4002 UV visible spectrophotometer (England).

The volume of methane produced was determined daily by a liquid displacement method, after first removing CO_2 by adsorption into NaOH solution [3,5].

2.5. Upflow Anaerobic Packed Bed Reactor (UAPBR)

This laboratory scale study was performed using two reactor designs (Figure 1). Each of the two reactors has a total liquid volume of 5.0 l and was each filled up to 4.3 l of their volume with plastic balls, with a rough surface to retain the bacterial biomass. The temperature of the reactors was maintained at mesophilic conditions (37 ^{o}C) by electrical heating mats. The feed was introduced through the bottom of each reactor by means of peristaltic pumps.

The Organic Loading Rate (OLR) applied to the first-stage reactor ranged from 2-15 g COD $l^{-1}day^{-1}$, corresponding to a Hydraulic Retention Time (HRT) of 120-72 hour. The OLR applied to the second-stage reactor ranged from 0.3-2.23 g COD $l^{-1}day^{-1}$ corresponding to an HRT of 120-72 hours.

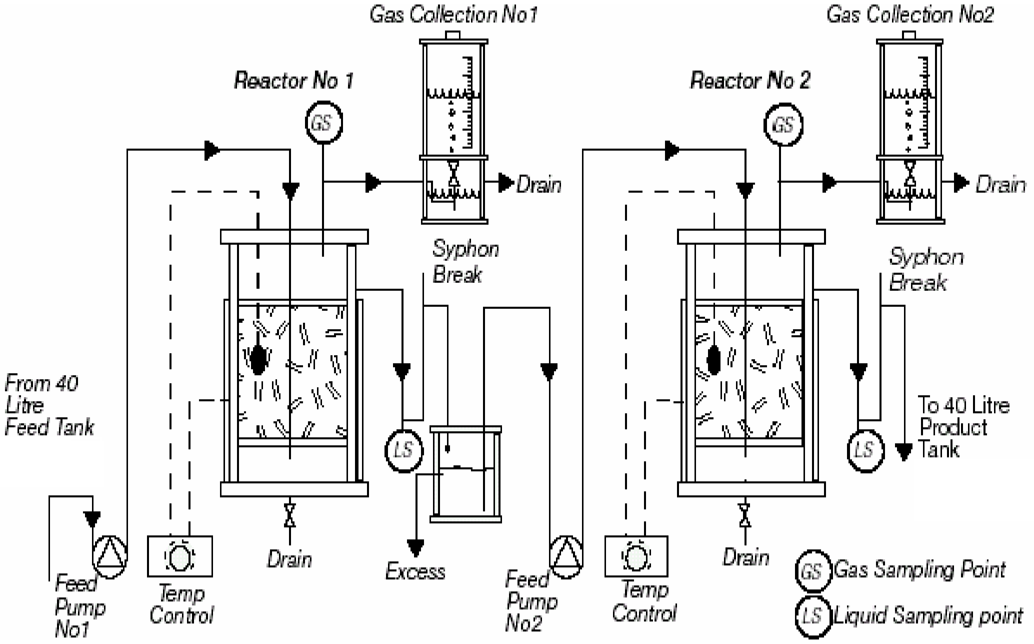

Figure 1. Upflow anaerobic packed bed reactor

2.6. Batch aerobic reactor experiments

This study was conducted to determine the aerobic post-treatability of cheese whey following anaerobic treatment, in order to provide discharge standarts. Experiments were conducted in 300 ml volumetric flasks. Sample volumes were 100 ml. The batch aerobic reactors were continuously shaken for 8 days in a shaker at 140 rpm at 25±1 ºC.

3. RESULTS AND DISCUSSION

3.1. Anaerobic treatment

Table 2 and 3 summarizes the HRT, applied organic loading rates, influent and effluent COD concentration, pH, bicarbonate alkalinity values and effluent VFA concentrations.

In the first reactor stage, COD removal was 85%, with an OLR 2 g COD l^{-1} day^{-1}during first 10 days. When the OLR was icreased until 8 g COD l^{-1} day^{-1} during 92 days, at the end of this time COD removal reached 94%. But, at an OLR of 10 g COD per day, decrease in efficiency was observed (91 %). Therefore OLR decreased from 10 to 9 g COD each day. In concequence of this, COD removal increased 93 %. Amounts of carbohydrate, protein and oil which is one of inhibitory compounds, in wastewater increased in concur with rise of OLR. Therefore, decrease of COD removal at 10 g COD l^{-1} day^{-1} OLR may be due to high oil content that affects microorganism growth negatively in wastewater (See Table 2). When OLR was decreased, improving of COD removal performance in reactor confirmed this case.
Lipids are potentially inhibitory compounds, which can always be encountered during anaerobic treatment of dairy wastewaters. There is little information avaliable in literature about the anaerobic digestibility of lipids. During anaerobic degredation, lipid is firstly hydrolyzed to glycerol and long chain fatty acids (LCFAs) followed by β-oxidation, producing acetate and hydrogen. Glycerol, a compound formed as a result of lipid hydrolysis, was found to be a non-inhibitory compound, while LCFAs were particularly reported to be inhibitory to methanogenic bacteria [1]. The inhibitory effects of lipids in anaerobic processes can mainly correlated to the presence of LCFAs, which cause retardation in methane production. Unsaturated LCFAs seemed to have a greater inhibitory effect than saturated LCFAs. Unsaturated LCFAs strongly inhibited methane production from acetate and moderately inhibited methane production from acetate and moderately inhibited β-oxidation [1].

Recently, the performance of an industrial-scale anaerobic filter treating raw milk discharged by quality control laboratories was reported [6]. Higher than 90% of COD removal could be attained, with an OLR maintained around 5-6 kg COD/(m^3 day). Moreover, the fat content in dairy wastewater could successfully be degraded by anaerobic filter reactor.

Viraraghavan and Kikkeri [7] was reported that a laboratory-scale plastic medium anaerobic filter reactor provided average COD removal rates between 78 and 92 %, at hydraulic retention time (HRT) of 4 days. In another research, the effect of porous and non-porous support media in anaerobic filter reactors on thermophilic anaerobic treatment of ice-cream wastes were investigated. At high loading rates, anaerobic filter with porous support media performed more satisfactorily [8]. The performance of porous and non-porous media in an upflow anaerobic filter (UAF) treating wastewaters from a milk bottling factory was also investigated.by Anderson et al. [9]. They reported that the reactor with non-porous packing showed instability above an organic loading rate (OLR) of 4 kg COD/(m^3 day), while the reactor with porous packing was stil stable at OLRs up to 21 kg COD/(m^3 day).

Kalyuzhnyi et al.,[3] investigated anaerobic treatment of high-strength cheese-whey (above 77 g COD l^{-1}) in laboratory and pilot upflow anaerobic sludge bed (UASB) reactors under mesophilic (35°C) and submesophilic (20-30 °C) conditions. They demostrated that a stable operation of the reactor with the treatment efficiencies higher than 90% on the total COD was up to the organic loading rates of 28.5 and 9.5 g COD/l day for mesophilic and submesophilic regimes, respectively.

Table 2. Results obtained under different experimental conditions in the first-stage UAPBR

Days	Influent parameters						
	HRT	COD	SS	OLR	pH	Alkalinity	Oil-grease
0-10	120	10000	650	2	6	2000	1400
11-23	120	15000	1000	3	6	2000	2100
24-35	120	20000	1300	4	6,1	2000	2800
36-50	120	25000	1600	5	6,2	2000	3600
51-62	120	30000	2000	6	6,1	2000	4300
63-75	120	35000	2300	7	6,2	2000	5000
76-92	120	40000	2600	8	6,3	2000	5700
93-108	120	50000	330	10	6,2	2000	7200
109-123	120	45000	3000	9	6,3	2000	6500
124-137	107	45000	3000	10,11	6,4	2000	6500
139-155	96	45000	3000	11,25	6,2	2000	6500
156-170	85	45000	3000	12,71	6,2	2000	6500
171-185	72	45000	1400	15	6,2	2000	6500

Effluent parametres								
COD	SS	Gas Production	pH	Alkalinity	VFA	Oil-grease	COD Removal (%)	VFA/ Alkalinity
1500	190	2,88	7,4	2200	260	400	85	0,11
1800	230	4,48	7,4	3300	228	580	88	0,07
1600	250	6,25	7,3	4800	354	750	92	0,07
1750	400	7,9	7,4	4600	380	900	93	0,08
1800	450	9,58	7,4	4500	450	1100	94	0,1
2100	460	11,17	7,3	4000	500	1200	94	0,12
2400	460	12,7	7,3	4100	500	1300	94	0,12
4500	600	15,12	7,2	4300	600	1700	91	0,14
3200	580	15,54	7,3	4800	540	1500	93	0,11
4000	990	14,4	7,1	4400	550	1600	91	0,12
4500	1250	14,19	7,1	4350	600	1700	90	0,14
4700	1300	13,8	7,05	4200	600	1750	90	0,14
6700	1400	13,1	7,05	4000	600	1740	85	0,15

HRT (hour), COD (mg l-1); SS (mg l-1); OLR (g COD l-1 day-1); Alkalinity (mg CaCO3 l-1); VFA (mg l-1); Gas Production l CH4 l -1 day-1

Table 3. Results obtained under different experimental conditions in the second-stage UAPBR

Days	Influent parameters							
	HRT	COD	SS	OLR	pH	Alkalinity	VFA	Oil-grease
0-10	120	1500	190	0,3	7,4	2200	260	400
11-23	120	1800	230	0,36	7,4	3300	228	580
24-35	120	1600	250	0,32	7,3	4800	354	750
36-50	120	1750	400	0,35	7,4	4600	380	900
51-62	120	1800	450	0,36	7,4	4500	450	1100
63-75	120	2100	460	0,42	7,3	4000	500	1200
76-92	120	2400	460	0,48	7,3	4100	500	1300
93-108	120	4500	600	0,9	7,2	4300	600	1700
109-123	120	3200	580	0,64	7,3	4800	540	1500
124-137	107	4000	990	0,9	7,1	4400	550	1600
139-155	96	4500	1250	1,13	7,1	4350	600	1700
156-170	85	4700	1300	1,32	7,05	4200	600	1750
171-185	72	6700	1400	2,23	7,05	4000	600	1740

Effluent parametres								
COD	SS	Gas Production	pH	Alkalinity	VFA	Oil-grease	COD Removal (%)	VFA/ Alkalinity
240	50	0,42	7,5	2300	130	100	84	0,05
300	75	0,50	7,6	3350	90	120	83	0,03
240	90	0,46	7,5	4900	140	180	85	0,03
250	100	0,5	7,5	4650	140	220	85	0,03
265	100	0,52	7,6	4600	130	290	85	0,03
350	110	0,59	7,7	4200	150	300	83	0,03
390	100	0,68	7,8	4300	150	300	83	0,03
600	160	1,2	7,8	4400	170	350	86	0,04
460	155	0,93	7,8	5076	120	400	85	0,02
480	205	1,3	7,7	4700	170	420	88	0,04
500	260	1,5	7,7	4300	240	450	88	0,05
520	300	1,6	7,7	4150	250	450	88	0,06
750	400	1,8	7,7	4100	250	440	88	0,06

HRT(Hour), COD (mg l^{-1}); SS (mg l^{-1}); OLR (g COD l^{-1} day^{-1}); Alkalinity (mg $CaCO_3$ l^{-1}); VFA (mg l^{-1}); Gas Production l CH_4 l^{-1} day^{-1}

In this study, the pH in the both reactors remained approximately constant for all of the HRT studied, with 7.05 and 7.8 as extreme values (Table 2 and 3). This stability can be attributed to carbonate/bicarbonate buffering. When alkalinity is above of 1000 mg l^{-1} the system has enough buffer capacity. The alkalinity of original wastewater was 2600±100 mg l^{-1}, therefore $NaHCO_3$ wasn't added to it. The buffering guards against possible acidification of the reactor giving a pH of the same order, are as optimal for methanogenic bacteria. The high pH values and the buffering capacity is a guarantee as opposed to an acidification of the reactor that could be caused by a sudden overloading of the reactor [10].

The VFA/alkalinity ratio can be used as a measure of process stability; when this ratio is less than 0.3-0.4 the process is considered to be operating favorably without acidification risk [10]. As was observed in Table 2 and 3, the ratio values were lower than the suggested limit value in all HRT studies.

The values of volumetric methane production rates for each OLR studied in the first-stage UAPB reactor and second-stage UAPB reactor are also given in Table 2 and 3. The methane yields in the first-stage APB reactor increased linearly with increasing OLR up to 15,54 l CH_4 g^{-1} COD day^{-1} at 2-9 g COD l^{-1} day^{-1}.

The second-stage UAPBR was fed the effluent from the first stage UAPBR. When considering the performance of the second-stage UAPBR a total COD removal efficiency of 83-88% is observable, an effluent quality which can't be directly discharged to a receiving environment (Table 3)

3.2. Aerobic treatment

Table 4 summarizes results obtained from aerobic treatment. Batch aerobic reactors were operated for 8 days. Effluent COD, oil-grease, were measured on every day. On day 5, the effluent COD concentrations were 110 mg l^{-1} as opposed to the influent 460 mg l^{-1}.The oil and grease effluent concentartions were 55 mg l^{-1} at this day versus 400 mg l^{-1}. The COD and oil-grease removal efficiencies were 76 and 85%, respectively. The overall COD and oil-grease removals anaerobic and aerobic treatment stages collectively were 99.8 and 99.2%, respectively. Malaspina et. al. [11], the anaerobic downflow-upflow hybrid reactor (DUHR) achieved 98% COD reduction at an OLR of 10 g COD per day. Post treatment was subsequently performed, resulting in more than 90% of both COD and nutrient removal rates.

Table 4. Results obtained from aerobic treatment

	Days								
Parameters	0	1	2	3	4	5	6	7	8
pH	7,8	7,7	7,7	7,6	7,7	7,8	7,8	7,7	7,7
Biomass (mg l^{-1})	2900	3100	3300	3700	3900	3800	3650	3650	3550
COD(mg l^{-1})	460	350	230	180	140	110	110	110	110
Oil-grease (mg l^{-1})	400	330	200	120	66	55	55	50	48

4. CONCLUSIONS

In this study, treatability of cheese whey was examined with a sequential UAPBR and batch aerobic reactor configuration.

The following conclusions can be drawn according to the experimental results obtained in this study:

1. A two-stage UAPBR configuration was efficient for cheese whey treatment at 9 g COD l^{-1} day^{-1} of OLR.
2. In application of a sequential biological (anaerobic/aerobic) treatment for the cheese whey, COD and oil-grease removal efficiencies were 99.8, 99.2%, respectively.
3. Effluent COD and oil-grease concentrations satisfied the effluent discharge limits.

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DECADES OF TIN MINING IN JOS PLATEAU NIGERIA AND A LEGACY OF IMPOVERISHED AGRICULTURAL LAND AND HIGH RADIOACTIVE ELEMENTS: AN OVERVIEW OF INFRASTUCTRAL NEGLIGENCE

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Geologically, the lithological formations of Jos Plateau are basement complex, biotite granite and new basalts. Tin and Columbite –ore are associated with greisesnized biotote granite, hence the Tin presence and its mining and exploration in the area which started in 1904. This mining operation was on for over 50 years until in 1974 when the radioactive nature of the Tin-ore and its tailings was realized. Before this realization the tailings were treated as non-radioactive and as such were used in building construction, farming and industries (furnace blasting). The decades of tin mining activities in the Jos area have left a legacy of polluted water supplies, impoverished agricultural land and soil containing abnormally naturally found radioactive elements metals in the area . Both agricultural food products and soil in the area contain high levels of natural radioactive elements which pose increased both internal and external radiation exposure health risks to the population. Food safety, security and health impacts and infrastructure in place to address years of negligence are being addressed in this paper.

Keywords: *Health, environment, mining, policy, radiation risk, food safety, Jos-Plateau, Nigeria.*

1.0 INTRODUCTION

Nigeria has a total land area of 923,773km^2 which can be divided into three major geographical zones. The semi-arid and dry sub-humid areas in the north; the humid areas and sub-humid areas in the central Nigeria and the very humid and flood areas in the south. From the mangrove and rain forests of the south through the savannahs and semi-arid ecosystem of the northern Nigeria, the nation is richly endowed with fishery resources, wildlife, timber, medical plants, mineral resources (oil and gas), water, ornamental and food crops etc. The economic growth and development of the country has since the colonial times depended on the exploitation of these resources. This model of economic development coupled with high population growth rate and urban migration has adversely affected the environment and social well-being of the nation. The challenge however is how to achieve growth in the present. It is now well known that human induced changes in the environment have always been profound and common in almost all parts of the globe. According to Gbadagesin (2002), the present environmental crises all over the world can be seen to be the result of human beings towards nature on premise that the natural resources of the environment are unlimited and human’s primary purpose in the environment is to produce and consume. Particularly, production and consumption must continue endlessly because of human’s ever-increasing material standard of living and also that humans need not adapt himself to the natural environment since he has the potential to remake it to suit his own needs using Science and Technology (ST).

This view of nature is popularly referred to as the environmental possibilism. However, the potential of human labour to transform nature and the capacity of people to create new systems of material production that transcends contemporary economic constraints as preached by the environmental possibilism paradigm was challenged by the human-ecology paradigm. This new paradigm not only preached the idea of a mutual adjustment between human beings and their environment but also dictated the various environmental movements witnessed in the latter part of the 20th century. One of such approaches to the new paradigm was the Agenda 21 tagged the RIO Declaration in Environment and Development in 1992. According to the World Bank (1997), these declarations are to guide countries in their thinking of environmental issues for sustainable development without compromising the ability and aspirations of the future generations to achieve their needs. In a very broad sense, the environment refers to natural resources which include soils and land, waters, forests, oil and minerals, fisheries, wildlife, plants, air and climate. These also include coastal resources, vegetation and manmade environments like cities. The environment in its totality is the geographical and physical location in which we live, work and produces, socialize, and derive our cultural heritage. The environment is therefore locale specific, but some aspects of it cut across different political boundaries, thereby necessitating cooperation between local communities and nations. Although the environment has a natural resilience and dynamic ability to adapt to changes, technological advancement and population growth are two major forces pushing the environment beyond its carrying capacity. Unless new strategies are evolved, it would be difficult for the environment to meet the needs of the future generations. Sustainable development is the term that was used to describe the right of the present and future generations to equitably meet their developmental and environmental needs. The global strategy is to integrate social, economic and environmental issues in national development planning. A development seeking country like Nigeria should therefore give utmost priority to environmental planning policy and management at all levels of government. The National Policy on the environment which was published in 1989 was designed to ensure sustainable development based on proper management of the environment. One of the strategies for achieving the objectives is the institution of environmental impact assessment (EAI) process in the national economy with the enactment of the environmental impact assessment Decree No 86 of 1992. The decree and the accompanying documents set out procedures, methods, standards and sanctions for non-compliance with the EIA requirements (Alayande, 2002).

This paper describes a study carried out in Jos Plateau where Tin mining activities took place and its effect on the radioactivity levels in food crops in the area, its implication on food security and safety and the lessons learned relevant for environmental development and sustainability in the country. Food is a major source of energy for metabolic activities in living organisms and as such it is an indispensable product for human existence. Ingestions of radionuclides through food intake account for substantial part of average radiation doses to various organs of the body and also represent one of the important pathways for long term health considerations (Hernandez et al, 2005). Radionuclides on farmlands or farm soil may enter human food through direct deposition on leaves or exposed parts of plants that are edible to humans or also due to persistence of the radionuclides based on their physical half lives in the layer of soil from which they are taken up into growing agricultural plants through root-uptake. Human dietary composition is quite variable from place to place even from an individual to another.

The natural radionuclides entering the food chain are contained in the soil and as a result, soil radionuclides content is a prime source of geographic variability. Also uptake varies from plant species; hence intake of different food products forms the second source of variability (Avadhani et al, 2001 and Breuninger et al, 2002).

2.0 Tin Mining on the Jos Plateau

Jos is situated at the geographical centre of Nigeria; about 288 km from Abuja, the nation's capital. Geologically, the lithological formations of Jos Plateau are basement complex, biotite granite and new basalts (Osin and Rahaman, 1986). Tin and Columbite –ore are associated with greisesnized biotote granite, hence the Tin presence and its mining and exploration in the area (Oresegun and Babalola, 1993). The geological formation and minerals of the Jos Plateau is shown in Fig 1.

The opening up of the Jos Plateau for Tin mining started in 1902. The use of heavy machinery on the mine fields aggravated the process through which land was destroyed. Although Plateau has always been vulnerable to erosion but the combination of heavy rainfall, Tin mining activities, deforestation and overgrazing speeded up the process and devastated the topsoil rendering it useless for any meaningful agriculture. The Tin mining carried out on the Jos Plateau disturbed some 320 km^2 of agricultural land (Pasquini and Alexander, 2005). The traditional farming system of the indigenes has become distorted toady as a result of shortage of land so that the people especially in the mining communities because of socio-economic pressure have to farm on the same piece of land yearly and with the poor quality of the land, produce yields have been very poor. And coupled with the present state of land shortage are mining ponds all over the place some of which have become death traps to both human and animal lives. The mining operation took place for over 50 years and not until in 1974 when the radioactive nature of the Tin-ore and its tailings was realized (Oresegun and Babalola, 1990, 1993).

Before this realization the tailings were treated as non-radioactive and as such were used in building construction, farming and industries (furnace blasting). During the milling of the Sn-ore to obtain tin and columbite, Monazite, Zircon and Ilemenite through electrostatic and magnetic separation using manual processing method in the open, resulting in the generation of dust that are spread into the environment. Mining is a capital intensive industry and also its aftermath is always devastating to the ecology of the host community. This appears to describe the scenario today in Jos-Plateau after decades of tin mining which has left the area impoverished and devastated unlike in the developed countries where remedial measures were taken in the course of mining to avoid environmental degradation. No formal attempts at reclamation of this land has been initiated a situation that impedes environmental sustainability and developments (Alexander, 2002).

3.0 MATERIALS AND METHODS

3.1 Sampling: The map of Jos-Plateau showing the location of Bitsichi the sampling site is shown in Fig 2. The local food crops grown in the area were identified and to ensure good coverage the entire area was divided into six grids of about 3 km^2. The full range of food items identified could not be collected at each sampling site, since, in a field situation it is not possible to have a grid where all the food samples are grown as the area covered a wide variety of agricultural and local and/or urban conditions. As much as possible effort was made to ensure adequate collection of representative samples of the identified food crops from the study area.

The different food items collected and the number of each sample is presented in Table 1. Soil samples were collected to a depth of 150 mm from 4 different points in the farms where food samples were collected and thereafter thoroughly mixed together to represent a sample for that site. Also aerial dose rate measurement was performed in the farms using a pre calibrated survey meter (Morgan Series 1000 – mini rad meter by Mini Instruments Ltd, England).

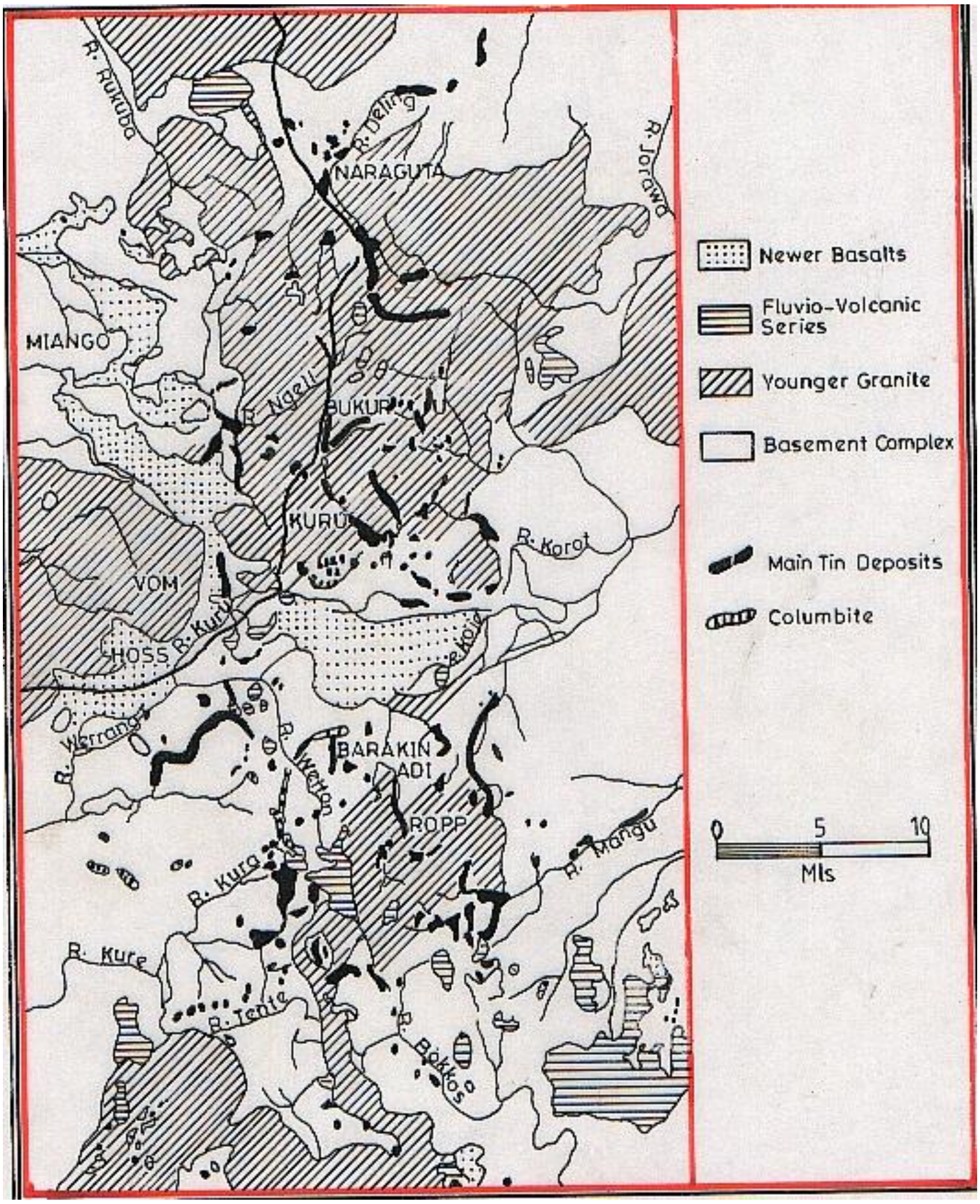
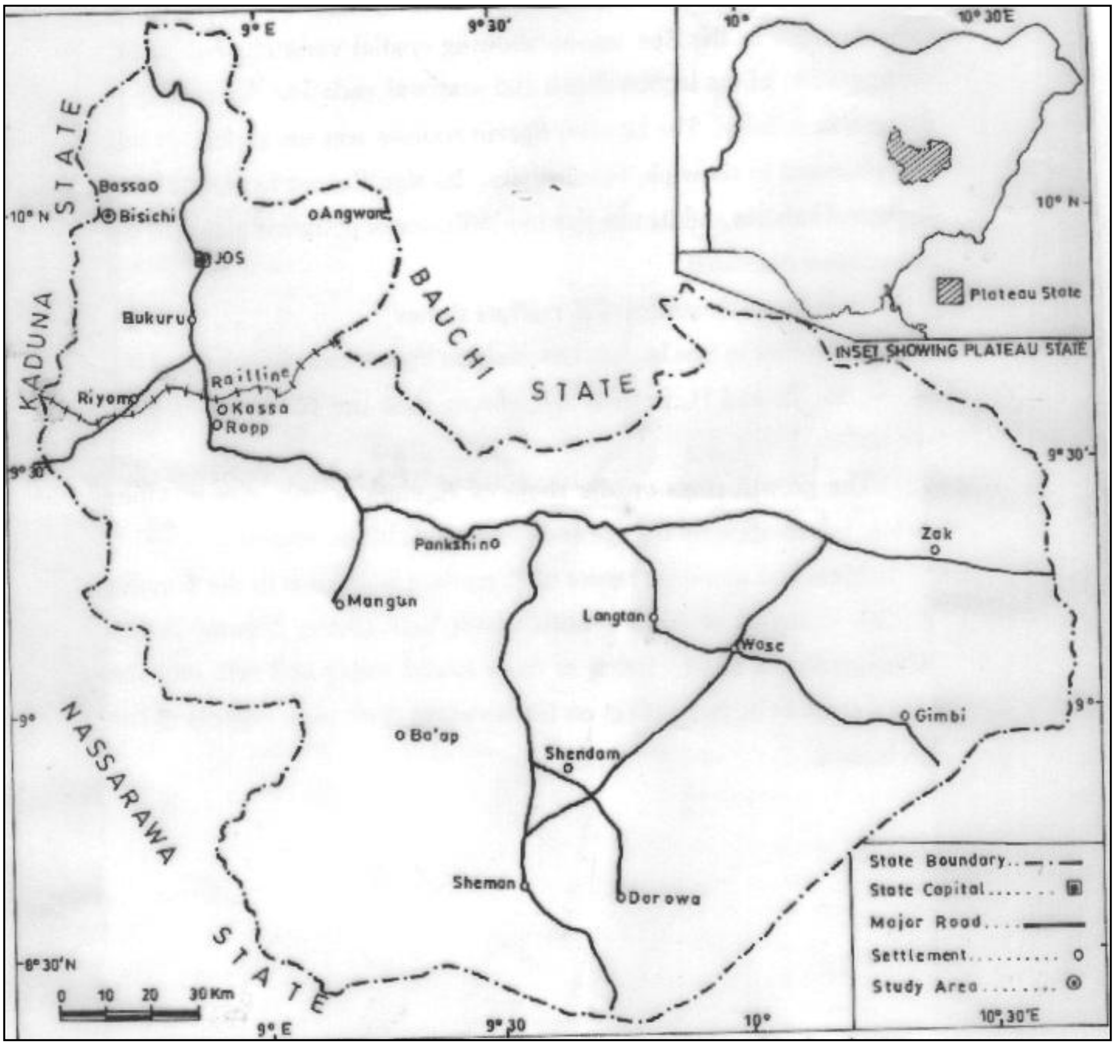


Fig 1. Geology and mineral distribution of Jos-Plateau.

The soil samples after drying for many days at room temperature until a constant weight was reached were crushed to pass 2mm mesh sieve. They were transferred into uncontaminated empty cylindrical plastic containers of uniform size (60 mm height by 65 mm diameter) and were sealed for a period of about 4 weeks. This was done in order to allow for Ra and its short-lived progenies to reach secular radioactive equilibrium prior to gamma spectroscopy. Since the study focuses on the pathway for human ingestion of these food items grown and consumed by the population in the area, only the edible parts of the food items were considered for preparation and analysis. For instance, the peels of cassava tuber, yam tuber and cocoyam were all discarded.



The items were thereafter air- dried to reach a constant weight, then, homogenized and

Fig 2. The map of Jos-Plateau showing Bitsichi the sampling site

transferred into the calibrated geometry sample containers and kept sealed as the soil samples.

3.2. Radioactivity determination: The samples (food and soil) were counted for 36,000 seconds (10 hrs) in a low-level gamma counting spectroscopy comprising of a 76 mm x 76 mm NaI (Tl) detector (Model No 802-series) by Canberra Inc., which is coupled to a Canberra Series 10 plus Multichannel Analyzer (MCA) (Model No 1104) through a preamplifier base. The detector has a resolution of about 8% at 0.662 MeV of ^{137}Cs which is capable of distinguishing the gamma ray energies used for the measurements. The photopeak at 1.460 MeV was used for the measurement of ^{40}K while those at 1.760 MeV peak from ^{214}Bi and 2.614 MeV from ^{208}Tl were used for the measurement of ^{226}Ra and ^{232}Th, respectively. The net area count after background corrections in each photopeak was used in the computation of the activity concentration of each of the radionuclides in the food and soil samples. The activity concentration in the samples was obtained using the expression (Akinloye and Olomo, 2000):

$$C\left(Bq.kg^{-1}\right) = \frac{C_n}{\varepsilon P_\gamma M_s} \qquad (1)$$

where C is the activity concentration of the radionuclide in the sample, C_n is the count rate under each photopeak due to each radionuclides, ε is the detector efficiency of the specific γ-ray, P_γ is the absolute transition probability of the specific γ-ray and M_s is the mass of the sample (*kg*). The mass of samples used ranged between 80 g and 200 g for the food samples while a uniform mass of 200 g was used for the soil samples.

4.0 RESULTS AND DISCUSSION

4.1. Radioactivity levels

The activity concentrations of the radionuclides in the soil samples are shown in Table 2 while those in the food items in the study area and the control sites are presented in Tables 3 and 4 respectively. The errors in Tables 2, 3 and 4 are combined uncertainties in the counting measurements. As could be observed in Table 2 the concentration of ^{232}Th was highest in virtually all the sampling sites. This appears not to follow the trend of ^{40}K contents that more often is usually higher environment where radioactive concentrations are within normal world average value (Jibiri and Bankole, 2006). The ^{238}U were equally high in its soil content in this area. It can also be observed from Table 3 that ^{40}K content was highest in all the food samples at variance with its content in the soil samples. This may be attributed to the heavy use of NPK fertilizers by the farmers in improving crop yield as the farm lands were considered infertile due to impoverishment of the soil by the decades of mining operation in the area and to which no effort was made in reclaiming it (Pasquini and Alexander, 2005). The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in the food crops from this area were about 10 orders of magnitude higher than those obtained in other parts of the country. For instance in tuber products the radionuclide levels varied from 10.6 to 46.4 Bq kg^{-1} for ^{40}K, 0.5 to 2.7 Bq kg^{-1}for ^{226}Ra and from BDL – 1.4 Bq kg^{-1} for ^{232}Th (Akinloye and Olomo, 2000) while in cereal crops the values of the radionuclides varied from 36.4 to 186.9 Bq kg^{-1} for ^{40}K, 0.2 to 1.4 Bq kg^{-1}for ^{238}U and from 0.3 to 1.8 Bq kg^{-1} for ^{232}Th (Arogunjo, 2003). It can also be observed from Table 4, that values of similar food items from the control site were also lower to those from the study area.

The activity concentrations of ^{40}K, ^{238}U and ^{232}Th measured in each of the soil samples from the farms is only an indication of the intensity of the radionuclides present and does not relate the effect of such level on bio-system. The important quantity to assess when considering radiation risk to a bio-system is the absorbed dose rate. The absorbed dose rate, D (nGy h^{-1}) in air at 1 m above the ground level due to the concentration of ^{238}U,^{232}Th and ^{40}K in the soil samples in each site was calculated using the equation (UNSCEAR, 2000):

$$D = 0.427.C_U + 0.662.C_{Th} + 0.043.C_K \tag{2}$$

where $C_{U,}$ C_{Th} and C_K are the concentration of ^{238}U, ^{232}Th and ^{40}K in the sample (Bq kg^{-1}), respectively. The absorbed dose rate (nGy h^{-1}) in air at 1 m above the ground determined at each farm does not directly give the radiological health hazard to which an individual is exposed. There are two additional factors that must be considered. The first is a factor which converts Gy to Sv that accounts for the biological effectiveness of the dose in causing damage in human tissue. The second is the occupancy factor that specifies the proportion of the total time spent outdoors. The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), recommended 0.7 Sv Gy^{-1} as the first factor and 0.2 as the second factor. According to Adejuwon (2002), an individual farmer is expected to spend about 8 hrs per day in the farm while a tractor base mechanized farming will spend half the period, however, about averagely 10 hrs per day is spent by farmers from this area and generally for peasant farmers in the country. As such an outdoor occupancy factor of 0.4 (≈10 hrs per day) has been assumed in this work to be more suitable. Adopting 0.7 and 0.4 occupancy factors the total gamma effective dose due to the concentration of the radionuclides in the soil at the different farms ranged between 0.07 μSv h^{-1} and 1.16 μSv h^{-1} giving an annual value of 228 μSv and 4065 μSv respectively. The aerial dose values obtained using a survey meter was found to vary between 0.50 μSv h^{-1} and 1.47 μSv h^{-1}. This dose values from both in-situ and soil measurements can be seen to be in agreement and therefore suggest that the area is suited in high background area since values are 20 orders of magnitude higher than world average terrestrial value of 0.055 μSv h^{-1} (UNSCEAR, 2000). The major contributor to gamma radiation exposure in the area is principally due to ^{232}Th.

Table 1. The different samples of food items collected and their food group

Food Group	Sub-food Group/Food type	Scientific Names	Number of samples
Grains/Cereals	Dyare	*	2
	Millet	*Pennisetum glaucum*	3
	Maize	*Zea mays*	4
	Guinea corn	*Sorghum bicolor L*	2
	Acha	*Digitaria exillis stapf*	4
Vegetables			
	Tuberous-Sweet potato	*Ipomoea batatas*	3
	-Irish potato	*Solanum tuberosum*	4
	General - Okra	*Abelmoshus*	3
	-Tomato	*esculentus*	3
	- Pepper	*Lycopersicon*	3
		esculentus	2
	- Garden egg	*Capsicum annum var*	
	Leafy	*abbrevatum*	
	- Kuca	*Solanum gilo*	3
		*	
Tubers	Yam	*Dioscorea sp*	4
	Cassava	*Manihot esculenta*	4
	Cocoyam	*Colocosia esculenta*	3
Legumes	Groundnut	*Arachis hypogeae*	3
	Local bean (Sword beans)	*Linn*	2
	Soya beans	*Canavalia ensiformis*	3
			3
		Clycine max merr	

* Dyare and Kuca are local kind of cereal and vegetable respectively.

Table 2. Activity concentrations of ^{40}K, ^{238}U and ^{232}Th in the soil samples and aerial dose rate levels in the agricultural farmlands in Bitsichi mining area.

Locations	^{40}K (Bq.kg^{-1})	^{238U} (Bq.kg^{-1})	^{232}Th (Bq.kg^{-1})	Aerial dose rate (μSv h^{-1})
Farm 1	93.0 ± 9.6	145.2 ± 16.3	373.5 ± 8.9	0.72 ± 0.02
Farm 2	135.7 ± 7.1	175.1 ± 19.6	515.2 ± 10.1	0.73 ± 0.04
Farm 3	166.4 ± 12.4	10.9 ± 15.2	122.7 ± 11.2	0.50 ± 0.01
Farm 4	128.8 ± 17.2	72.5 ± 13.8	168.4 ± 7.8	0.89 ± 0.05
Farm 5	BDL	427.1 ± 12.4	1036.5 ± 8.8	1.01 ± 0.05
Farm 6	55.1 ± 11.5	470.6 ± 10.9	2189.5 ± 9.2	1.47 ± 0.05

Table 3. Activity concentrations of the radionuclides in the food samples and annual effective dose.

Food items	^{40}K (Bq.kg^{-1})	^{226}Ra (Bq.kg^{-1})	^{232}Th (Bq.kg^{-1})	Ingestion dose (µSv y^{-1})
Cereals/Grains				
Maize	243 ± 21	34± 14	BDL	63
Millet	144 ± 13	5 ± 3	BDL	39
Acha	BDL	BDL	BDL	-
Dyare	179 ± 25	5 ± 1	8 ± 3	2
Guinea corn	86 ± 26	5 ± 1	8 ± 2	112
Rice	117 ± 30	6 ± 3	6 ± 3	
Tubers				
Yam	685 ± 41	84 ± 10	90 ± 6	2164
Cocoyam	537 ± 18	34 ± 15	33± 7	81
Cassava	540 ± 21	27 ± 9	22 ± 5	519
Sweet potato	424 ± 31	24 ± 11	36 ± 12	170
Irish potato	494 ± 22	11 ± 4	17 ± 10	22
Vegetables				
Okra	213.0 ± 19	BDL	BDL	*
Tomato	159 ± 29	149 ± 6	10 ± 4	27
Pepper	132 ± 19	5 ± 3	BDL	9
Garden egg	122 ± 22	32 ± 19	BDL	*
Kuca	81 ± 17	10 ± 7	BDL	*
Legumes				
Soya beans	546.8 ± 28.6	8 ± 4	BDL	9
Groundnut	398.6 ± 12.9	7 ± 3	10 ± 3	13
Local beans	453.6 ± 15.8	9 ± 2	19 ± 6	0.2

BDL- Below detection limit

Table 4. Activity concentration of radionuclides in food from Kaduna State (control site)

	Activity concentration (Bq kg^{-1})		
Food samples	^{40}K	^{226}Ra	^{232}Th
Acha	24 ± 3	6± 1	6 ± 2
Cassava	94 ± 3	2 ± 1	2 ± 1
Sweet Potato	113± 3	BDL	7± 2
Guinea corn	38 ±2	BDL	6 ± 2
Maize	38 ± 3	3± 1	5 ± 2
Millet	38 ± 3	3± 1	BDL

4.2 Effective dose due to ingestion

Effective dose is a useful concept that enables the radiation doses from different radionuclides and from different types and sources of radioactivity to be added. It is based on the risks of radiation induced health effects and the use of International Commission on Radiological Protection (ICRP) metabolic model that provides relevant conversion factors that permits the calculation of effective doses from the total activity concentrations of the radionuclides measured in food items (ICRP, 1994, 1996). The estimation of the radiation induced health effects associated with intake of radionuclides in the body is proportional to the total dose delivered by the radionuclides while resident in the various organs. The radiation dose delivered by taken in food is obtained by measuring how much is in the food (Bq kg^{-1}) and multiplying it by how much food is consumed over a period of time (kg d^{-1} or kg y^{-1}) and then by a dose conversion physical factor (Sv Bq^{-1}) which gives an indication of how much dose is caused by the radioactivity in the body organ. Thus according to Till and Moore (1988) the ingested dose is given by:

$$H_{T,r} = \left(U^{Bl} \times C_r^{Bl} + U^{Pf} \times C_r^{Pf} + U^{Mi} \times C_r^{Mi} + \ldots\ldots \right) \times g_{T,r} \qquad (3)$$

Thus equation 3 can rewritten as:

$$H_{T,r} = \sum \left(U^i \times C_r^i \right) \times g_{T.r} \qquad (4)$$

where, *i* denotes a food group, the co-efficients U^i and C^i_r denotes the consumption rate per year (kg) and activity concentration of the radionuclide (Bq) respectively and $g_{T\ r}$is the dose coefficient for intake by ingestion of radionuclide *r* (Sv Bq^{-1}). The values of g for ^{40}K, ^{238}U, ^{232}Th and ^{137}Cs are respectively, 5.9 x 10^{-9} Sv Bq^{-1}, 4.8 x 10^{-8} Sv Bq^{-1}, 2.3 x 10^{-7} Sv Bq^{-1} and 1.3 x 10^{-8} Sv Bq^{-1} respectively for members of the public (adult) (ICRP 1996; RIFE, 2005).

Using these conversion factors the effective dose due to ingestion was estimated and they are presented also in Table 3. The estimated total effective dose due to intakes of radionuclides varied from 0.2 μSv y^{-1} in local beans and 2164.1 μSv y^{-1} in yam. The tuber crops were found to deliver more dose than the other crop types. The food consumption statistics used for the different food crops in Nigeria based on Federal Office of Statistics (FOS) and Food and Agriculture Organization (FAO). In this study, the calculation of individual doses and risks from ingestion pathways carried out were based on the assumption that all food consumed is produced at the point of consumption and that the required amount of food is produced in the given location. In essence the consumption of such foodstuff is sustained wholly by local sources. Furthermore, in the estimate of doses to individuals in agricultural food products, it is usually important to consider the peculiarity of the food availability to such an individual and the nature of the environment from which he derives his food products. The three type of individual usually considered are:

(i) A control individuals whose diet consists of food grown on undisturbed soil.
(ii) A local individual who obtains 10 % of their food from a disturbed soil
(iii) A theoretical maximum exposed individual whose diet is obtained solely from food grown on disturbed soil.

Based on the conditions that the study involves mining areas (disturbed soil) the assessment of dose is based on the assumptions of (ii) and (iii) that the individuals derives all its nutritive requirement from the crops analyzed and the he solely resides in that environment. However, a maximum exposed individual does not exist in reality, but from radiation protection perspective, conservative estimate of dose is important in relation to Protective Action Guide (PAG) and other scenarios such as planning and legislation of food policy and administration (Fernandez et al, 2004). Protective Action Guide (PAC) is referred to as an action or measure taken to avoid exposure to radiation that would occur from future ingestion of foods contaminated with radioactive materials due to local or international releases.

Generally, the dose from intakes of radionuclides can be considered to be low when compared to natural external radiation of about 2000 μSv y^{-1} to which no harmful effects will occur directly given the realities of diet habits, food choice, etc. Also the cereals crops which constitute the major food types of nutritive importance in the area were low in radionuclide concentrations (Maziya-Dixon et al 2004). Although not all crops were sampled such as rice though not grown in the area, the total effective dose estimated in this study is seen to represent a reasonable range due to intakes in the area. Nevertheless, it represents a useful small database that will allow more thorough investigations in future works in the area.

The small database is also seen to be useful to the newly established Nigerian Nuclear Regulatory Authority (NNRA) in their food policy, administration and regulatory functions or other environmental monitoring institutions for effective management of the environment for sustainable development. However, Effective management of the environment for sustainable development does not just happened. It is created. Moreover, it is created by hard work and vision within governmental and non-governmental organizations striving to protect the environment from degradation. The policy framework within which this can be achieved has four aspects: (i) *Risk Assessment:* which defines the types and magnitude of environmental problems and priorities them, (ii).*Visioning, Planning and Decision making:* which define goals and workout strategies for achieving the goals, (iii) *Implementation:* which translates plans and decision into actions at field levels and (iv) *Evaluation:* which access the performance of the adopted strategies in achieving the desired goals. These four important aspects of the policy process depend critically on the Government Administrative procedure which provides opportunities and constrains for efficiency and effectiveness. Government Administration for environmental management unlike other sectors is complicated by the following factors:

- The environment is a complex dynamic system. Therefore, government administration should be knowledge-based and not bureaucratic. It should also be flexible with potentials for change and growth.
- Environmental issues affect almost everyone, every agency, every voluntary group, industry, and every government ministry and/or department. Hence, the institutional arrangement should have a broad base, bottom-up approach to planning, implementation and evaluation.

- Environmental protection is wide ranging in scope and complex in its relationship with different sectors of national life. This requires that there should be a clear allocation of roles and responsibilities. Such a definition of task is needed between Federal, State, and Local Government and between sector agencies as well as non-governmental organizations to facilitate the necessary cooperation, coordination and efficient use of scarce financial and knowledge resources.

As posited by Aina et al (1994), environmental planning and management practice in Nigeria has to do with enforcement of policies and regulations and strong commitments to achieving the goals set forth in the regulations.

5.0 CONCLUSION

The effective dose due to ingestion of crops grown in an old Tin mining area in Jos-Plateau, Nigeria has been estimated based on measured radionuclide concentrations of ^{40}K, ^{238}U and ^{232}Th in the different food crops. The concentration of ^{40}K was highest in all the food crops and this could be due to the use of fertilizer by farmers to improve crop yields in the farms. Tuber crops were found to deliver more dose than cereal crops which constitute the major food type of nutritive importance of the area under study. The external dose on the farms due to soil radioactivity and internal dose in the food products were relatively high when compared to studies in other parts of the country. However, they are considered to be low to which no harmful effects will occur directly given the realities of diet habits, food choice and residence time in the farms by an individual. To ensure food security and safety, adequate institutional framework should be in place and strong commitments to effectively manage the environment if sustainable development in the area is desired.

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PARTICULATE MATTER and PAH POLLUTION IN AN INDUSTRIAL TOWN: DILOVASI CASE

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Dilovası is an industrial coastal town with a population of 35000 in western part of Turkey The primary cause of the deaths in the town was attributed to cancer according to the investigation made by the ministry of the Health. 167 industrial facilities were identified in the area. In addition to industrial emissions, two major highways pass through the town. The aim of this study is to determine the amount of particulate matter from major pollutant sources and to measure the particulate matter (PM) concentrations in the ambient air and polycyclic aromatic hydrocarbon (PAH) content of PM. In recent years, PAHs have received increased attention in air pollution studies because some of these compounds are highly carcinogenic and mutagen and listed as probably and possibly carcinogenic by the International Agency for Research on Cancer (IARC). Daily particulate and vapor-phase PAH samples were collected on quartz fiber filters and PUF plugs using high volume sampling device at two sampling locations (Dilovası and Gebze) for the selected periods in each season. The fillters and PUF plugs were extracted and the extracts were subjected to GC/MS to determine the concentrations of 16 PAH given in the EPA's priority list.

Keywords: polycyclic aromatic hydrocarbons (PAH), particulate matter, Dilovası

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of compounds which consist of two or more fused aromatic rings made entirely from carbon and hydrogen. The physical and chemical properties of the individual PAH vary extensively. They are released into the atmosphere during incomplete combustion of organic matter. Major PAH sources are natural (forest fires, volcanic eruptions) and anthropogenic (engine exhaust, metal industry, waste incineration, tobacco smoke, domestic heating and food smoking) processes. Concentrations and profiles of PAHs in ambient air are dependent on their sources and environmental variables [1], which vary from region to region. In European cities, vehicle exhaust, wood/coal combustion for space heating, and some stationary point sources, such as metal smelting/process operation, are determined as the principal PAH sources .[2]

Atmospheric PAHs are partitioned between particulate matter and the gas phase. PAHs are mainly adsorbed to airborne particulate matter [3]. Due to their wellknown carcinogenic and mutagenic properties, polycyclic aromatic hydrocarbons (PAHs) were widely studied regarding their environmental effects [4]. Some of PAHs are listed as probably (Group 2A) and possibly (2B) carcinogenic by the International Agency for Research on Cancer (IARC) In particular, benzo[a]pyrene (BaP) has been identified as being highly carcinogenic. (Fang and Wu et all,2003)

This study aims measurements of TSP and PAH in Dilovası. Ambient particulate and gaseous air samples are collected and the samples are analyzed in terms of total organic matter content and 16 PAHs taking place in the EPA priority list. The sampling location is one of the seriously polluted areas in Marmara Region of Turkey. Uncontrolled emissions from the industry, use of fossil fuels for domestic heating together with the unfavored meteorological and geological conditions for air circulation have given rise to serious public health problems. An investigation by The State Health Department revealed the fact that cancer is the reason for the half of the deaths in the region. The role of air pollution can only be understood by intensive monitoring programs of the ambient air. Therefore the results of this study carry important insights in terms of determining and evaluating the current air quality of the area.

2. Experimental

2.1. Sampling program

Dilovası is an important coastal town situated in the northern part of Turkey and is located by the Marmara Sea with longitude between 29°15' and 29° 30', and latitude between 40°45' and 41°00' covering a total area of 2000 hectare.

Two sampling sites were selected to characterize the PAHs concentrations in ambient air in Dilovası, Turkey. Location of sampling sites in Dilovası are given in Figure 1. The first site is situated in a location with a high population density and downstream of the major pollutant sources. The second site was situated on a remote site to measure the background air quality in the region. A sampling program of 20 days for each season from the two sites has been conducted.

Figure 1. Location of sampling sites in Dilovası.

2.2. Sample collection

Atmospheric particulate-and vapor- phase PAH samples were collected using PUF Sampler (GPS1). Airbone particulate were collected on quartz microfiber filter.(Whatman QMA 11,0 quartz microfiber filter). PUF and XAD resins are two of the adsorbents commonly used in high-volume air samplers for gas PAH sampling. Sampler is modified by placing XAD-2 resin (Supelco Amberlite XAD-2)) between two PUF slices to improve the collection of lower moleculer weight PAHs. The PUF Sampler was calibrated with the calibrated orifice and rechecked prior to each sampling period. Each particulate sample was collected for a period of around 24 h with the average sampled air volume of 250-300 m^3.

2.3. Chemical analysis

Filters were pre-heated at 550 ^{o} for least 10 h. Before extraction the weight of total suspended particles (TSP) on the filters was determined by weighing the filters before and after sampling (following 24 h conditioning at 20 ^{o} C in desiccators). During the measurement campaign, every other day only filtered samples were taken and organic matter (OM) of the TSP was determined by weighing the fitler content after 550 C heat treatment. For the other days only TSP and PAH content were determined. Prior to extraction of filter and PUFs internal standart was added to each filter and PUF. The filters were kept in acetone-hexane mixture (50/50, v/v) for 24 h. The filters were extracted for 30 min in an ultrasonic bath. PUF were extracted separately for 24 h using a Soxhlet apparatus containing acetone/hexane mixture (300/300, v/v). Each sample was then concentrated to a volume of 5 ml hexane by using a rotary evaporator. Then they were concentrated further with ultra pure nitrogen to 2 ml. They cleaned by clean columns which consist of sodium sulfate, alumina, silica gel and glass wool. During clean up 40 ml DCM and 40 ml PE were used and obtained extract reconcentrated with ultra pure nitrogen to exactly 1 ml using a procedure that was described in Lee et al., 1995 and US EPA, 1999. The samples collected at sites were analysed by GC/MS (Agilent 6850 N) including 16 US EPA priority PAH.

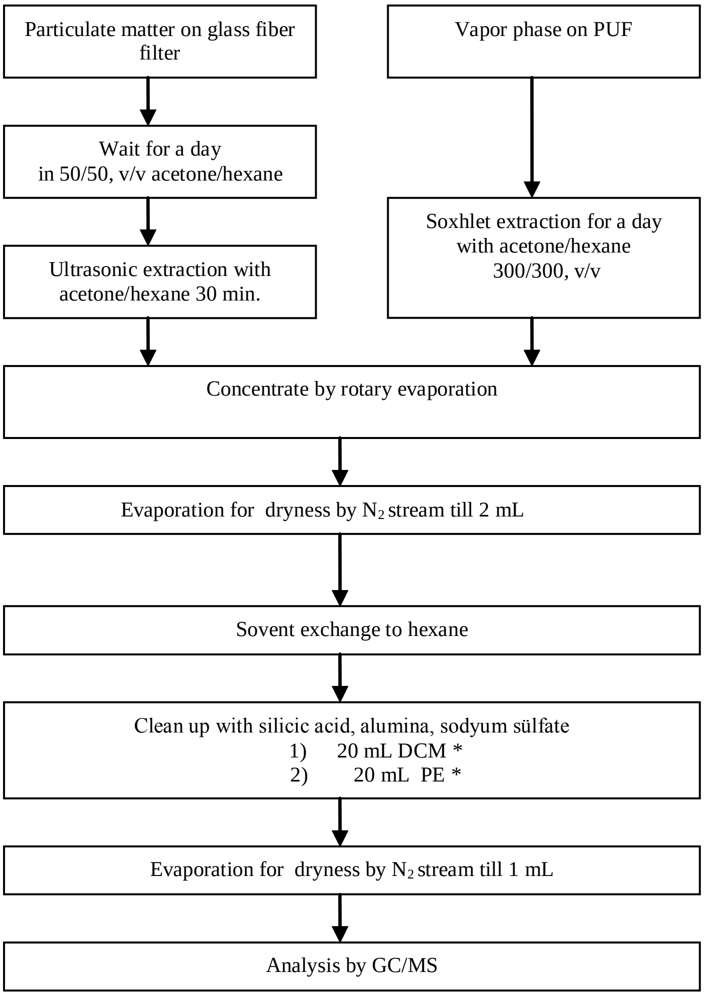

Figure 2.Analiytical procedure used for PAH analysis.* DCM: diclhloromethane *PE: Petrolium ether

3.Results and Discussion

Figure 3 shows the TSP and OM amount of the TSP at GYTE site for one week measurement period in July. TSP concentrations vary from 50 µg/m^3 to 179 µg/m^3 while averaged OM is **51,83** µg/m^3. One week measurements made in October at DLV site however shows higher TSP concentrations with a maximum of 300 µg/m^3 (Figure 4)

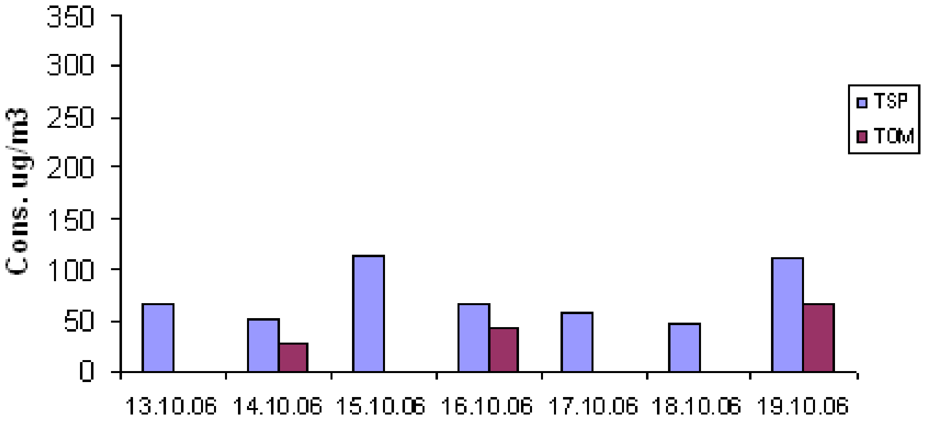

Figure 3. Daily summer season TSP and TOM concentrations at GYTE site.

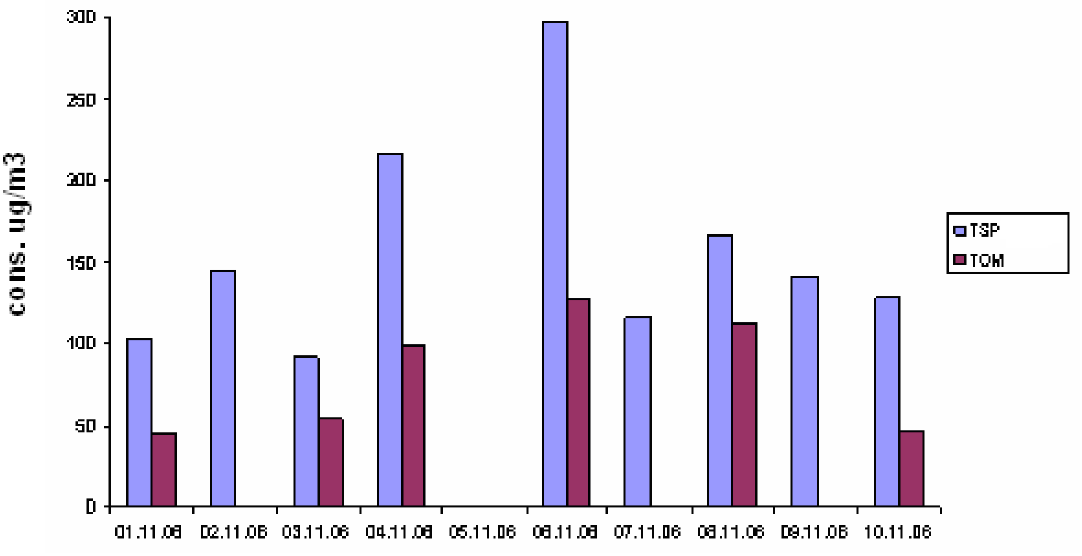

Figure 4. Daily fall season TSP and TOM concentrations at DLV site.

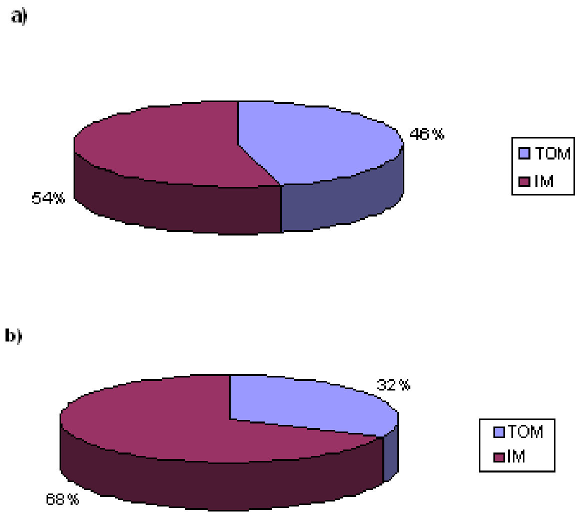

Figure 5. Percent total organic and inorganic content of TSP at DLV site **(a)** and at GYTE site **(b)**

Organic content of the particulate matter is approximately 32 % of the total PM at GYTE and 46 % at Dilovası as can be seen in Figure 5a and 5b respectively. Organic content seems to be higher in Dilovası compared to TSP at GYTE site.

The average concentrations of selected PAH in particulate and vapor phase at DLV site are presented in Table 1. NAP, ACY, ANTH, PHEN and FLT show the highest concentration and particulate PAH concentrations are higher than vapor phase for all selected PAHs.

Table 1
Average total(particulate+vapor) PAH concentrations in DLV

PAH	Abbrev.	Particulate(ngm^{-3})	Vapor(ngm^{-3})	Total(ngm^{-3})
Napthalene	NAP	256,33	22,20	228,82
Acenapthene	ACY	157,71	0,71	129,72
Acenapthylene	ACE	18,60	0,43	16,86
Fluorene	FLU	85,68	0,34	86,03
Anthracene	ANTH	178,14	5,82	183,96
Phenanthrene	PHEN	29,41	1,41	30,83
Fluoranthene	FLT	104,20	24,40	128,60
Pyrene	PYR	72,48	24,85	97,34
Benz[a]anthracene	BaA	1,85	35,50	37,35
Chrysene	CHR	3,43	36,45	39,88
Benzo[b]fluoranthene	B(b)F	0,35	27,09	27,44
Benzo[k]fluoranthene	B(k)F	0,31	24,84	25,15
Benzo[a]pyrene	B(a)P	0,15	21,59	21,74
Dibenz[ah]anthracene	DBahA	0,22	17,60	17,82
Indeno[1,2,3-cd]pyrene	IND	0,50	6,11	6,61

The average concentrations of selected PAHs at GYTE site are presented in Table 2. Almost same PAH profile can be seen at GYTE site. However all individual total (particulate + vapor) PAH concentrations show lower values compared to PAH concentrations at DLV site.

Table 2.

Average total(particulate+vapor) PAH concentrations GYTE

PAH	Abbrev.	Particulate(ngm^{-3})	Vapor(ngm^{-3})	Total(ngm^{-3})
Napthalene	NAP	73,75	22,46	96,21
Acenapthene	ACY	13,28	2,06	15,34
Acenapthylene	ACE	6,51	1,20	7,71
Fluorene	FLU	10,84	0,37	11,20
Anthracene	ANTH	52,46	1,97	54,44
Phenanthrene	PHEN	3,74	0,62	4,36
Fluoranthene	FLT	25,45	2,75	28,20
Pyrene	PYR	14,12	1,83	15,95
Benz[a]anthracene	BaA	0,53	1,41	1,93
Chrysene	CHR	1,53	2,96	4,49
Benzo[b]fluoranthene	B(b)F	0,58	1,95	2,54
Benzo[k]fluoranthene	B(k)F	0,39	0,59	0,97
Benzo[a]pyrene	B(a)P	0,12	0,93	1,06
Dibenz[ah]anthracene	DBahA	0,40	1,21	1,61
Indeno[1,2,3-cd]pyrene	IND	0,93	0,29	1,21

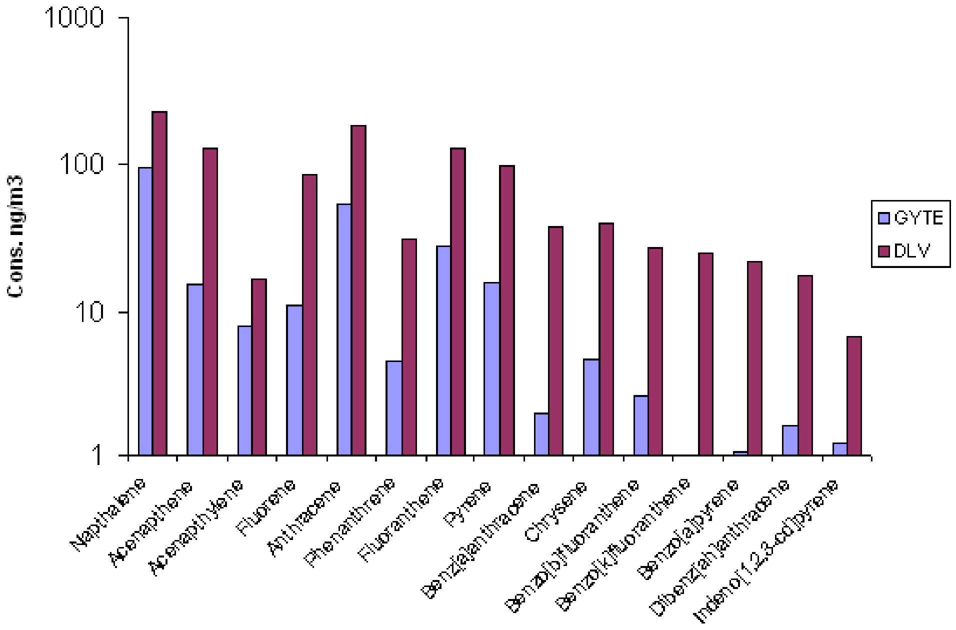

Figure 6. GYTE PUF-Filter PAH concentrations.

Figure 6 shows averaged total PAH concentrations for two sites. The difference between the sites can be seen clearly. Especially for Benzkfluoranthen and Benzopyrene DLV sites show extremely higher concentration values while at GYTE these individual PAH concentrations are quiet small.

These preliminary results show that there is a significant difference between Dilovası and GYTE sites in terms of gaseous and particulate PAH content. All 16 PAHs analyzed in this study show higher concentrations values in Dilovası site based on one week intensive measurement campaigns at each site.

However it is important to monitor the area for longer terms and future sampling for one year period is expected to give a more comprehensive picture of the air quality in the area.

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AN INTEGRATED PREVENTIVE PRODUCTION PLANNING PROGRAM WITH WASTE MINIMIZATION

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The manufacturing process is considered as one of the important sources of environmental impacts of the industrial production. Companies working with hazardous materials in their production have begun to consider the alternatives of minimising the waste at the origin, in the production process. This study focuses on developing an alternative production planning and scheduling technique aiming to prevent the production of hazardous materials while covering the needs of production planning principles. A case study is realised in a battery manufacturing company whose wastes are classified as hazardous. In the first part of the study, the production planning methods adopted in the facility are examined to find out their relations with waste minimisation and an optimisation model is generated. In the second part, the benefits obtained as a result of the application of the optimum scheduling plan is determined in terms of waste and cost minimisation. This study is unique as being one of the few studies aiming the design of job scheduling to reduce waste at the source.

1. Introduction

Industry is aware of the importance of the cleaner production (CP) or pollution prevention (P2) in protecting the limited environmental resources, increasing the reputation of the firm and maintaining the production sustainable. The truth about old fashion waste management alternatives is that they don’t prevent the formation of the waste. Companies adopting old fashion waste management techniques do not only have to pay for inefficiencies of production but they also have to carry the charge of waste removal. For these reasons, the companies using hazardous materials in their production have started to consider waste management alternatives from P2 perspective.

This study aims to establish “cleaner production” methods preventing the production of waste at the origin instead of refining or removing the waste already produced. The production/waste management policy proposed in this study will give the chance to protect limited environmental resources by means of environmental sensitive production techniques.

One of the sources of environmental impacts in the industrial production is the manufacturing process, which is simply turning the raw materials into finished products. Among many other options, the production planning and scheduling are the most important factors due to their significance in manufacturing. This study focuses on developing an alternative production planning and scheduling aiming to prevent the production of hazardous materials while increasing the productivity.

Productivity is simply a measurement of an organisation’s ability to turn inputs into outputs. For example, if a worker produces 50 items in a seven-hour shift, the workers productivity (often called labour productivity) is 7,1 units per hour. Industries monitor their productivity closely because productivity, together with innovation and quality of working life, is the major indicator of the organisational performance [3-5].

Since the productivity is due to many different types of input and outputs and working conditions, the measurement methods and tools will vary between sectors. Some of the tools and data collection systems used in productivity measurement are as follows: work measurements determining the time needed to perform a task, flow process charts showing all activities involved in a process, Gantt charts indicating the relative timing of various activities [9].

Organisations develop productivity measures for all factors of production, including people, raw materials, and equipment [1]. If productivity is low, that does not necessarily mean that the labour resource is performing poorly. More likely, the management system is deficient. The system is fair to provide high-quality tools, timely information, equipment, materials, training, designs, technical support, strategic guidance, and proper motivational climate [6].

Increasing the productivity will increase an organisation’s operational capabilities in order to permit an organisation to meet even higher goals in the future [5]. From the standpoint of management, productivity growth is a way to increase profits. As a matter of fact, in some cases increased productivity may be a better way to improve profits than increased sales [7]. That’s why one of the biggest purpose of industrial engineering is to increase manufacturing department’s productivity.

Manufacturing department’s management is generally done by the production planning department. The purpose of production planning is to assure that all resources needed to produce the requires items (determined by the forecast) are at the right place at the right time and in the needed quantities and furthermore, that waste of resources (idle time and overly large inventories of material and product etc.) is minimised [9]. Production planning activity is important due to its ability to maximise the economic utility of a productive system [2]. An integrated production planning and control system includes demand forecasting, operations planning, inventory planning and control, and operations scheduling. Operations Scheduling is the final step in production planning and indicate the starting and completion time of each product’s production. Scheduling seeks to achieve several conflicting objectives: high efficiency, low inventories, and good customer service. Efficiency is achieved by a schedule that maintains high utilisation of labour, equipment, and space. Of course, the schedule should also seek to maintain low inventories, which may lead to low efficiency due to lack of available material or high setup times. Thus, a tradeoff decision in scheduling between setup times and inventory levels is required to increase the productivity of a production system [1,9].

The adjustment of setup times in the production of sequential products is important in production planning and it is usually tried to be minimised in Pinedo (2005). Minimisation of setup time may correspond to reduction of setup wastes for the industries producing sequential products requiring similar production techniques. In that case where setup costs are sequence dependent, the number of waste produced can be held at a minimum level. But this solution may not be relevant for all types of productions. For example in certain cases, the amount of setup waste is constant no matter the sequence of production chosen.

Since the amount of setup waste is determined by quality regulations and is constant, one way of minimising setup waste may be to decrease the number of machine adjustment, which means, changing the production scheduling policy.

The production scheduling policy used in most of the industries is based on a system where monthly demands are divided into short periods in which a predetermined amount of each product is produced. Although this policy is appropriate for the flexibility of the scheduling, it may cause production of abundant numbers of setup waste. The reason of this is that as period of scheduling plan becomes smaller, the number of machine adjustments becomes higher, which in turn increases the number of setup waste. Therefore, the scheduling periods and number of setup waste are inversely proportional.

If longer scheduling periods are chosen, then the production of setup wastes will be decreased but the flexibility of the scheduling will be lost and new costs such as inventory holding costs will appear. On the other hand, if the scheduling period is shortened, then the scheduling will be more flexible and the number of setup waste will increase. For this reason, there is a need to find out an optimum scheduling plan taking into account the waste production.

The objectives of the study are twofold: (i) to show the relation between the production planning and waste generation, (ii) to develop an alternative production plan integrated with waste minimisation.

In the first part of the study, the production planning methods adopted in factories were examined to find out their relations with waste minimisation and waste management. It was noticed that hazardous waste is primarily produced as a result of the machine setup operation in the production line. Whenever a new type of product is produced, machines require an adjustment and certain number of products has to be wasted *(setup waste)* during the pilot run. The formation of setup waste also happens after a two-hour work of the production line.

In the second part, a comprehensive analysis is carried out to determine the optimum scheduling period and its benefits obtained as a result of the application of the optimum scheduling plan in terms of waste and cost minimisation.

2. Company Description

Yiğit Battery, founded to produce Starter Type Batteries in a small workshop in 1976, has become today an international trademark, occupying a total space of 22.500 m^2 in its sized-up plant in Ankara.

Commodities produced by Yiğit Battery are various types of batteries from sealed maintenance calcium batteries to batteries produced using expended metal technologies. Yiğit Battery also supplies different types of semi-finished products like grids of different type and dimensions, raw plates, charged plates as well as lead monoxide.

With its 2200 sales points and well organised service network all around Turkey, Yiğit Battery is now exporting to more than 27 countries around the world. The success of the company is obviously due to the modern technologies used in production and the use of computer integrated equipment. With the company's computer controlled casting machines, it is possible to produce 3.500 kg/band per hour; which is equivalent to 4.500.000 batteries per year.

Another leading reason of the success of the company is the environmental awareness of its qualified employees and the company's strong willing about continuous improvements. Yiğit Battery has been improving its technical substructure, which is necessary for the high quality production, with experienced staff, modern production facilities and equipment [10].

Now having its powerful technical substructure on hand, Yiğit Battery is at a point where the reduction of waste production is one of the targets. The use of the modern machines obviously helps to reduce the amount of waste, but since production involves the use of hazardous materials, it is necessary to consider more effective solutions.

It is necessary to produce two semifinished products while making machine adjustments in assembling and wet charge operations in the production line of a battery. Since those semifinished products are not suitable to be reincluded to the production line, they are considered as "setup wastes" as described in the previous section. Those setup wastes consist of alloyed lead and polypropylene. Lead is a toxic material that causes pollution and deterioration of both human health and environment [3]. Because of the toxic materials they have, Yiğit Battery send its setup wastes to a removal facility in Eskişehir. The transportation and the removal of these wastes create a cost that will be named as waste removal costs in this study.

Since it is difficult and expensive to remove the materials left over or wasted in this sector, the company's aim is to prevent the production of waste as much as possible. A way to prevent those kinds of productions may be to change the production scheduling policy as described in the previous section. The company is using the production scheduling policy giving the highest number of wastes, which means the *One-Week Alternative.*

3. Methodology

The relation between the scheduling period and setup waste amount is established and optimised in this study. Knowing that the number of scheduling period in a month affects the number of setup waste generated, alternatives should be recommended to show the optimum scheduling plan taking into account the waste removal cost and inventory holding costs.

To determine the optimum scheduling period, different scheduling scenarios are analysed. These scenarios are based on a week, two, three and four weeks. Once the first alternative is clarified, then monthly demand is divided to four and one quarter of the demand of each product is produced in each period (one week). The same logic is applied to other alternatives.

Although Yiğit Battery is producing more than fifty types of products, it is decided to consider thirty types of products which are considered as main commodities in this study.

Since demands in some months are close to each other, Yiğit Battery describes those groups of months as “periods”. Therefore, three periods consisting of four months is considered instead of twelve separate months in the computations. The values related to period are computed calculating the average of values of the months considered.

Considering the availability of selling amounts of the year 2005 for each product at each period, it is assumed that those amounts are constant for each year and that they are relevant also for the year elaborated. Therefore, real selling amounts of the previous year are determined to be the real demand of the current year.

To evaluate the four alternatives, monthly demands are firstly divided into the numbers needed to find unit demands of each alternative. The production amount needed is then found out for each product at each period for each alternative.

Computations of the unit demand of product i for each alternative are stated as follows:

- For the *One-Week-Alternative*, monthly demand is divided to 4 and quarter of the production demand must be realised each week. Since the unit production time is one week, it is necessary to repeat this operation four times in a month

$$U_{i,j} = \left(\frac{1}{4} * D_{i,j}\right) \qquad D_{i,j} = \left(\frac{1}{4} * D_{i,j}\right) * 4 \qquad (1i)$$

where i = index showing the type of product, i=1,…,30
j = index showing the period number, j=1,2,3
$D_{i,j} = \text{Demandof producti, in period j}$
$U_{i,j} = \text{Unit Demandof producti, in period j}$

- For the *Two-Week-Alternative*, monthly demand is divided to 2 and one half of the production demand must be realised during the period. Since the unit production time is two week, it is necessary to repeat this operation two times in a month.

$$U_{i,j} = \left(\frac{1}{2} * D_{i,j}\right) \qquad D_{i,j} = \left(\frac{1}{2} * D_{i,j}\right) * 2 \qquad (1ii)$$

- For the *Three-Week-Alternative,* monthly demand is divided into 2 parts: In the first part is three quarter of the demand is produced in three weeks, and in the second part one quarter of the demand is produced in the last week of the month.

$$D_{i,j} = \left(\frac{3}{4} * U_{i,j} + \frac{1}{4} * U_{i,j} \right) \qquad D_{i,j} = U_{i,j} \qquad (1iii)$$

- For the *Four-Week-Alternative*, the total monthly demand is produced in a single period.

$$D_{i,j} = U_{i,j} \qquad (1iv)$$

Having the monthly production quantities of each product for each alternative on hand, it is possible to calculate the number of setup waste derived for each alternative tested. When looking at quality regulations it was found that before starting at a product's production, two setup wastes are produced while machine adjustments are made. Additionally, the production of two setup waste also happens after a two-hour work of the production line.

Calculations for the number of setup waste are made as follows:

- Since it is stated in the quality regulations that setup wastes are produced after two-hour work of the production line, number of products produced in two hours should be taken into account. By observing the production speed of each product, it is possible to determine the number of setup waste per unit production. For example, it is known that 800 units of a certain product are produced in each shift. Considering that a shift is 8 hours, it can easily be said that the speed of production of that product is 100 units / hour. Therefore setup wastes will be produced after 200 units production of this product is manufactured. The same logic is used while computing other products' control periods.

$$K_i = \text{Control Period for Each Product i (units/hour)}$$

$$K_i = \frac{(\text{Shift Capacity})_i}{8} * 2 \qquad (2)$$

- After computing each product's control period, the number of controls made in each production-planning alternative is calculated. For this process, unit demand is divided to the control period and the result is rounded down.

$$N_i = \text{Number of Control Times for Each Product i}$$

$$N_i = \left\lfloor \frac{\mathrm{U_i}}{\mathrm{K_i}} \right\rfloor \qquad (3)$$

- After computing each alternative's control numbers, total waste number is calculated. Two setup waste is produced when the production of a new product is started and at each control time 2 additional setup waste is produced. This circumstance is expressed as: (N_i * 2 +2). This amount is multiplied by the number needed to complete the production planning time to one month (2 * 2 weeks, 4 * 1 week etc.)

$$T_i = \text{Total Waste Produced for Each Product i}$$

For One-Week Alternative: $T_i = (N_i * 2 + 2) * 4$ (4*i*)

For Two-Week Alternative: $T_i = (N_i * 2 + 2) * 2$ (4*ii*)

For Three-Week Alternative: $T_i = (N_i * 2 + 2) * 1$ (4*ii*)

For Three-Week Alternative: $T_i = (N_i * 2 + 2) * 1$ (4*iv*)

Now that setup waste quantities are computed, the total cost can be calculated. The sum of inventory holding cost and waste removal cost will give the total cost. Those costs are calculated as below:

$$Z_i = I_i + W_i$$
$$Z_i = \text{Total Cost of Product i}$$
$$I_i = \text{Inventory Holding Cost of Product i}$$
$$W_i = \text{Waste Removal Cost of Product i} \qquad (5)$$

In the calculation of the inventory holding cost, it is needed to express this cost as the selling price's ratio. Since the inventory holding cost changes due to the time of holding inventories, bank credit is designated as the coefficient showing changes in holding cost. Knowing that bank credit is approximately 20% for one month, we converted this percentage to weeks. The weekly cost of holding inventory is then calculated for each product as

$$P_i = \text{Selling Price of Product i}$$
$$I_i = 0{,}05 * P_i \qquad (6)$$

The waste removal cost is expressed as the function of the selling price. In the case of Yiğit Battery, 85% of the selling price indicates the production price and 20% of the production price denotes the waste removal cost. This cost remains the same for each period and each alternative. Therefore, waste removal cost can be computed as follows:

$$W_i = P_i * 0{,}85 * 0{,}20 \qquad (7)$$

Following the computation of the cost, it is possible to find how much time will take to produce the products, and also how much inventory will be carried for how long.

Since computations of holding inventories and producing wastes are based on weekly units, the hourly calculated production time is converted to weekly production time.

The company's weekly working policy is to work 24 hours during 6 days (1 week=144 hours or 1 hour=1/144 week). Therefore inventory holding cost for each scenario is calculated as follows:

- One-Week-Alternative: *Inventory Holding Cost For One Month*

$$IH_1 = \frac{(0{,}05P_i)\left[(week) - \frac{1}{144}S_i * \frac{1}{4}U_i\right]}{2}4 \qquad (8i)$$

- Two-Week Alternative: *Inventory Holding Cost For One Month*

$$IH_2 = \frac{(0{,}05P_i)\left[(2weeks) - \frac{1}{144}S_i * \frac{1}{2}U_i\right]}{2}2 \qquad (8ii)$$

- Three-Week Alternative: *Inventory Holding Cost For One Month*

$$IH_3 = 0{,}05P_i * (\text{week}) + \frac{0{,}05P_i\left[(3\text{ weeks}) - \frac{1}{144}S_i * \frac{3}{4}U_i\right]}{2} + \frac{0{,}05P_i\left[(\text{week}) - \frac{1}{144}S_i * \frac{1}{4}U_i\right]}{2}$$

(8*iii*)

- Four-Week Alternative: *Inventory Holding Cost For One Month*

$$IH_4 = \frac{0{,}05P_i * \left((4\text{ weeks}) - \frac{1}{144}S_i * U_i\right)}{2}$$

(8iv)

where $IH_a = \text{Monthly inventory holding cost for alternative a}$

and $S_i = \text{production time (hr)}$

4. Results and Discussion

As a result of the calculations, One, Two and Four-Week Alternatives' inventory holding costs are found to be equal and much more less than the Three-Week Alternative's one. Therefore One, Two and Four-Week Alternatives are optimal in terms of inventory carrying costs (Figure 1).

On the other hand, while looking at waste removal costs one can see that Three and Four-Weeks Alternatives are clearly optimal. It is also noticeable that the alternative currently carried out in the company, the One-Week Alternative is, the policy that gives the highest waste (Figure 2).

The results indicate that the Four-Week Alternative is the optimal solution for most of the products. The One-Week Alternative is the policy that gives the highest total cost for each period. This fact is shown in Figure 3.

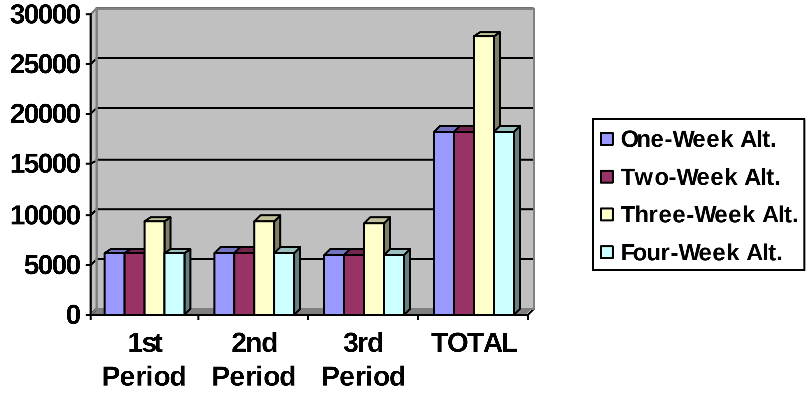

Figure 1. Periodic Representation of Inventory Holding Costs

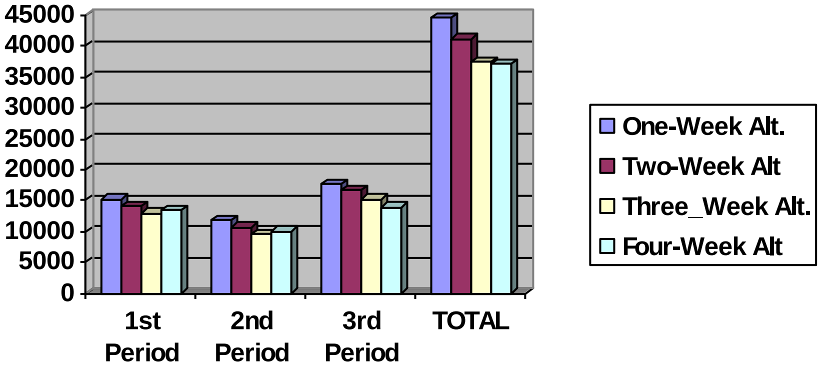

Figure 2. Periodic Representation of Waste Removal Costs

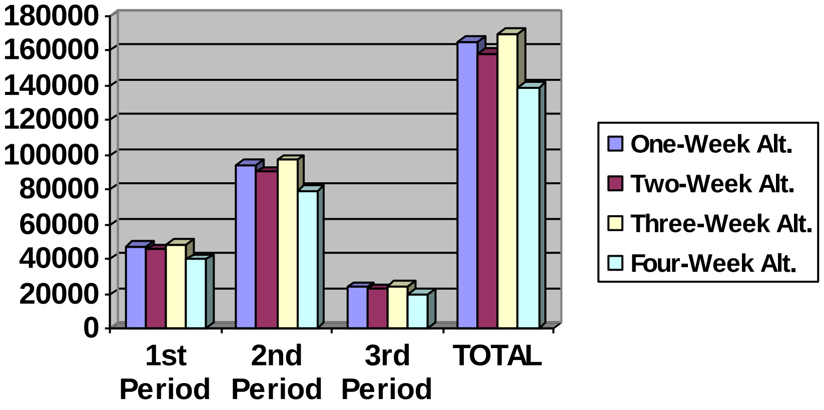

Figure 3. Periodic Representation of Total Costs

In this study, the optimal alternative calculated is the one giving the best solution for both waste removal and inventory carrying. As told in the first section, the lowness of the cost may be an indicator of its low flexibility. The Four-Week Alternative, calculated as the optimal option, is not providing an applicable solution due to its low flexibility. The economic lot size model study done by Wagner and Whitin can be examined and the waste minimisation point of view may be adapted to this model.

The proportion between waste removal and inventory holding costs is a very important factor in the computation of the optimal alternative. If the waste removal costs were higher than the actual one, no matter the inventory carried, the alternative giving the less waste would give the optimal solution. The same logic is true for inventory carrying costs. Therefore it is important to accurately calculate the costs associated to waste production to attain results representing real world.

The approach can be used for different industries using hazardous materials. In the beginning of the pollution prevention study, the production process and machine setup operations must be analysed. After the problem and the work area are defined, setup wastes’ ratio can be calculated from quality regulations or production planning principles. Inventory holding and waste treatment costs should be computed as a final input. After the collection and the calculation of inputs, the algorithm proposed in this study can be applied to find an alternative giving the equilibrium between the waste removal and inventory holding costs.

4. Results and Discussion

One of the biggest problems in production industries is the waste removal. The conspicuous nature of the problem is due to the liability to carry both waste production and waste removal charges. Especially firms working with hazardous materials are aware of the need to find new techniques to handle waste. This paper showed that using production planning optimisation opportunities by taking into account the minimization of waste can be an economical solution of the waste management problem.

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LEVELS OF HEAVY METALS IN WATER AND FISH (*CARASOBARBUS LUTEUS* HECKEL, 1843) WERE SAMPLED FROM GÖLBAŞI LAKE, HATAY, TURKEY.

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Aquatic organisms are widely used to biologically monitor variation in environmental levels of anthropogenic pollutants. Much of the variability in trace metal tissue concentrations in aquatic organisms has been attributed to variability in size and age of individuals, feeding habits and to the season of captured. In this study, seasonal concentrations of some heavy metals such as Ag, Cd, Cr, Cu, Fe, Ni, Pb and Zn were investigated from the water and liver, gills, skin, gonads and muscle of himri (*Carasobarbus luteus* HECKEL, 1843) samples (Gölbaşı Lake, Hatay-Turkey). Samples were analyzed seasonal from September 2003 to June 2004 using Inductively Coupled Plasma Atomic Emission Spectrophotometer. The average levels showed that concentrations of heavy metals in *C. luteus* varied depending of different organs. Generally, liver, gonads and gill tissues showed higher metal accumulations than muscle tissues. The mean highest levels of Ag, Cd, Cr, Fe and Cu are found in the livers, followed by the gills, the skin and the muscles. The mean highest Zn was found in the skin. The values of heavy metals in muscle were lower than the recommended limits for the aquatic products. It may be said that Gölbaşı Lake has not a risk that threats the biological balance for examined metals in study period.

Key words: *Heavy metals, Gölbaşı Lake, Carasobarbus luteus*

1. Introduction

Heavy metals from geological and anthropogenic sources are increasingly being released into natural waters (Nimmo et al., 1998). Under certain environmental conditions, heavy metals may accumulate to toxic concentrations and cause ecological damage (Karadede and Ünlü, 2000). Marine organisms, among them fish, may accumulate heavy metals through direct absorption or via their food chain and pass them to human beings, by consumption, causing chronic or acute diseases (Chen et al., 2000; Calza et al., 2004). The metals bioaccumulation causes biochemical or pathological effects in individual fish, resulting in decrease of growth, fecundity and survival (Al-Yousuf et al., 2000). Heavy metals are taken up through different organs of the fish because of the affinity between them. In this process, many of these heavy metals are concentrating at different levels in different organs at the fish body (Karadede& Ünlü, 2000; Yılmaz, 2003; Henry et al., 2004; Yılmaz, 2005). Therefore fish have been extensively used in marine pollution monitoring programs (e.g., OECD, 1991; UNEP, 1993). Two main objectives are being pursued in these programs, (i) to determine contaminant concentrations in fish muscle in order to assess the health risk for humans, and (ii) to use fish as environmental indicators of aquatic ecosystems quality (Adams, 2002).

The Hatay region of the South-Eastern Turkey is heavily industrialized and considered to have bad environmental qualities (Kargın, 1996; Yılmaz, 2003). The lake Gölbaşı which is located in Hatay region has importance of irrigation and drinking purposes. In the present study, it was aimed to evaluate the pollution level of this aquatic ecosystem via determining the accumulation of Ag, Cd, Cr, Cu, Fe, Ni, Pb and Zn in the water and fish (*Carasobarbus luteus* HECKEL, 1843) samples of Lake Gölbaşı.

2. Materials and Methods

2.1. *Study area*

Gölbaşı Lake is located 50 km from the city of Antakya and 10 km from the city of Kırıkhan. The lake is approximately 6m deep in winter and covering an area of 1200 ha. It is artificial in origin and one of the largest freshwater lake in Hatay. The water of the lake is used for irrigation and drinking purposes. In addition to these, fish species (*Carasobarbus luteus* HECKEL, 1843; *Clarias gariepinus* BURCHELL, 1822) present in this lake.

2.2. Materials

Carasobarbus lutes (Karaman,1971) from the Euphrates in Turkey (Kuru, 2004) is a barbell endemic to the Mesopotamian Rivers. It is also known himri, *Barbus luteus* (Heckel), Beckman (1962) reported its presence in the Orontes River. The selected specie (*C. luteus*) is popular with amateur sport fishermen. This fish is highly valued as it is high demand as food (Hazzaa, 2005). *C. luteus* is herbivorous, feeding on benthic (Barak and Mohammed, 1982; Geldiay and Balık, 1988).

2.3. Sample collection and preparation

Some physico-chemical parameters of Lake Gölbaşı were determined during the sampling period. Dissolved oxygen and temperature were measured by an YSI-52 type oxygen-meter, pH by a Lutron pH-206 model pH-meter. Three surveys were carried out on the selected station (Gölbaşı Lake) in September 2003, January, March and July 2004. Surface water samples were collected in polyethylene bottles (washed deionized water before and after 5% HNO_3 and finally surface water) and acidified by adding 0.5% concentrated nitric acid. At each sampling period, *C. luteus* were caught throw net. Water and fish samples were transported to the laboratory in a thermos flask with ice on the same day. Male (♂) and female (♀) fish were grouped in sex and size. Ten samples were obtained for each season. Total fish length and weight were measured to the nearest millimeter and gram before dissection. For analysis, whole gonads, liver, gills, a bit of skin and approximately 5 g samples of muscle (edible parts) each fish were dissected, weighed and dried at 120 ^{0}C until they reached a constant weight. The separate organs were digested using concentric nitric acid and hydrogen peroxide (1:1) v/v according FAO methods (Yılmaz, 2005). They were evaporated to dry on hot plate then dissolved and diluted to 50 ml with 2.5% of nitric acid. The chemicals used for sample dissolution were analytical grade.

Deionized water was used throughout the study. High purity argon was used as inert gas. All samples were analyzed for Ag, Cd, Cr, Cu, Fe, Ni, Pb, Zn by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), (Varian Model- Liberty Series II). The following absorption lines were used; silver 328. 1 nm, cadmium 228.8 nm, chromium 267.7 nm, copper 324.7 nm, iron 259.9 nm, nickel 231.6 nm, lead 353.2 nm, zinc 213.9 nm. Standard solutions were prepared from stock solutions (Merck, multi element standard). Replicate analysis of the reference material showed good accuracy, with recovery rates for metals between 90-100%. Metal concentrations were calculated in microgram per gram wet weight (µg/g wet wt.). Statistical Analysis of data was carried out with SPSS statistical package program. Oneway ANOVA and Duncan Multiply Comparison Test were used to compare data among seasons.

3. Result and discussion

The physico-chemical parameters determined in Gölbaşı Lake are given in Table 1. According to these parameters, the temperature varied between 17.5 and 23.5 ^{0}C; the pH between 7.1 and 8.4; the dissolved oxygen between 6.8 and 7.9 mgl^{-1}; the hardness 34.4 and 53.6 Fr during the study period in Lake Gölbaşı.

In this research, the heavy metals concentrations (Ag, Cd, Cr, Cu, Fe, Ni, Pb, Zn) in water (Gölbaşı Lake) and in the tissues (liver, gills, skin, gonads and muscle) of *Carasobarbus luteus* HECKEL, 1843 were investigated seasonally between October (2003) and July (2004).
The concentrations of heavy metals in water and fish samples collected from Lake Gölbaşı are given in Tables 2 and 3. In water samples, the average concentrations of Cd, Cr, Cu, Fe and Pb in Lake Gölbaşı were 5.75, 10.25, 52.5, 94.5, 23, 49.5 µgl^{-1}, respectively (Table 2). In Lake Gölbaşı, Fe had the highest concentration and Cd the lowest concentration in water samples. The seasonal concentration in water samples were statistically significant ($p<0.05$). According to the heavy metal concentrations given Table 2, the water of Lake Gölbaşı was included to the second class category and the heavy metal concentrations such as Cu and Pb were found to be above for permissible level of drinking water in international criteria's such as WHO, EU and EPA (USA), but Fe, Cr and Zn concentrations were almost in the permissible levels for drinking.

Table 3 shows sampling months, the mean body weight and total length as well as standard deviations for the himri samples. The metal concentration-size correlations depend on several factors, such as (i) the specific metabolism of the metal in the fish and tissue type considered, (ii) the competition between the opposing effects of ageing and tissue growth and (iii) the availability of the metal in the environment (Evans et al., 1993).

In Table 4, mean heavy metal concentrations (Ag, Cd, Cr, Cu, Fe, Ni, Pb, Zn) and their standard deviations for *C. luteus* tissues (liver, gill, skin, muscle and gonads) samples are presented. The heavy metal accumulations in *C. luteus* were determined on wet basis. Some metals (Ag, Cd and Ni) were below the limits of detection in some seasons. According to these data, iron has the highest concentration, followed by zinc, copper and chromium.
As in other studies (Canlı et al., 1998; Karadede & Ünlü, 2000; Henry et al., 2004; Yılmaz, 2005), we observed higher levels of metals in liver and gonads than in the muscle tissues. Target organs, such as liver, gonads, kidney and gills, have a tendency to accumulate heavy metals in high values, as shown in many species of fish in different areas (Kargın, 1996;

Yılmaz, 2003; Abdel-Moniem et al., 1994). It is generally accepted that muscle is not an organ in which metals accumulate (Legorburu et al., 1988). Similar results were reported from a number of fish species showing that muscle is not an active tissue in accumulating heavy metals (Karadede and Ünlü, 1998; Karadede and Ünlü, 2000, Ünlü et al., 1994; Kargın and Erdem, 1991). Skin is not much studied in previous works, although it is a consumed part of the fish. Yılmaz (2003 and 2005) indicated that concentrations of heavy metals were higher in all of the skin samples than in muscles. The present results indicate that the lower concentrations of the heavy metals were usually recorded in muscle rather than the skin and gill while the higher values were recorded in the gonads and liver for all seasons. The concentrations of metals of the gill reflect the concentrations of metals in the waters where the fish live; whereas, the concentrations in liver represent storage of metals (Rao & Padmaja, 2000). The differences in concentrations are at least one order of magnitude and originate from differences in physiological functions of muscle and liver (Henry et al., 2004). Thus, the liver is often recommended as a target tissue when monitoring metal concentrations in aquatic environments.

The lowest and highest iron concentrations were found to be 82.64-355.75 μg g^{-1} in liver, 28.65-72.86 μg g^{-1} in gill, 11.47-57.43 μg g^{-1} in skin and 19.9-48.02 μg g^{-1} in gonads, respectively. Our iron values in liver were higher than those detected *C. luteus* in Atatürk Dam Lake (Karadede&Ünlü, 2000). The concentrations of Fe obtained in gill and muscle in present study were lower than those given for *C. luteus* from Atatürk Dam Lake (Karadede et al., 2004). Iron is present in soil, water and the atmosphere, and its compounds occur in several industrial processes. It participates in hepatic process, and is also associated with haemoglobin through oxygen transportation (Calza et al., 2004).
Table 1

Some physico-chemical parameters of Lake Gölbaşı

Table 1

	TurkishEnvironmental Guidelines			October (2003)	January(2004)	April (2004)	July (2004)
	Class I	Class II	Class III				
Temperature(C^0)	25	25	30	21,30	17,50	18,20	23,50
D.O. (mg/L)	8	6	3	7,20	7,90	7,85	6,80
pH	6,5-8,5	6,5-8,5	6-9	8,40	7,07	7,09	7,51
Hardness (Fr)	<10	10-22	22<	36,30	53,60	34,40	39,20

Table 2

Mean heavy metal concentrations and their standard deviations (Mean ± S.D) of Lake Gölbaşı for four seasons (concentration unit is in mgl^{-1}) and Turkish Environmental Guideline (µgl^{-1}).

Metals	Turkish Environmental Guidelines (µgl^{-1}) (1998)			SEASONS				
	Class I	Class II	Class III	October (2003)	January (2004)	April (2004)	July (2004)	Average Conc. ((µgl^{-1})
Ag				-*	-	-	-	-
Cd	3	5	10	0,002±0,01 ^{b**}	0,002±0,05 ^{b}	0,001±0,05^{a}	0,018±0,02^{c}	5.75
Cr	20	50	200	0,003±0,09 ^{a}	0,004±0,01 ^{a}	-	0,034±0,04 ^{b}	10.25
Cu	20	50	200	0,038±0,07 ^{a}	0,039±0,01 ^{a}	0,037±0,02 ^{a}	0,096±0,03 ^{b}	52.5
Fe	300	1000	5000	0,082±0,06 ^{a}	0,111±0,19^{b}	-	0,090±0,05^{a}	94.5
Ni	20	50	200	-	-	0,013±0,32	-	-
Pb	10	20	50	0,039±0,35^{b}	0,033±0,21^{b}	0,015±0,04 ^{a}	0,005±0,03 ^{a}	23
Zn	200	500	2000	0.037±0,02^{a}	0,065±0,07^{b}	0,043±0,06^{a}	0.053±0,035^{b}	49.5

*: Not detected

**: Means in the same line with different superscripts were significantly different (P<0,05) between the seasons.

Table 3

Sample characteristics (The sampling seasons, number of specimens, female and male, average wet weights and total lengths of *Carasobarbus luteus* HECKEL, 1843 were measured^{a})

Seasons	n	♂/♀	L± S.D			W± S.D		
			Min.	Max.	Ort.±Sd*	Min.	Max.	Ort.±Sd
October (2003)	--*	--	--	--	--	--	--	--
January (2004)	10	4/6	19,20	22,40	20,56±0,57	96,10	120,15	107,58±4,98
April (2004)	10	6/4	16,90	20,90	18,58±0,74	43,75	70,50	52,97±4,59
July (2004)	10	8/2	18,80	23,30	20,56±0,83	84,24	130,05	106,48±9,12

^{a} number of fish (n); (♂) male and female (♀); L- mean total length (cm); W - mean body weight (g); S.D.- standard deviation; * no sample.

Table 4

Mean concentrations (µg metal.g^{-1}w.w.) and associated standard deviations (Mean±S.D) of heavy metals (Ag, Cd, Cr, Cu, Fe, Ni, Pb and Zn) in the liver (L), gill (G), skin (S), muscle (M) and gonads (O) of *Carasobarbus luteus* collected for four seasons in the Lake Gölbaşı.

Heavy Metals	Tissues	October (Mean±S.D)*	January (Mean±S.D)	April (Mean±S.D)	July (Mean±S.D)
Ag	L	--***	-	1,14±0,32*	-
	G	--	0,09±0,08 ^{a**}	0,78±0,28^{b}	-
	S	--	-	0,59±0,07	-
	M	--	-	0,20±0,05	-
	O	--	0,93±0,29 ^{a}	0,65±0,64 ^{a}	-
Cd	L	--	-	-	1,24±0,26
	G	--	-	-	1,33±0,14
	S	--	-	-	1,14±0,40
	M	--	-	-	0,09±0,01
	O	--	-	-	-
Cr	L	--	2.65±0,27^{a}	-	2,26±0,31^{a}
	G	--	0,81±0,47^{c}	0,09±0,08 ^{a}	2,92±0,37^{b}
	S	--	0,14±0,08 ^{a}	-	2,48±0,85 ^{b}
	M	--	0,06±0,02 ^{a}	-	0,86±0,11 ^{b}
	O	--	2,28±0,89 ^{a}	1,36±0,57 ^{a}	0,91±0,29 ^{a}
Cu	L	--	35,45±7,52^{a}	25,73±9,6^{a}	40,59±25,4 ^{a}
	G	--	10,83±5,66 ^{a}	10,79±12,2 ^{a}	6,45±3,54 ^{a}
	S	--	10,94±16,7 ^{a}	10,46±14,1 ^{a}	3,33±0,93 ^{a}
	M	--	4,55±1,23^{ab}	4,79±1,70 ^{b}	2,68±1,06 ^{a}
	O	--	7,78±1,55 ^{a}	9,16±2,00 ^{a}	9,47±1,89 ^{a}
Fe	L	--	355,75±28,9^{b}	218,52±27,2^{ab}	82,64±27,3 ^{a}
	G	--	28,65±6,15 ^{b}	72,50±50,4 ^{a}	72,86±24,7 ^{a}
	S	--	57,43±3,56 ^{b}	23,72±4,33 ^{a}	11,47±3,18 ^{a}
	M	--	18,51±10,3 ^{b}	8,70±3,90 ^{a}	7,58±0,89 ^{a}
	O	--	42,56±3,58 ^{b}	48,02±5,73 ^{b}	19,9±7,35 ^{a}
Ni	L	--	3,97±4,26	-	-
	G	--	3,49±4,91	-	-
	S	--	0,39±0,46	-	-
	M	--	0,44±0,26	-	-
	O	--	0,69±0,11 ^{ab}	1,39±0,41 ^{b}	0,35±0,08 ^{a}
Pb	L	--	-	0,47±0,41^{b}	0,23±0,15^{ab}
	G	--	-	-	0,36±0,24
	S	--	0,36±0,27 ^{a}	0,28±0,18 ^{a}	0,34±0,24 ^{a}
	M	--	0,02±0,03 ^{a}	0,20±0,16 ^{b}	0,07±0,03 ^{a}
	O	--	1,04±0,17 ^{a}	2,11±0,89 ^{a}	1,35±0,26 ^{a}
Zn	L	--	66,44±20,1^{b}	37,73±14,6^{ab}	17,40±10,54 ^{a}
	G	--	29,21±7,89^{b}	15,07±4,10^{a}	11,65±6,94^{a}
	S	--	83,34±10,6^{a}	177,83±71,6^{b}	74,12±40,7^{a}
	M	--	8,45±0,73^{b}	13,06±4,30^{c}	4,68±0,46^{a}
	O	--	62,86±15,84 ^{a}	48,82±16,41 ^{a}	50,83±24,99 ^{a}

(Mean±S.D)* Mean concentrations (µg metal.g^{-1}w.w.) and associated standard deviations
** Means in the same line with different superscripts were significantly different ($P<0.05$) between the seasons.
*** N.D = Not detected..

Mean Zn content of different tissues varied from 4.68 to 177.83 µg g^{-1} in *C. luteus*. Our results of Zn in the samples of muscle were similar to these reported in fish tissue from Atatürk Dam Lake (Karadede&Ünlü, 2000; Mendil et al., 2005) higher than those detected fish species (Calza et al., 2004). However, the mean highest Zn was found in the skin. The highest concentration of Cu was observed in liver (40.59 ±25.4). Considering all tissues investigated, and the average of concentrations, Cu accumulation follows the sequence: liver>gill>gonads>skin>muscle. Cu and Zn are essential elements and are carefully regulated by physiological mechanism in most organisms (Eisler, 1988). However, they are regarded as potential hazards that can endanger both animal and human health. Knowledge of their concentrations in fish is therefore important both with respect to nature management and human consumption of fish (Amundsen et al., 1997).

The seasonal variations observed in the heavy metal load of the himri lead back to changes in the feeding rate, as well as the lipid dynamics of tissues and the growth of fish (Farkas et al., 2003). Season may influence body burdens of heavy metals. This seasonal variability may result from either internal biological cycles of the organism or from changes in the availability of the metals in the environment of the organism. The present study shows a significant seasonal variation ($p<0.05$) in the concentration of the studied metals in the selected tissues, except gonads ($p >0.05$).

Muscle is commonly analyzed because it is the main fish part consumed by humans and is implicated in health risk. The European Community (EC, 2001) proposed threshold values of metal concentrations in fish muscle only for nonessential metals (0.05 for Cd and 0.2 for Pb µg metal.g^{-1}w.w.) The permissible limits proposed by the FAO, WHO and Turkish legislation established the following maximum levels for the metal studied, above which consumption is not permitted: 0.1 µg g^{-1} for Cd, 5 µg g^{-1} for Cu, 50 µg g^{-1} for Zn and 0.5 µg g^{-1} for Pb (FAO/WHO, 1989; WHO, 1993; Institute of Turkish Standards for food (ITS,2000). The concentrations of these metals in the muscle of *C. lutes* were lower than the ITS establish maximum levels. The metal with the concentration in muscle closest to the legal limit was Cu.

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IMPACTS OF SOLUTION PH ON ARSENIC REMOVAL BY NANOFILTRATION AND TIGHT-ULTRAFILTRATION MEMBRANES

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In order to comply with the new arsenic standards (10 µg/L for the USA, 50 µg/L for the South Korea), numerous studies have been undertaken to develop novel treatment technologies for the removal of arsenic from surface and groundwaters. In this study, the impacts of solution pH on the rejection of arsenite [As(III)] and arsenate [As(V)] in synthetic model solutions (deionized water, DI) by nanofiltration (NF) and tight-ultrafiltration (TUF) membranes were investigated through a series of bench-scale experiments. For all experiments, test solution temperature, cross-flow, and permeate flowrate were consistently maintained at 25 °C, 400 mL/min, and 4.5 mL/min, respectively. The tested pH values were 6, 8 and 10. Concentrations of As(III) and As(V) in separate feed solutions were 250 µg/L. As(III) and As(V) concentrations were measured by inductively coupled plasma–mass spectrometry (ICP/MS). The rejection of both As(III) and As(V) increased with increasing pH from 6 to 10 for both membranes tested. The rejection of As(III) was affected by its charge valency in solution. It was found that both As(III) and As(V) rejections by NF membrane were higher than those by TUF membrane at all pH values. Furthermore, As(V) rejections were consistently higher than As(III) rejections for both membrane types. Higher removal efficiencies of As(V) by the NF membrane than the TUF membrane show the importance of size exclusion for As(V) rejections. Results overall indicated the additional benefit of size exlusion over charge exclusion for the removal of arsenic species from waters by the membrane processes. Apparently, the redox conditions and the pH of waters affect the distribution of arsenic species, thus their rejections by high-pressure membrane processes.

Keywords: Arsenic, Nanofiltration, Ultrafiltration, Water

1. Introduction

Various industries and natural activities are the major contributors to arsenic contamination in drinking water (Saitua *et al.*, 2005). Arsenic exists naturally in rocks, soils, water and sedimentary deposits, air, and biota (Ergican *et al.*, 2005, Gecol *et al.*, 2004). The concentration of arsenic in soil and on the earth's crust range between 0.1-8,000 mg/kg and 1.5-5 mg/kg, respectively (Ergican *et al.*, 2005). The interactions between water and geographic compositions, atmospheric precipitation, soil erosion and leaching, volcanic emission, agricultural runoff, and industrial effluents contribute to the release of arsenic into the aquatic systems. Figure 1 shows the input of arsenic into waters, and the global arsenic cycle (Shih, 2005). The concentrations of arsenic range 0.2–264 ppb in rivers, 0.38–1000 ppb in lakes, 1–1000 ppb in groundwaters, and 0.15–6 ppb in seawaters (Gecol *et al.*, 2004). Many factors influence the concentration of arsenic in the natural environment, such as organic and inorganic components of the soils, as well as redox potential status (Shih, 2005). High arsenic concentration in water resources increases the treatment cost and the expenses related to its effect on human health, animals, and crops (Gecol *et al.*, 2004).

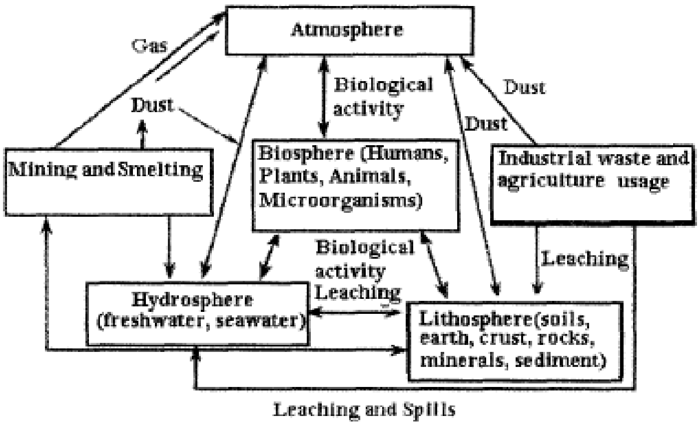

Figure 1. The global arsenic cycle (Shih, 2005).

Arsenic exists in a variety of inorganic forms and oxidation states in water (Ergican *et al.*, 2005). Since the speciation of arsenic is controlled by both acid/base and oxidation/reduction chemistry, various arsenic species may be present in natural waters (Brandhuber and Amy, 2001). In general, the trivalent form, arsenic (III) species are dominant under relatively reducing conditions while the pentavalent form, arsenic (V) species are dominant under relatively oxidizing conditions. Depending on redox condition, pH range, presence of complexing ions and the microbial activity of the environment, As (V) species may exist as arsenic acid (H_3AsO_4) and arsenate ions ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}). Similarly, As (III) species may be present as arsenious acid (H_3AsO_3) and arsenite ions ($H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}) (Ergican *et al.*, 2005, Gecol *et al.*, 2004) (Fig. 2). At typical pH values in natural waters (pH 5–8), As (V) exists as anions while As (III) remains as a neutral molecule. Pentavalent arsenic has a negative charge over pH 9.2 (Sato *et al.*, 2002, Brandhuber and Amy, 1998). Both dissolved As(V) and As(III) species have been found to simultaneously exist in many contaminated groundwaters. It is believed that arsenate is the major water-soluble species in groundwaters, and there is increasing evidence indicating that arsenite might be more prevalent than has been previously understood since groundwater is often reducing (negative Eh value). Pentavalent arsenic species are generally dominant in surface waters (Shih, 2005).

Arsenic contamination in drinking water has been reported in many parts of the world including Argentina, Australia, Bangladesh, Chile, China, Hungary, India, Mexico, Peru, Thailand, and the United States of America. Arsenic due to its toxicity may cause serious problems to human health (Ergican *et al.*, 2005). Arsenic is known as a carcinogen that causes skin cancer and various internal cancers. The International Agency for Research on Cancer (IARC) classified inorganic arsenic compounds as skin and lung (via inhalation) carcinogens that also have multitude of non-cancer effects. Inorganic arsenic is more toxic than organic arsenic, and arsenite is more toxic than arsenate (Sato *et al.*, 2002). Due to the long-term toxicological and carcinogenic effects of arsenic in drinking water, the United States Environmental Protection Agency (US EPA) reduced the maximum contaminant level (MCL) for arsenic in drinking water from 50 µg/L to 10 ppb in January 2001 (Saitua *et al.*, 2005, Ergican *et al.*, 2005, Gecol *et al.*, 2004, US EPA, 2001). The World Health Organization (WHO) has established a provisional arsenic limit of 10 µg/L because of the epidemiological evidence of arsenic carcinogenicity (Saitua *et al.*, 2005 , WHO, 2004).

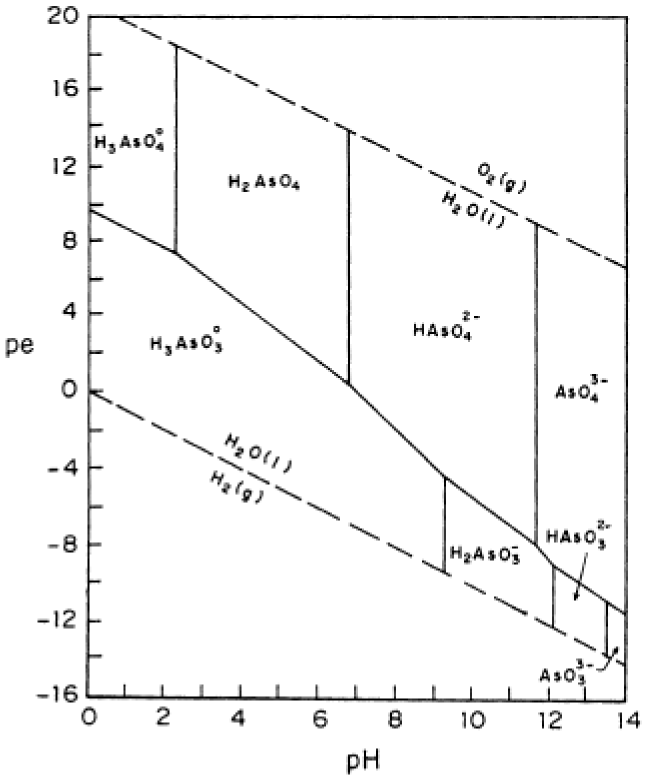

Figure 2. pe–pH diagram of arsenic in water at 25 °C (Kumaresan and Riyazuddin, 2001).

A variety of treatment processes have been developed and used for arsenic elimination from water, including coagulation (precipitation), adsorption (by iron oxide-coated sand, natural iron ores, manganese greensand, etc), ion exchange, membrane filtration, electrocoagulation, biological processes, high gradient magnetic separation (Kosutic *et al.*, 2004, Song *et al.*, 2006, Floch and Hideg, 2004). Arsenate ions can be more easily removed from water than arsenite ions with conventional arsenic removal processes (i.e., chemical precipitation, adsorption, ion exchange, and membrane filtration). Developments in membrane technology have produced nanofiltration (NF) membranes with higher selectivity and increased water flux at much lower operating pressures. In addition, as arsenic is typically present in natural waters as a divalent oxyanion ($HAsO_4^{2-}$), there has been much interest in the use of NF membranes which are known to be quite effective at removing divalent ions (Saitua *et al.*, 2005, Vrijenhoek and Waypa, 2000, Urase and Yamamoto, 1998). Thus, the main objective of this study was to investigate the effectiveness of NF and tight-ultrafiltration (TUF) membranes for removal of As(III) and As(V) at different pH levels.

2. Methodology

Single solute model solutions were used in this study. Arsenite and arsenate standard solutions were prepared by dissolving primary arsenic trioxide (As_2O_3) (Aldrich) and sodium salt hyptahydrate ($Na_2HAsO_4.H_2O$) (Aldrich) in deionized water, respectively. Hydrochloric acid (Merck) and sodium hydroxide (Duksan) were used to adjust pH. Arsenite and arsenate were analyzed using Agilent 7500ce inductively coupled plasma-mass spectrometer (ICP/MS). All water samples were analyzed without dilution. Stock solutions containing arsenic were prepared at fixed concentrations of 1, 5, 10, 25, 50 and 100 ppb.

A laboratory scale cross flow membrane test unit was used for all the experiments. The membrane test unit system was capable of providing pressures up to 1000 kPa and a maximum crossflow of 1.5 L/min. Mono-tech Eng. Com. Circulator MCH-011 D and PolyScience KR-50 A were used to control temperature. A digital flowmeter (Optiflow 1000, Agilent) was used to measure permeate flowrate. In all the experiments the test solution temperature, crossflow velocity and permeate flowrate were consistently maintained at 25 °C, 400 mL/min, and 4.5 mL/min, respectively. Concentrate and permeate were returned back to the feed tank. For all sets of experiments, membranes were operated for 2 hours with DI water for stabilization. All measurements were performed in parallel. Reported removals are the averages of the parallel measurements. A NF (NE 70, Saehan, Korea) and a TUF (GM, Desal. Osmonics, USA) membrane was used in this study. The membrane properties are listed in Table 1, and Figure 3 shows the results of the zeta potential of membranes. To investigate the removal efficiencies of arsenite and arsenate as a function of pH for each membrane, 250 μg/L of arsenite and 250 μg/L arsenate solutions were filtrated for 1 hour at pH 6, 8 and 10. At the end of the 1-hour filtration, samples were taken from the permeate.

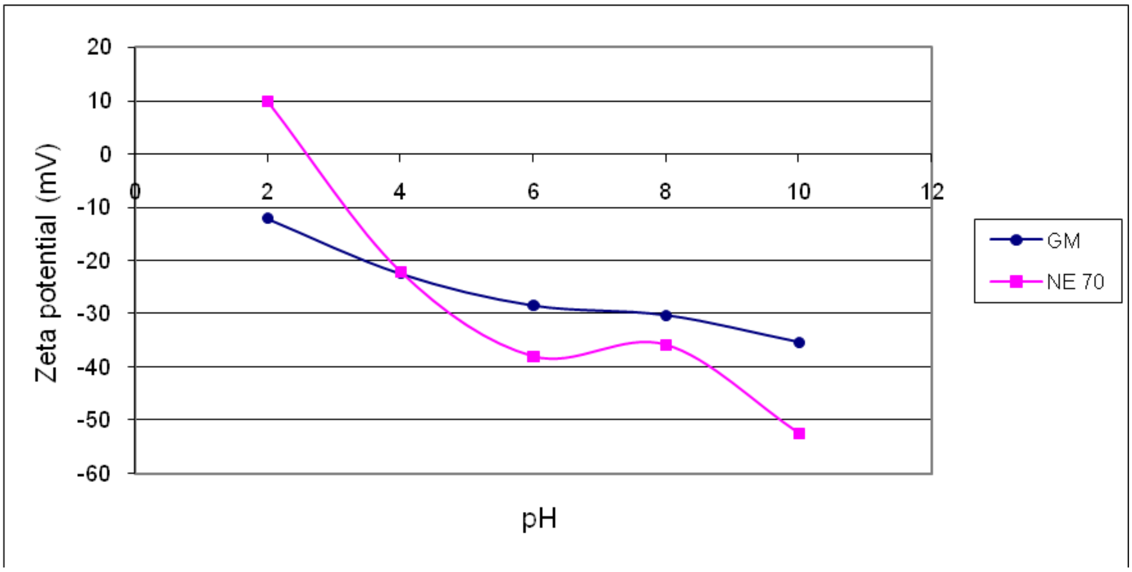

Figure 3. Zeta potential of membranes

Table 1. Membrane properties

Membrane	**Material**	**MWCO[1] (Da)**	**Zeta Potential (mV) at pH 6**	**PWP[2] (L/d-m^2-kPa)**
TUF (GM)	Polyamide TFC	8000	-28.42	3.20
NF (NE 70)	Polyamide TFC	350	-37.95	2.46

[1] MWCO = Molecular weight cut-off
[2] PWP = Pure water permeability

3. Results and Discussion

The removals of As(III) and As(V) by both membranes at different pH values are shown in Table 2. While As(III) concentrations in permeate samples ranged between 92 and 160 ppb for the NE 70 membrane, such range was 122-159 ppb for the GM membrane. Removals were much higher for As(V); permeate As(V) concentrations as low as 5 ppb were achieved by the NE 70 membrane. The rejection of solutes by NF membranes is a rather complicated phenomenon mainly influenced by two basic membrane characteristics, membrane charge and membrane pore size. These characteristics control two main solute retention mechanisms, charge exclusion and size exclusion. Charge exclusion is caused by electrostatic interactions between a charged membrane and charged species from the permeated solution, and size exclusion or sieving is based on the relation between the pore size and the size of permeating particles. A highly charged membrane is able to exclude ions better, particularly co-ions, and a membrane with smaller pores is able to retain the uncharged solute molecules better (Kosutic *et al.*, 2004). Consistent with these mechanistic theories, the rejections of As(V) were always higher than those of As(III) for both membrane types and at each pH.

Table 2. Removals of As(III) and As(V) by both membranes at different pH levels (initial As(III) and As(V) concentrations were 250 ppb).

Membrane Type	**pH**	**As(V)**		**As(III)**	
		Permeate Conc. (ppb)	**% Removal**	**Permeate Conc. (ppb)**	**% Removal**
NE 70	6	11.3	95	159.1	36
	8	11.4	95	159.9	36
	10	5.2	98	92.3	63
GM	6	65.0	74	159.4	36
	8	36.5	85	157.5	37
	10	15.0	94	122.5	51

Figure 4 and 5 show the rejections of As species at tested pH values by the NF and TUF membranes, respectively. The rejection of As(III) by the NF membrane increased with pH, from 36% at pH 6 to 63% at pH 10. Similarly, the rejection of As(III) by the TUF membrane also increased with increasing pH. The percent rejections of As(III) were about constant (36%) at pH 6 and 8, independent of the membrane type. On the other hand, at pH of 10, As(III) rejection was higher by the NF membrane (63%) than the TUF membrane (51%). This result is expected since while most of the As(III) is in the monovalent anion form at pH of 10, neutral As(III) species dominate at pH of 6 and 8, given that the pKa of arsenite is 9.1 (Urase and Yamamoto, 1998). Thus, the rejection of As(III) is strongly affected by its charge valency in the solution.

Similar to the results obtained for As(III) species, the rejections of As(V) also increased with increasing pH for both membrane types. For the NF membrane, the impact of pH was minimal; As(III) rejection increased from 95% at pH 6 to 98% at pH 10. For the TUF membrane, such increase was from 74% to 94%. Apparently, the positive impact of increasing pH on rejections was less pronounced for arsenate species having higher charge valency than arsenite species. Furthermore, higher rejections of As(V) by the NF membrane at each pH indicated that the importance of size exclusion mechanism for As(V) species. However, for the TUF membrane having larger pore size, charge exclusion is also effective for As(V) rejection, given the fact that rejections increased with increasing solution pH. At all pH values, both As(V) and As(III) rejections were generally higher by the NF membrane than the TUF membrane, further highlighting the additional benefit of size exlusion over charge exclusion.

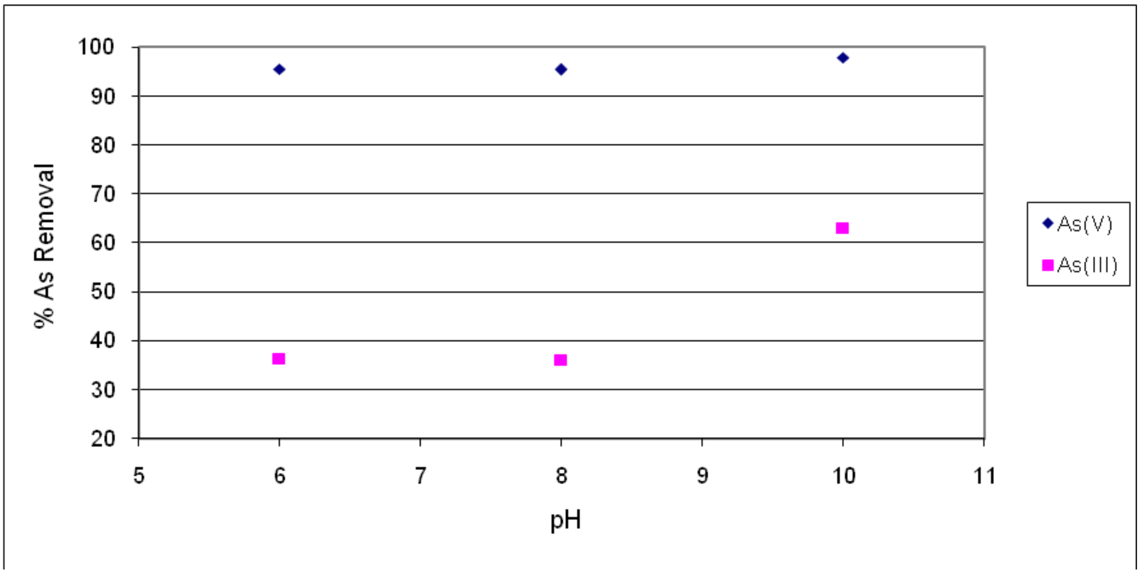

Figure 4. The rejections of As(III) and As(V) by the NF (NE 70) membrane.

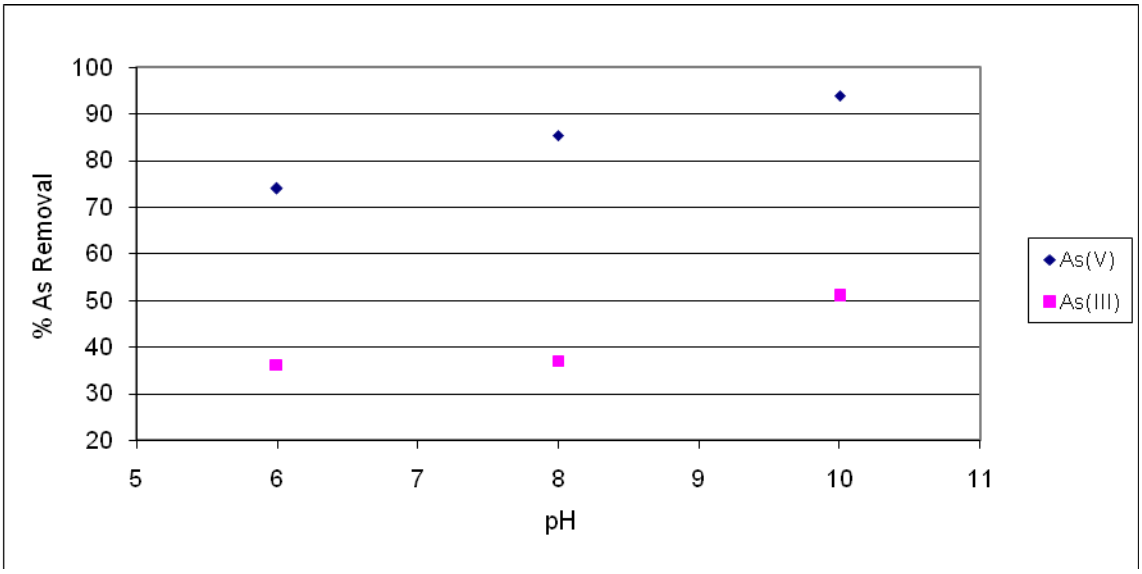

Figure 5. The rejections of As(III) and As(V) by the TUF (GM) membrane.

4. Conclusions

The rejection of As(III) by the NF membrane increased with pH, from 36% at pH 6 to 63% at pH 10. Similarly, the rejection of As(III) by the TUF membrane increased with increasing pH. While the rejections of As(V) also increased with increasing pH for both membrane types, the positive impact of pH was less compared to As(III). For the NF membrane, As(III) rejection increased from 95% at pH 6 to 98% at pH 10. For the TUF membrane, such increase was from 74% to 94%. The rejections of As(V) were always higher than those of As(III) for both membrane types and at each pH. Both As(V) and As(III) rejections were generally higher by the NF membrane at each pH. Results overall indicated the additional benefit of size exlusion over charge exclusion for the removal of arsenic species from waters by the membrane processes.

5. Acknowledgments

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NONDESTRUCTIVE TEST TO TRACK POLLUTANT TRANSPORT INTO LANDFILL LINERS

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Since the beginning of the eighties, waste disposal has become a particularly sensitive issue. This led to the development of new legislation in the international law, which resulted in new regulations concerning landfill liner design. Algeria, as many countries in the world, faces serious environment threats like domestic and hazardous waste disposal. To limit these threats, the creation of controlled landfills is necessary. These landfills prevent the pollution of groundwater using impermeable base and side liners.

hydraulic conductivity of the liner material in order to reduce flow rates. This approach is simplistic and does not consider the effect of diffusion of chemical solutes through liner, witch can occur at significantly faster hydraulic flow rates.

Traditional methods of liners charactrisation involve soil sampling and chemical analysis, which are costly, destructive and time-consuming process. New techniques are being investigated to provide non-destructive, liners characterisation.

This paper describes the recent development in landfills. Particular emphasis is stressed on new legislation to design safe landfills and several types of natural or engineered liners. The interrest on this work to evaluate the potential application of electrical conductivity to track ionic movement through landfill liners. The effect introduced on the mesured of the electrical conductivity by frequency, degree of saturation, electrolyte type and it's concentration.

Key words : *landfill, diffusion, electrical conductivity, transport.*

1. Introduction :

Clay plays an important role in negating the movement of contaminants from landfill sites when used as bottom or slope lining. Current practice in landfill liner design is to minimise the hydraulic conductivity of the liner material in order to reduce flow rates. This approach is simplistic and does not consider the effect of diffusion of chemical solutes through the liner, which can occur at significantly faster hydraulic flow rates. Moreover, the flow conditions within the liner can be further complicated by the effects of coupled flow caused by the combination of hydraulic, chemical and even thermal gradients. Little information is available to assist in evaluating which flows, or combination of flows, are significant for a given set of circumstances. The critical parameter in liner design is the time for contaminant breakthrough and to ensure that this is less than that of the design life of the liner.

In order to collect relevant data to produce liner specifications, their long-term performance should be studied preferably using in situ, nondestructive, monitoring techniques. The alternatives are to excavate sections of the liners (which must be replaced) or to construct purpose built test sites. Previous studies have shown that electrical conductivity can be used to describe particle alignment. Previous studies have shown that electrical conductivity can be used to describe particle alignment during consolidation (Blewett et al., 2001). This particle alignment, or tortuosity, will also define the flow characteristics of the deposit either under hydraulic, electrical, thermal or chemical gradients or any combination of these. It is set against this background that the current work presents laboratory studies on the application of electrical conductivity techniques to monitor diffusive driven ionic migration within saturated (sand + bentonite clay). The advantage of conductivity measurements is that they are relatively straightforward to make in terms of accuracy and instrumentation required McCarter and Desmazes, (1997) ; Blewett et al., (2001). Ultimately, a simple approach is preferred such that the technology can readily be transferred to field monitoring systems, although certain technical issues must be resolved regarding electrical measurements and are discussed below.

The electrical conductivity of soils arises from the motion of ions, which are displaced from their original position by an applied electric field. The most relevant works related to the electrical conductivity for different soils in the frequencies of interest here have been presented by Smith-Rose (1933, 1935), Mitchell and Arulanandan (1968), McCarter (1984), Shang et al. (1995) and Abu-Hassanein et al. (1996). From these works, the reported factors that affected electrical conductivity in soils and rocks are: void ratio, degree of saturation, soil structure and fabric, salt concentration of the pore fluid. The aforementioned parameters also have a significant influence on the mechanical and physical behavior of compacted soils. Thus, McCarter (1984) and Abu-Hassanein et al. (1996) Discussed the potential application of electrical conductivity to evaluate soil compaction. In general, for a given soil, a good correlation between electrical conductivity and volumetric water content was found. Yet, the relationship between electrical conductivity and degree of saturation was observed not to be unique, except at large water contents where the conductivity of soils can be considered independent of the compaction energy (McCarter 1984). Only for some soils, a good correlation between hydraulic and electrical conductivity was found (Abu-Hassanein et al. 1996). According to the knowledge of the writers, little attention has been given to the influence of salt type and concentration in pore water and soluble salts in the soils on the electrical conductivity of soils. In this aspect, Mitchell and Arulanandan (1968) Showed that these parameters have a significant effect on the electrical conductivity of sodium kaolinite. Furthermore, Sen et al. (1988) attribute the observed nonlinear relationship between the conductivity of clay bearing sandstones and the conductivity of the pore fluid to saline concentration. Monitoring compaction using electrical methods is advantageous since control in the field can be performed from the surface to any depth by working with different electrode separations when any of the four-electrode configurations is adopted. On the other hand, according to the experience of the writers, measurement of conductivity is fast and little data processing is required in order to obtain accurate and repeatable results.

The purpose of this work is to present a fundamental laboratory study about the ohmic conductivity of a compacted sand bentonite clay to evaluate the potential application of the electrical methods for monitoring track ionic movement through landfill liners by diffusion. Thus, a large number of samples were compacted at maximum dry density with optimum moisture content and different concentrations of sodium chloride electrolyte. Electrical conductivity was measured in a two-electrode cell in the frequency range of 5 Hz to 550 kHz. The effects of frequency and electrode polarization on the measured electrical conductivity are discussed. Thus, the influence of soluble salts in soil conductivity was studied.

2. Literature review :

The practice of compacted clay liners (CCL) started in the last three decades Daniel, (1993). Since then, a large number of landfills have been constructed worldwide. Based on the performance of the constructed facilities and extensive research, standard specifications were proposed for design and construction of new facilities. Because a leakage from a landfill liner can cause adverse and harmful impact on the environment, strict specifications are imposed on the selection of a liner material, design and construction of the compacted clay liners. The compacted clay liner must have a low hydraulic conductivity to control leachate from the waste Mitchell et al., (1995). The hydraulic conductivity must not increase due to chemical and biological attack from waste leachate. Furthermore, the CCL must be designed to accommodate the landfill settlement and have sufficient shear strength to resist bearing capacity and slope failures. Soils that possess the properties shown in Table 1 will generally satisfy the above requirements Daniel, (1993); Rowe et al., (1995).

Natural clays usually satisfy the above requirements; however, highly plastic clays that desiccate are not preferable because the desiccation cracks can increase the amount of leachate. Also, the hydraulic conductivity of some clays that contain active clay minerals such as montmorillonite can increase drastically if the soil is permeated with chemical solutions due to the relatively high reactivity of these clay minerals Stern and Shackelford, (1998). The hydraulic conductivity of clays containing less reactive clay minerals such as kaolinite, illite and attapulgite (palygorskite) were found to be unaffected by chemical solutions Stern and Shackelford, (1998); Broderick and Daniel, (1990).

3. Diffusive transport in soil :

For uniaxial, diffusive driven flow into a semiinfinite, isotropic medium, Fick's second law for nonreactive solutes

$$\frac{\partial c}{\partial t} = D^{*} \frac{\partial^{2} c}{\partial x^{2}} \qquad (1)$$

where, D* is the effective diffusion coefficient, C is the concentration of the ionic species under study, t is
time and x is the depth. The solution to Eq. (1) is (Crank, 1979),

$$\frac{C}{C_0} = erfc\left[\frac{x}{2\left(D^{*}t\right)^{1/2}}\right] \qquad (2)$$

C_0 : Concentration of non reactive solute; C corresponding concentration et time t and location x; erfc the complementary error function ; D* effective diffusion coefficient and t : transit time.

4. Ohmic Conduction in Soils :

Conduction phenomena in materials is due to the movement of Conduction phenomena in materials is due to the movement of electric charges (e.g., ions and electrons) which displace from their original equilibrium position under an applied electric potential between two electrodes. In such a case, the electrical conductivity (σ_o) can be defined as the coefficient that relates the potential gradient (ΔVe) and the electric current density (i) as conductivity is written Rinaldi and Francisca 1999 as :

$$i = \sigma_0 \; \Delta Ve \qquad (3)$$

Eq. 1 is the well-known Ohm’s law. This equation can be considered as valid in ionic conductors, when one type of charge is mobile, or at high enough frequencies where different charges may displace, but there is no time for changes to accumulate at electrodes or to create concentration gradients of ionic species space type of polarization. Thus, no electrochemical diffusion forces can be acting in the system Raistrick et al. 1987 In coarse soils where the surface charge of particles is negligible, ions can displace through the pores with little interaction.

Therefore, electrical conduction is governed mainly by the nature of the pore fluid, void ratio, and degree of saturation. In fine grained soils, electrical conduction becomes more complex since double layers are developed around the particles of colloidal size with negative surface charge.

At frequencies below a few kilohertz, ions in the double layer follow the variation of the electric field and the conduction of particles can be considered as ohmic, as described by Eq. 1. At large frequencies, ions in the double layer cannot follow the variation of the electric field, energy is dissipated, and conductivity increases. Therefore, conduction and polar losses contribute to the electrical conductivity of soils (σ^*). In complex notation, conductivity is written Rinaldi and Francisca 1999

$$\sigma^*_s = \sigma_0 + j\, \varepsilon_0\, k^*\omega \qquad (4)$$

where σ_0 = ohmic low-frequency conductivity or the conductivity at frequencies much lower than that corresponding to the relaxation process; k* = k’+j k” frequency dependent complex dielectric permittivity of the medium k’ and k” real and imaginary permittivities, respectively; ε_0 vacuum permittivity 8,853 F/m ; j = complex number ; and ω angular frequency.

Th real component of Eq. 2 can be determined by introducing the real (k') and imaginary (k") components of the complex permittivity k* :

$$\sigma^*_s = \sigma_0 + \varepsilon_0 \omega k'' \qquad (5)$$

In most soils, at frequencies below 100 kHz, the second term of Eq. 3 vanishes and the total conductivity is governed by the ohmic term (σ_0) which is frequency independent. However, at very low frequencies, electrode polarization may be also present. This mechanism occurs in soils at frequencies below 2 or 3 kHz when conductivity measurements are performed using a two electrode cell Dias 1972.

A simple parallel resistor capacitor RC circuit can be used to approach the effect of electrode polarization Rinaldi and Francisca 1999. This circuit should be connected in series with the resistor that represents the ohmic conduction (σ_o) of the bulk sample.

5. Soil description and measurement of Electrical Conductivity :

The samples of sand and bentonite mixture were air dried, sieved through sieve No. 40, and then oven dried at 105°C as suggested by ASTM 1991 Air-dried samples cannot be used here since the soil must be thoroughly mixed with electrolytes at different concentrations and no water may be initially present. The dried soil was then mixed with the different volumes of the electrolytes.

The standard Proctor test ASTM 1991 yielded a maximum dry density of 1,8 g/cm^3 at the optimum moisture content of ω 15%. The prepared soil specimens were compacted to the desired density in the cells showed in Fig 1.

The prepared soil specimens were compacted to the desired density in cells showed in Fig.1. The sample length was varied between 50 and 250 mm, depending on volumetric liquid content and electrolyte concentration. In general, larger samples were prepared when electrolytes of high concentration were used in order to obtain a resistance in the range of measurement of the analyzers within the 5% error.

The measurements were performed using a Hewlett–Packard HP4800 impedance analyzer in the range of 5 Hz to 550 kHz.

To facilitate electrical measurements, the column had pairs of stainless steel square plate electrodes positioned at discrete heights within the column (see Fig. 1). The electrodes were positioned flush with the sides of the column. Electrical measurements were taken normal to the direction of diffusion.

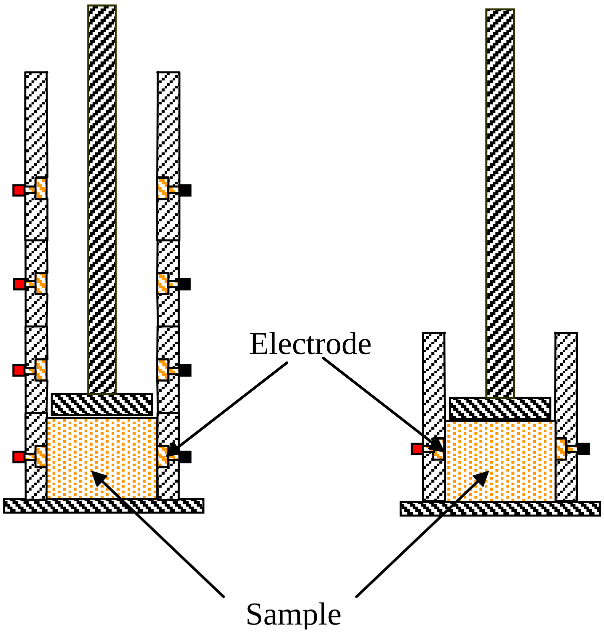

Fig. 1 : Two-electrode cell used in this work to measure electrical conductivity of soils and electrolytes

6. Test Results

6. 1. Effect of Frequency on Conductivity of Soil

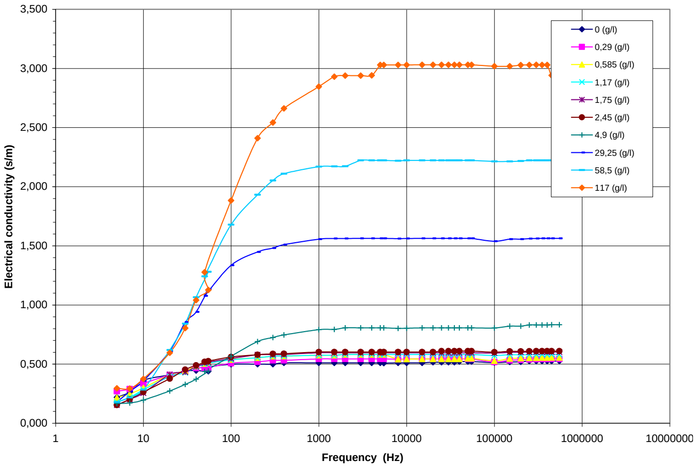

Fig. 2. Variations of electrical conductivity with frequency for sample at constant moisture content
(18%), constant unit weight of 1,81 kN/m3, and different NaCl concentrations

Fig. 2 shows the variations of conductivity with frequency for samples specimens at constant moisture content (18 %) and at different NaCl concentrations. In this case, samples were mixed with the electrolyte and compacted to the same density (1,81 g/cm3). It is observed that the conductivity of the samples saturated with an electrolyte of concentration, 0 and 117 g/l, is almost frequency independent in the whole frequency range 1 to 55 kHz of this work. The samples saturated with higher electrolyte concentration, develop a nonlinear behaviour at frequencies below 1 kHz. Such behaviour can be attributed to electrode polarization. Therefore, the measurement of electrical conductivity in loess at frequencies larger than 1 kHz was considered to be free from electrode effects is illustrated in Fig 3, who shows a typical curve of conductivity that may be observed in clayey soils and the limiting frequencies at which electrode polarization. All measurement of electrical conductivity in this work is taken in the rage of ohmic conduction (1 kHz to 55 kHz).

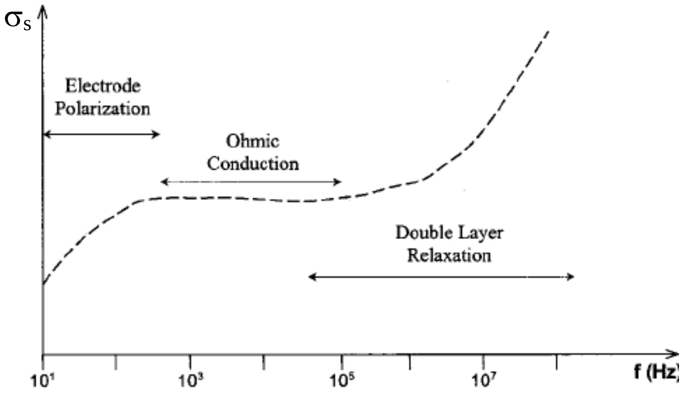

Fig. 3. Typical curve of conductivity to be observed in clayey soils measured in two blocking electrode cell Rinaldi et al 2002

The relation obtained between concentration and electrical conductivity at 20 KHz is polynomial relation as fellow with a correlation coefficient $r^2 = 0{,}99$

$$\textbf{Conc.} = 2{,}491.EC^3 + 0{,}3846.EC^2 + 17{,}75.EC - 9{,}7213 \quad (5)$$

Conc. : concentration du NaCl (g/l)
EC : Electrical Conductivity (S/m)

6. 2. Diffusion test:

The sand bentonite sample is compacted in the column and solution of 29,5 g/l of NaCl is placed over the sample thereby inducing a diffusive flow of NaCl into the saturated sample. The top of the column was sealed to prevent evaporation of liquid and the solution was replaced daily to ensure a constant 29,5 g/l driving solution. As shown in fig 4.

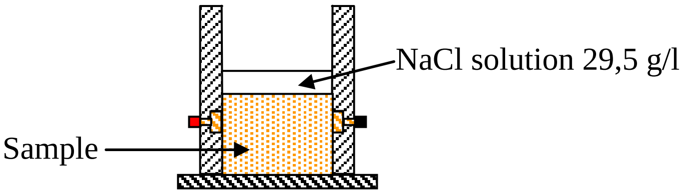

Fig. 4. Schematic arrangement of diffusion column.

Electrical impedance measurements were taken using Hewlett–Packard HP4800 impedance analyzer. Sample impedance measurements at 20 KHz. every 24 h over the test period, which, in this work, was 20 days.

Fig. 6 presents the values obtained from Eq. (5) at the electrode level. The theoretical concentration versus time profiles at the electrode level, C(x,t), predicted using Eq. (2) are presented in this figure using a diffusion coefficient $D^* = 1.5 \times 10^{-10}$ m^2/s, with x taken as the distance to the mid-point of the electrode.

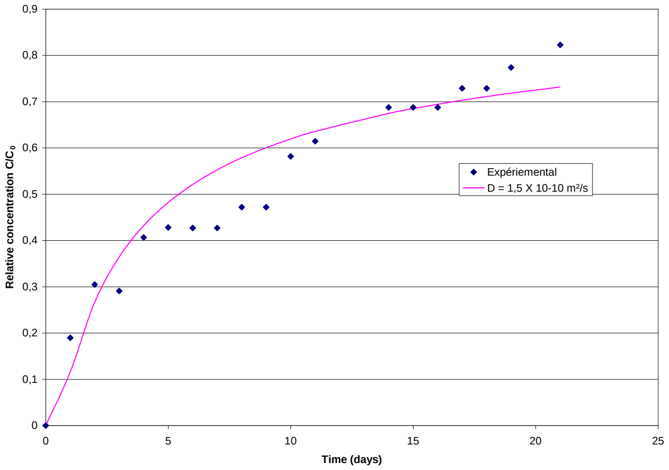

Fig. 5 : Concentration versus time calculated from conductivity results in (b) and predicted curves based on a diffusion coefficient D*= $1,5x10^{-10}$ m²/s.

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Conclusions :

The basic mechanisms of electrical conduction in soils were reviewed in this work. The influence of measurement frequency, and electrolyte concentration was determined for the silty clay studied. Additionally, it can be concluded that a two-electrode cell, the measurement of electrical conductivity is not affected by electrode polarization at frequencies larger than 3 kHz in the soil tested;

In addition to electrode polarisation effect and temperature correction procedures—it was shown that conductivity measurements could be used to track ionic movement through clay liners during diffusion in a simple yet informative manner. This was undertaken for compacted sand bentonite liners.

Although the work presented is specific to the diffusion of NaCl, the work highlights that and, for the concentrations employed, increasing concentration within the pore fluid can be correlated with increasing bulk conductivity. The simplicity of the testing system thus offers the potential for adapting as a field monitoring technique.

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INVESTIGATION OF BIOACCUMULATION OF COPPER AND NICKEL IONS BY *RHIZOPUS DELEMAR*

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In this study, the bioaccumulation of Cu(II) and Ni(II) ions by *Rhizopus delemar* from growth media was investigated in media containing molasses in batch-stirred reactor systems. *R. delemar* can grow at low pH values which is suitable for acidic character of waste waters.
In the first stage of studies, the effects of initial pH, substrate (sucrose) concentration on specific growth rate and maximum concentration of fungus in the absence of metal ions were investigated. Maximum microorganism growth was obtained at pH 4.0. Specific growth rate and maximum microorganism concentration increased with increasing sucrose concentration up to 20 g/L.

In the next stage of studies, to investigate the bioaccumulation of Cu(II) and Ni(II) ions from single metal ion systems, the initial concentrations of single metal ions were varied between 50 and 250 mg L^{-1}, whereas the substrate concentration in each growth media containing molasses was held constant at 10 g L^{-1}. Microorganism growth rate in the presence of single metal ions was observed to decrease with increasing concentrations of metal ions. Maximum growth rates in the presence of 50 mg L^{-1} Cu(II) and Ni(II) ions were found to be 0.291 $h^{-1,}$ 0.257 $h^{-1,}$ respectively. Cu(II) bioaccumulation efficiency in the presence of 50 mg L^{-1} Cu(II) was determined as 74.2%. Ni(II) bioaccumulation efficiency in the growth medium containing 50 mg L^{-1} Ni(II) ions singly was lower than that of Cu(II) ions and found to be 51.8%.

1. Introduction

Rapid increase in the population of the world and the inadequacy of waste treatments causing environmental problems that getting larger by the time and the water pollution is one major item of it. Heavy metal ions are widely used in many industries and so they cause water pollution. Wastewater that containing heavy metal ions is toxicologic and acidic so must be controlled according to water standards and concentration of them must be reduced under limiting values. Classical methods that used for removing heavy metal ions from wastewater (precipitation, ion exchange, reverse osmosis, charcoal adsorption etc.) are not economical because of many reasons as low wastewater treatment yield, high investment and operating cost, composed of new pollutants after treatment. Nowadays, some studies getting important by using microorganisms which have the ability of bioaccumulate heavy metal ions and can grow in wastewater that acidic and containing heavy metals (Yu et al., 1999; Anand et al., 2006; Kobayashi et al., 2006). Microorganisms need carbon source to grow and in such studies synthetic nutrients are used like glucose and sucrose. If molasses, sugar industry waste, containing high level sucrose and salts is used in this studies, microorganism growing will be more economical. Fungi can be used for bioremedation of heavy metals from waste waters. They can grow at low pH values and have the ability of accumulating metals. They are also inexpensive and readily available biomasses (Weber, JR, 1972; Mejare and Bülow 2001).

Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemicals concentration in the solution. Bioaccumulation begins when a chemical passes from the solution into an microorganism cells. Uptake is a complex process and still not fully understood. Because of concentration gradient chemicals can diffuse passively from high concentration to low concentration. The force or pressure for diffusion is called as the chemical potential, and it works to move a chemical from outside to inside a microorganism cell (Vasconcelos et al., 2001; Ortiz and Alcañiz, 2006).

2. Materials and methods

2.1. Microorganism growth and preperation of microorganism for bioaccumulation

R. delemar used in this study was kindly supplied by United States Department of Agriculture (NRRL). Growth medium of *R. delemar* composed of 10 g/L molasses sucrose, 0.5 g/L K_2HPO_4; 0.5 g/L KH_2PO_4; 0.2 g/L $MgSO_4.7H_2O$; 2.0 g/L yeast extract. Prepared mediums were sterilized in autoclave for 15 minutes at 121°C and 1.2 atmospheric pressure.

2.2. Bioaccumulation studies

Bioaccumulation studies were performed in 250 mL erlenmayer flasks that have 100 mL working volume at 25°C constant temperature and 150 rpm stirring rate in shaker as batch system. Inoculum was carried out aseptically with the cells reached exponential growth phase. Before inoculum, the cells were adapted metal ion containing medium. Bioaccumulation experiments were started by adding 1 mL of microorganism solution. Samples were taken aseptically from growth media at certain times and centrifuged. The supernatant was analyzed for the determination of unbioaccumulated metal ion concentration and sucrose concentration. The solid phase was used for the measurement of microorganism concentration.

2.3. Measurements of heavy metal ion, sucrose and microorganism concentrations

The concentrations of unbioaccumulated Cu(II) and Ni(II) ions in the sample supernatant were determined using an atomic absorption spectrophotometer with an air-acetylene flame. Cu(II) and Ni(II) ions were measured at 324.8 and 232.0 nm, respectively. Sucrose concentratios in the sample supernatant was determined spectrophotometrically. The coloured complexes of sucrose with dinitrosalicylicacid was read at 575 nm. Turbidity of the culture medium was measured at 360 nm spectrophotometrically (Snell and Snell1959).

2.4. Modelling

The most widely used equation for substrat limited growth of microorganisms is the Monod equation.

$$\mu = \frac{\mu_m S}{K_s + S}$$

where μ is the specific growth rate (h^{-1}), K_s is the saturation constant ($g\ L^{-1}$), μ_m is the maximum specific growth rate when $S >> K_s$ (Shuler and Kargi, 2002).

3. Results and discussion

3.1. Effect of initial pH

The pH of the growth media was varied over the pH range of 2.0-5.0 to determine the effect of pH on the maximum microorganism concentration and the specific growth rate. The maximum concentration and the specific growth rate of *R. Delemar* strongly depends on medium pH value. The maximum specific growth rate and maximum microorganism concentration was observed at pHs in the range 4.0-5.0 as shown in Fig. 1.

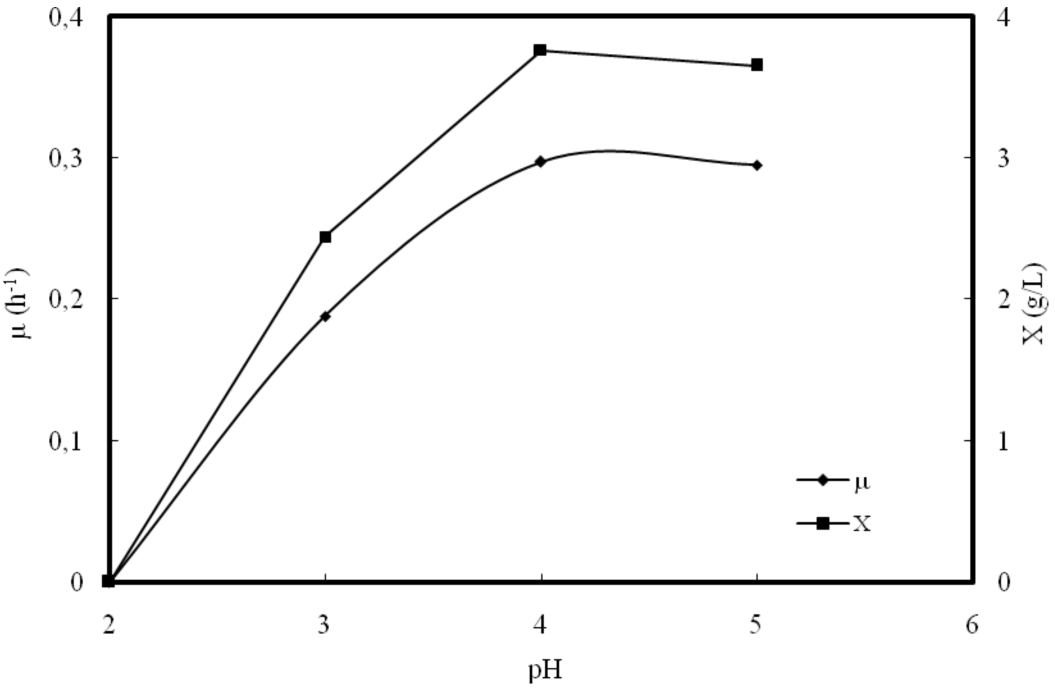

Fig.1 Effect of initial pH value on specific growth rate and the maximum microorganism concentration (So=10 g/L).

3.2. Effect of initial sucrose concentration

The effects of initial molasses sucrose concentration on the specific growth rate and maximum microorganism concentrations were investigated at the initial molasses sucrose concentrations in the range 1-20 g/L and the results were given in Table 1. The specific growth rate and the maximum microorganism concentration increased with increasing initial molasses sucrose concentration, and reached a plateau value of 0.350-0.365 h^{-1} and 4.24 and 4.55 g/L, respectively at the sucrose concentrations in the range 15.08-19.91 g/L.

Table 1. The specific growth rates and maximum microorganism concentrations of *R. delemar* obtained at different initial molasses sucrose concentrations.

S_o g/L	μ h^{-1}	X_m g/L
1,03	0,085	0,98
2,48	0,145	1,67
5,04	0,212	2,55
9,98	0,297	3,76
15,08	0,350	4,24
19,91	0,365	4,55

The values of maximum specific growth rate and saturation constant were determined from Monod equation giving the relation between specific growth rate and sucrose concentration and were found to be 0.406 h^{-1}, 24.182 g L^{-1}, respectively.

3.3. Effect of initial copper and nickel concentration on growth and bioaccumulation

Bioaccumulation of Cu(II) and Ni(II) ions by *R. delemar* was investigated at 10 g/L initial molasses sucrose concentration, at pH 4.0 and at the initial metal ion concentrations in the range 50-500 mg/L. Change of the specific growth rate and the maximum microorganism concentration with initial metal ion concentrations is given in Figures 2 and 3, respectively. The specific growth rate and the maximum microorganism concentration decreased with increasing initial Cu(II) and Ni(II) ion concentrations up to 500 mg/L. Increasing concentrations of metal ions in the growth medium inhibit the growth of microorganisms. The inhibition effect of Ni(II) ions at all initial metal ion concentrations was higher than that of Cu(II) ions. While the specific growth rate and the maximum microorganism concentration were 0,276 h^{-1} ve 3,37 g/L, respectively at 100 mg/L initial Cu(II) ion concentration, the specific growth rate and the maximum microorganism concentration reduced to 0,222 h^{-1} ve 2,36 g/L, respectively at 100 mg/L initial Ni(II) ion concentration.

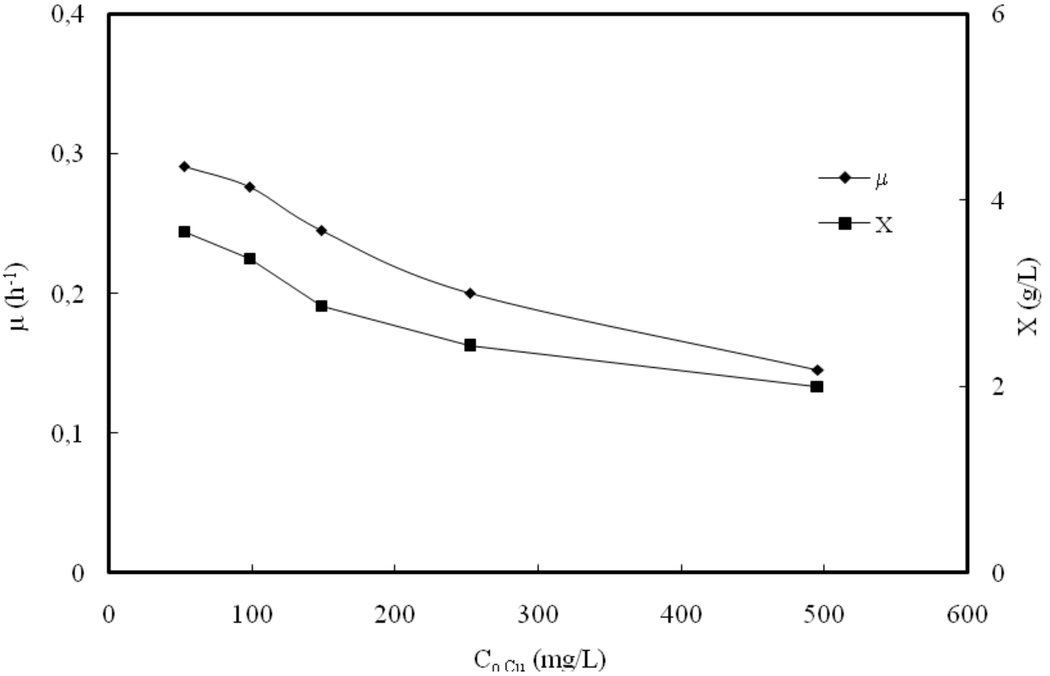

Figure 2. Effect of initial concentration of copper on specific growth rate and maximum microorganism concentration of *R. Delemar* (So=10 g/L).

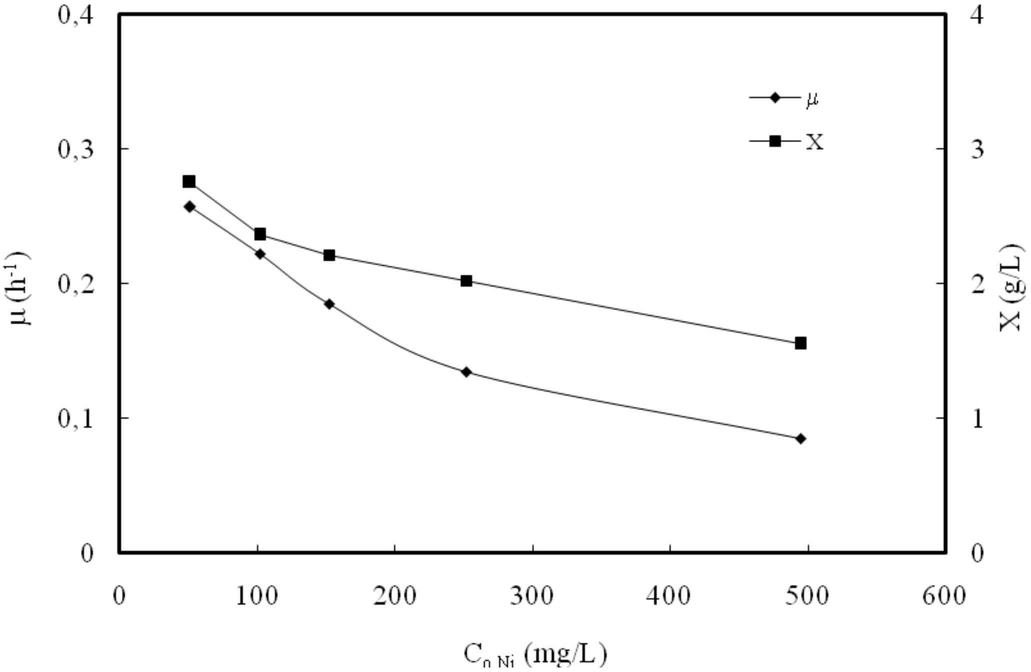

Figure 3. Effect of initial nickel concentration on specific growth rate and maximum microorganism concentration of *R. Delemar* (So=10 g/L).

Plots of bioaccumulated metal ion concentrations versus initial metal ion concentrations for Cu(II) and Ni(II) ions and the amounts of Cu(II) and Ni(II) bioaccumulated per unit dry weight of fungal cell (bioaccumulation capacity) versus initial metal ion concentrations for Cu(II) and Ni(II) ions are given in Figures 4 and 5, respectively. The bioaccumulated metal ion concentrations and the amounts of Cu(II) and Ni(II) bioaccumulated per unit dry weight of fungal cell increased with increasing Cu(II) and Ni(II) ion concentrations up to 500 mg/L. The bioaccumulation capacity of *R. delemar* for Cu(II) ions was higher than that for Ni(II) ions. While the bioaccumulated Cu(II) ion concentrations and the amounts of Cu(II) bioaccumulated per unit dry weight of fungal cell at 100 mg/L initial Cu(II) ion concentration were 69,8 mg/L and 20,72 g Cu(II) /g dry weight of microorganism, respectively, the bioaccumulated Ni(II) ion concentrations and the amounts of Ni(II) bioaccumulated per unit dry weight of fungal cell at 100 mg/L initial Ni(II) ion concentration were found to be 48,8 mg/L ve 20,67 g Ni(II) /g dry weight of microorganism. As the inhibition effect of Ni(II) ions on the specific growth rate of *R. delemar* was higher than that of Cu(II) ions, lower metal accumulations in the presence of Ni(II) ions were observed.

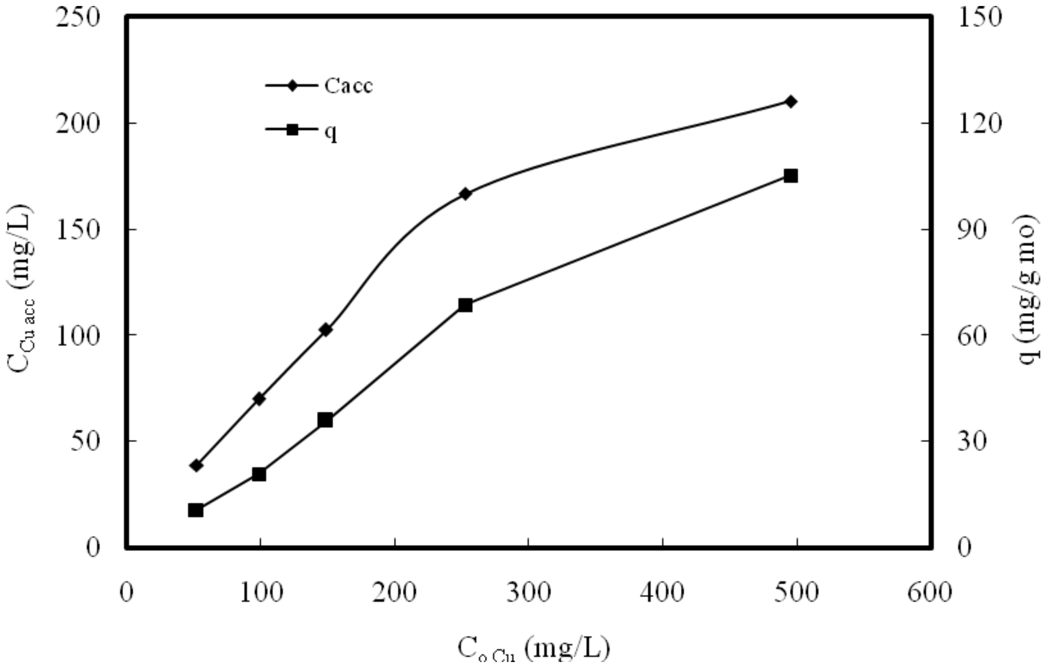

Figure 4. Effect of initial concentration of copper on bioaccumulated copper concentration and the amount of bioaccumulated copper per unit dry weight of microorganism (So=10 g/L).

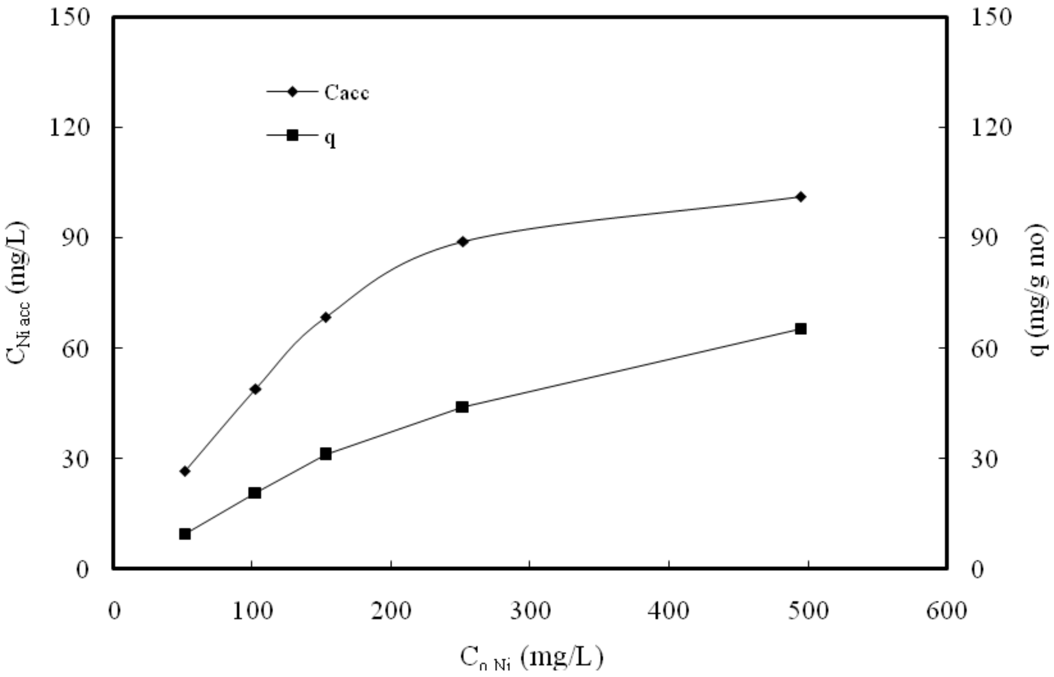

Figure 5. Effect of initial concentration of nickel on bioaccumulated nickel concentration and the amount of bioaccumulated nickel per unit dry weight of microorganism (So=10 g/L).

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COMPARISON OF BIOACCUMULATION AND BIOSORPTION OF COPPER IONS BY *CANDIDA LIPOLYTICA*

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In this study, the biaccumulation and biosorption of Cu(II) ions frequently encountered in waste waters by *Candida Lipolytica* was investigated in batch stirred reactors. *C. Lipolytica* can grow at low pH values and extreme growth media which suitable for waste waters containing heavy metal ions, can also accumulates and adsorbs heavy metal ions from liquid media. Molasses obtained from Ankara Sugar Factory as main carbon source was used in the growth media preparing for bioaccumulation and biosorption.

In the first stage of the studies, the effects of initial pH and substrate (sucrose) concentration on specific growth rate and maximum concentration of the yeast was investigated. Maximum microorganism growth was obtained at pH 4.0. When sucrose concentration was increased from 1 to 20 g L^{-1}, specific growth rate and maximum microorganism concentration increased. Using the Monod equation, maximum specific growth rate of the yeast and saturation constant was found to be 0.335 h^{-1}, 32.33 g L^{-1}, respectively. In the next stage, the bioaccumulation studies of Cu(II) ions from single-systems were carried out in the growth media containing 10 g L^{-1} molasses sucrose, at pH 4.0, maximum growth pH. Although the bioaccumulated metal ion concentration increased with increasing initial metal ion concentration in the range 50-250 mg L^{-1}, specific microorganism growth rate decreased and was found to 0.155 h^{-1} in the growth medium containing 250 mg L^{-1} Cu(II) ions. In the second stage of the studies, the biosorption of Cu(II) ions from single-metal systems was investigated. When the initial metal ion concentration was held constant at 100 mg L^{-1}, maximum biosorption capacity was also obtained at pH 4.0. The biosorption equilibrium data were fitted to Langmuir and Freundlich adsorption models and the values of model constants were determined. The biosorbed metal ion concentration also increased with increasing metal ion concentration. Biosorbed metal ion amount per unit dry weight of microorganism was 2.5 times higher than the bioaccumulated metal amount per unit dry weight of microorganism at 100 mg L^{-1} initial metal ion concentration and determined as 53.0 and 21.54 mg Cu(II) g (dry weight of microorganism)$^{-1}$, respectively. Moreover, biosorption was faster than the bioaccumulation. Ultimate bioaccumulation equilibrium was reached within 10 days whereas the biosorption equilibrium was established within 1 day.

1. Introduction

Environmental pollution is one of the main poblems for all living species on the world today and one major item of it water pollution. Especially heavy metal ions cause water pollution and that must be solved. In order to purifing water, using microorganisms as biosorbents for heavy metals offers a potential alternative to existing methods for detoxification and recovery of these components from industrial waste waters and is a subject of extensive studies. The special surface properties of microorganisms enable them to adsorb or bioaccumulate heavy metal ions from solutions. If metal ions in the solution bind surface of the microorganism, this process is called biosorption. If metal ions in the solution passes through cell membrane of the living microorganism into the cell and are bound some sites in cell cytoplasm, this process is called bioaccumulation.

In these methods: the process does not produce chemical sludges, it could be highly selective, more efficient, easy to operate and hence cost effective for the treatment of large volumes of wastewaters containing low pollutant concentrations. Especially yeasts can grow in low pH values which is suitable for the heavy metal containing waste water's acidic character. So yeast can be used for bioaccumulation of heavy metals. Yeasts biosorption capacity is also high at low pH values. Also this ability of it gives permition to be used as biosorbent (Weber, JR, 1972; Walker, 2000; Lee and Wang 2001; Veglio et al., 2003).

Biosorption of heavy metals is affected by several factors such as pH, initial metal ion concentration, sorbent concentration, temperature. The amino groups of the proteins on the cell wall and the nitrogen and oxygen of the peptide bond also could be available for binding of metallic ions (Mejare and Bülow, 2001). Such bind formation could be accompanied by displacement of protons dependent in part on the extent of protonation as determined by the pH. This process continues until the equilibrium established between the ions in the solution and the ions biosorbed on the biomass surface (Pal et al., 2006; Pamukoglu and Kargi, 2006).

Bioaccumulation of metal ions is also more complex and not fully understood process. Metal ions in the solution firstly biosorbed living microorganism cell membrane and then passes through membrane of it and enters the cytoplasm of the cell. Concentration gradient of metal ions in the solution and in the cell cytoplasm may be the cause of bioaccumulation. Some nourishment transporter enzymes on the cell membrane may be transport metal ions inside the cell. This process also continues until equilibrium established (Al-Saraj et al., 1999; King et al.,1999).

2. Materials and methods

2.1. Microorganism growth and preperation of microorganism for bioaccumulation

Candida lipolytica used in this study was kindly supplied by United States Department of Agriculture (NRRL). *C. lipolytica* was grown in an agitated liquid medium containing the following ingredients (g L^{-1}) : molasses sucrose 10; KH_2PO_4 1.0;. $(NH_4)_2SO_4$ 1.0. Prepared growth mediums were autoclaved for 15 minutes at 121^{o}C and 1.2 atmospheric pressure.

2.2. Bioaccumulation studies

The 250 mL flasks containing 100 mL of the growth liquid medium were incubated on a rotary shaker at 25^{o}C and 150 rpm. The cells were firstly adapted metal ion containing medium. Inoculum was carried out aseptically with the cells at the early exponential growth phase. The optimum inoculum ratio (Volume of inoculum / production volume of bioreactor) was determined as 10/1000, and all bioaccumulation experiments were started using this inoculum ratio. Samples were taken aseptically from growth media at certain times and centrifuged. The supernatant liquid was analyzed for the determination of unbioaccumulated metal ion concentration and sucrose concentration. The solid phase was used for the measurement of microorganism concentration.

2.3. Measurements of heavy metal ion, sucrose and microorganism concentrations

The concentrations of unbioaccumulated Cu(II) ions in the sample supernatant were determined using an atomic absorption spectrophotometer with an air-acetylene flame. Cu(II) ions were measured at 324.8 nm. Sucrose concentratios in the sample supernatant was determined spectrophotometrically. The coloured complexes of sucrose with dinitrosalicylicacid was read at 575 nm. Turbidity of the culture medium was measured at 360 nm spectrophotometrically (Snell and Snell, 1959).

2.4. Modelling of bioaccumulation

The most widely used equation for substrat limited growth of microorganisms is the Monod equation.

$$\mu = \frac{\mu_m S}{K_s + S} \qquad (1)$$

where μ is the specific growth rate (h^{-1}), K_s is the saturation constant (g L^{-1}), μ_m is the maximum specific growth rate when $S >> K_s$ (Shuler and Kargi, 2002).

2.5. Biosorption studies

For biosorption studies, 1.0 g of dried cells was suspended in 100 mL of distilled water and homogenized. The microorganism suspension (10 mL) was mixed with 90 mL of the desired metal solution in an Erlenmeyer flask. The dry cell weight in each sample was constant at 1.0 g /L. Biosorption studies were performed in 250 mL erlenmayer flasks that have 100 mL working volume at 25°C constant temperature and 150 rpm stirring rate in shaker as batch system. Before the microorganism suspension and the metal-bearing solution were mixed, a 3-mL sample was taken from the metal-bearing solution. Subsequently, samples were taken at 5-min intervals at the beginning of biosorption and at 25-30-min intervals after samples reached equilibrium. The samples were centrifuged at 6000 x g for 3 min and the supernatant liquid was used for metal analysis.

2.5.1. Modelling of biosorption

Rapid equilibrium is established between adsorbed metal ions on the yeast cell and unadsorbed metal ions in solution. This equilibrium can be represented by the adsorption isotherms. The most widely used isotherm equation for modeling of the biosorption equilibrium data is the Langmuir equation (Langmuir, L., 1916).

$$q_{eq} = \frac{Q^{\circ} b C_{eq}}{1 + b C_{eq}} \qquad (2)$$

where q_{eq} is the adsorbed metal ion quantity per unit weight of dried biomass at equilibrium (mg g^{-1} dry cell); Q^o is the amount of adsorbate per unit weight of adsorbent to form a complete monolayer on the surface (mg g^{-1} dry cell); and C_{eq} is the unadsorbed metal ion concentration in solution at equilibrium (mg L^{-1}).

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. The Freundlich equation is commonly presented as (Freundlich, 1907)

$$q_{eq} = K_F C_{eq}^{\frac{1}{n}} \quad (3)$$

The magnitude of K_F and 1/n shows easy separation of metal ions from waste water and favourable adsorption. K_F is an indication of the adsorption capacity of the adsorbent, and 1/n indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity. If sorption is favourable, then n>1.

3. Results and discussion

3.1. Bioaccumulation of copper

3.1.1. Effect of initial pH

Effect of pH the specific growth rate of *C. lipolytica* and the maximum microorganism concentration was studied in the pH range 2.0-5.0. The maximum specific growth rate and maximum microorganism concentration was obtained at pHs in the range 4.0-5.0 as shown in Fig. 1. The values of maximum specific growth rate, μ_{max}, and saturation constant K_s were determined from the Monod equation and were found to be 0.335 h^{-1}, 32.331 g L^{-1}, respectively.

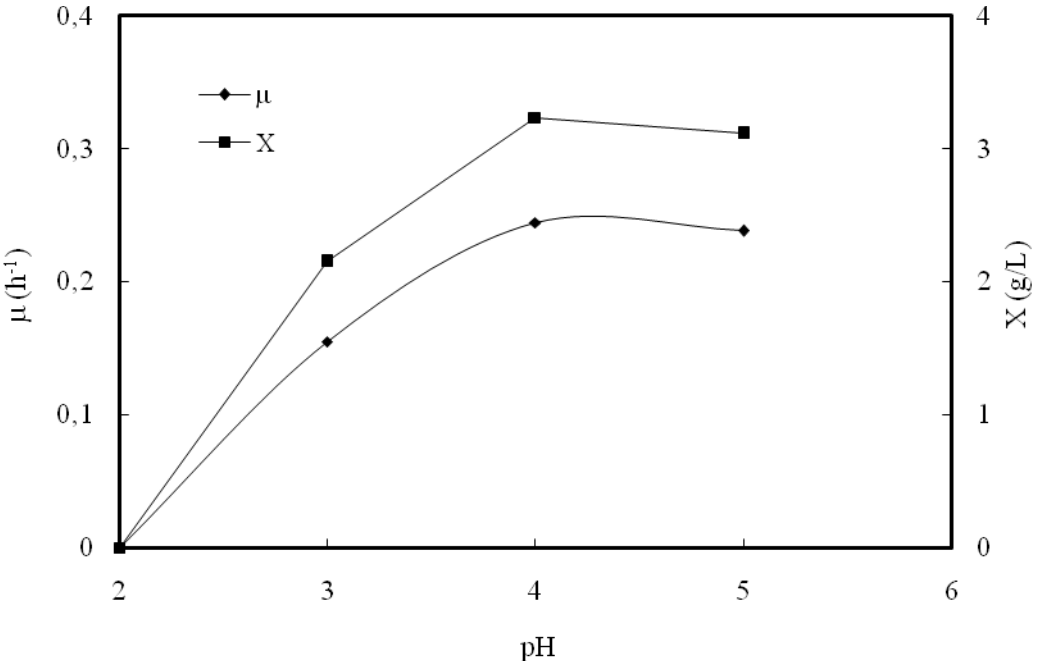

Fig. 1 Effect of initial pH value on specific growth rate and the maximum microorganism concentration (So=10 g/L).

3.1.2. *Effect of initial copper concentration on growth and bioaccumulation*

Bioaccumulation studies were performed at pH 4.0, which was observed the maximum specific growth rate and microroganism concentration, and at 10 g/L molasses sucrose concentration. Initial Cu(II) ion concentrations were varied over the range 50-250 mg/L. Change of the specific growth rate and maximum microroganism concentration versus initial Cu(II) ion concentration is given in Fig. 2. The specific growth rate and maximum microorganism concentration decreased with increasing initial Cu(II) ion concentration up to 250 mg L^{-1}. Presence of increasing concentrations of Cu(II) ions in the growth medium inhibits the microorganism growth. While the specific growth rate and maximum microorganism concentration at 50 mg/L initial Cu(II) ion concentration was 0,271 h^{-1} and 3,11 g/L, respectively, these values reduced to 0,155 h^{-1} ve 2,22 g/L, respectively, at 250 mg/L initial Cu(II) ion concentration. The effect of initial Cu(II) ion concentration on the bioaccumulated Cu(II) ion concentration and the bioaccumulated Cu(II) quantity per unit dry weight of yeast (bioaccumulation capacity) is given in Fig. 3. Both the bioaccumulated Cu(II) ion concentration and the bioaccumulated Cu(II) quantity per unit dry weight of yeast increased with increasing initial Cu(II) ion concentration up to 250 mg/L.

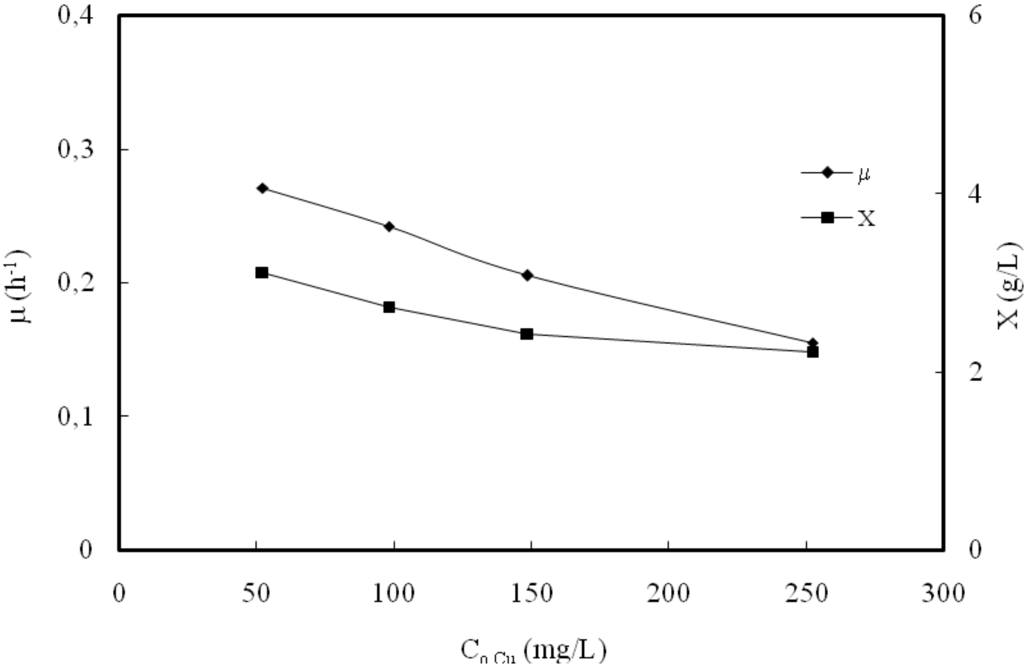

Fig. 2. Effect of initial Cu(II) ion concentration on the specific growth rate and the maximum microorganism concentration (So=10 g/L).

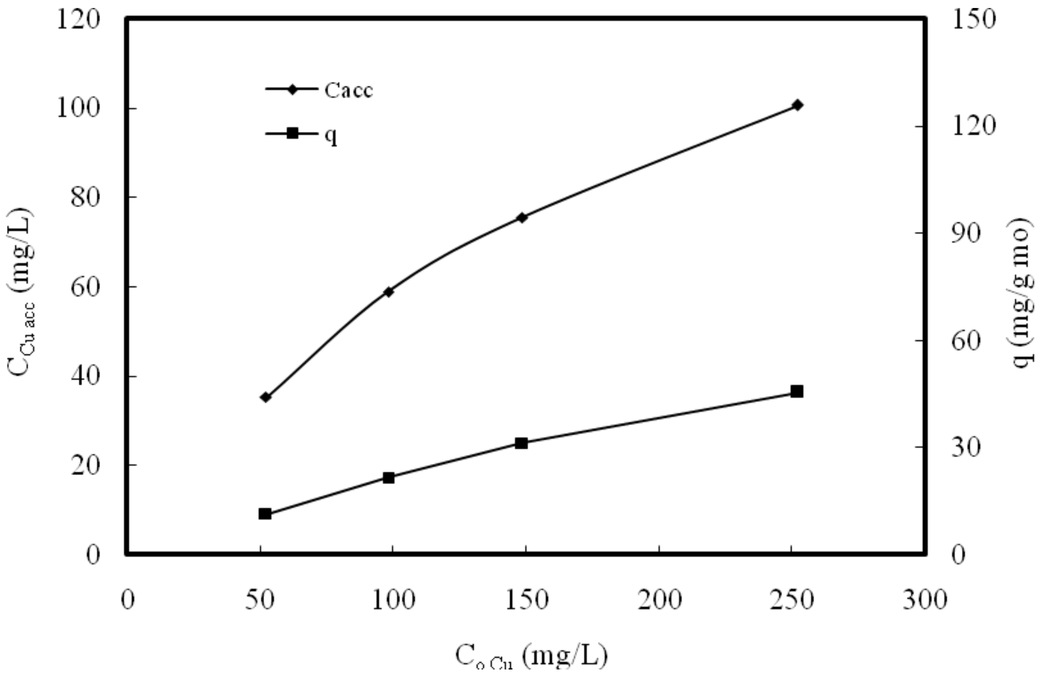

Fig. 3. Effect of initial Cu(II) ion concentration on the bioaccumulated Cu(II) ion concentration and the bioaccumulated Cu(II) quantity per unit dry weight of yeast (bioaccumulation capacity).

3.2. Biosorption of copper

3.2.1. Effect of initial pH

The effect of pH of biosorption medium on the initial biosorption rates of Cu(II) and the biosorbed Cu(II) ion concentration was studied in the pH range 2.0-5.0 and at 100 mg/L initial Cu(II) ion concentration. Maximum initial biosorption rate and the biosorbed Cu(II) ion concentration was obtained at pH 4.0 as shown in Table 1.

Table 1 Effect of pH of biosorption medium on the initial biosorption rates of Cu(II) and the biosorbed Cu(II) ion concentration

pH	r_{ad} mg/g min	$C_{ad\ Cu}$ mg/L
2,0	1,75	16,0
3,0	2,61	24,0
4,0	4,72	49,0
5,0	4,55	47,0

3.2.2. Effect of initial copper concentration

To determine the effect of initial Cu(II) ion concentration on the biosorption capacity of *C. lipolytica*, while the initial Cu(II) ion concentration was increased in the range 50-250 mg/L, the pH of biosorption medium was held constant at pH 4.0. Effect of initial Cu(II) ion concentration on the initial biosorption rates and the biosorbed Cu(II) quantity per unit weight of yeast (biosorption capacity) is presented in Fig. 4. Both the initial biosorption rates and the biosorbed Cu(II) quantity per unit weight of yeast increased with increasing initial Cu(II) ion concentration up to 250 mg/L.

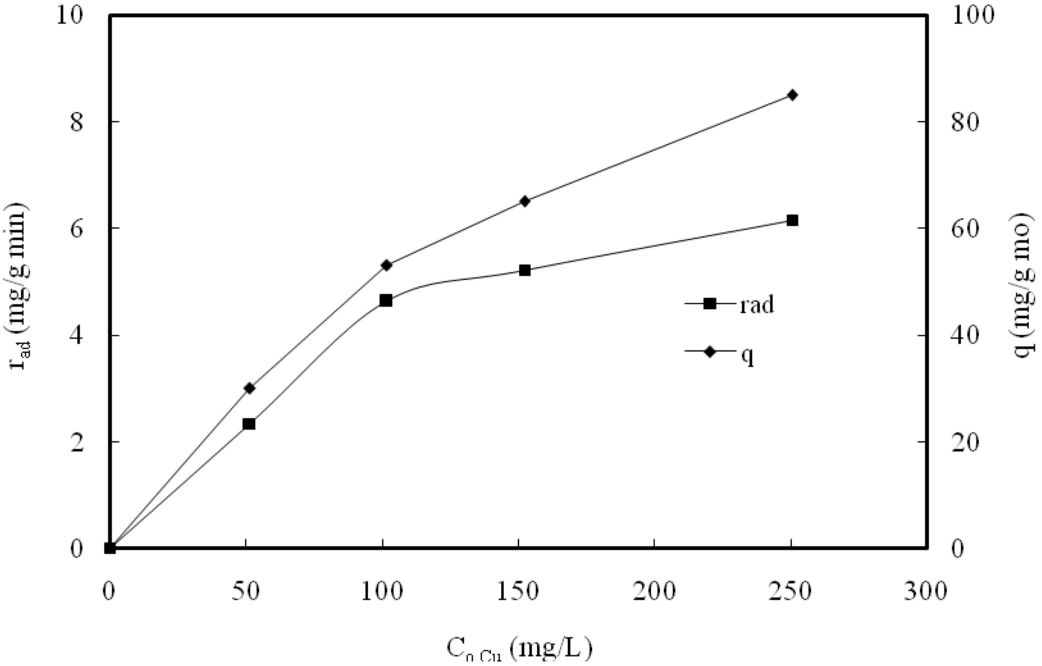

Fig. 4. Effect of initial Cu(II) ion concentration on the initial biosorption rates of Cu(II) ions and the biosorbed Cu(II) quantity per unit dry weight of yeast (biosorption capacity).

The sorption constants calculated according to the Langmuir and the Freundlich adsorption models at different pH 4.0 and 25^{o}C are listed in Table 2. The Langmuir constant, Q^o, represents the sorption capacity when the surface is saturated with metal ions. It is roughly an indicator of the ultimate sorption capacity. The Langmuir constant, b is the ratio of adsorption/desorption rates and reflects the affinity between the yeast cell and Cu(II) ions. As the value of Freundlich sorption constant, n, for Cu(II) ions was found to be higher than 1, this value indicate favourable sorption. High K_F value obtained for the sorption of Cu (II) ions also verify high biosorption capacity of *C. Lipolytica*.

Table 2 The adsorption isotherm coefficients of Langmuir and Freundlich adsorption models.

Langmuir		Freundlich	
Q^o (mg/g)	b (L/mg)	K_F ($mg^n g^{-1} L^n$)	n
114.942	0.016	7.646	2,23

3.3. Comparison of bioaccumulation and biosorption of copper

In Table 3, the biosorbed Cu(II) quantities per unit dry weight of yeast at the end of 24 hours obtained at different initial Cu(II) ion concentrations were compared with the bioaccumulated Cu(II) quantities per unit dry weight of yeast at the end of 240 hours. The biosorbed Cu(II) quantities per unit dry weight of yeast were higher than the bioaccumulated Cu(II) quantities per unit dry weight of yeast. Moreover, ultimate biosorption equilibrium established in short time, compared with ultimate bioaccumulation equilibrium. Passive metal uptake taking place non-metabolism dependent uptake mechanisms such as precipitation, physical adsorption, ion exchange, complexation is relatively rapid process and can be reversible. However, growth of the biomass, centrifuge of the cells at the end of the stationary phase of growth of biomass, chemical or heat treatment of resting cells and preparation of killed cells for biosorption takes extra time. Bioaccumulation or metabolism dependent uptake occurs by active metal uptake mechanisms such as transport across cell membrane, precipitation. It is an energy-driven process. Growth and bioaccumulation occurs simultaneously in the natural growth media, and bioaccumulation does not require additional time. However, downstream processes, separation of living cells from the growth medium should also be required in the bioaccumulation process.

Table 3 Comparison of the biosorbed Cu(II) quantities per unit dry weight of yeast with the bioaccumulated Cu(II) quantities per unit dry weight of yeast

İnitial copper concentration (mg/L)	Biosorption		Bioaccumulation	
	q (mg/g mo)	Time h	q (mg/g mo)	Time h
50,0	30,0	24	11,3	240
100,0	53,0	24	21,5	240
150,0	65,0	24	31,1	240
250,0	85,0	24	45,3	240

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ENVIRONMENTAL IMPACTS OF FLY ASHES FROM THERMAL POWER STATION

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Environmental concerns regarding the potential contamination of soil, surface and groundwater due to the presence of soluble metal species in the fly ash leachate is of great importance. The batch leaching method was used to determination the potential mobility of Ca, Cd, Cu, Pb, Cr, Co, Ni, Zn and Mn in fly ash samples, originated from Yatağan Power Plant in Turkey, in order to assess their leachability when these wastes are disposed of. The concentrations of these metals released in leaching solutions with initial pH values 2, 4 and 7 were used to assess the influence of pH conditions on element mobility from fly ashes. A mathematical model for leaching of these metals has been used and leaching intensities (I_i) has been calculated for each metals. Some metals such as Pb show the highest leaching intensity and such as Cu the lowest for pH=2. The results show that initial pH of the solution, leaching time and properties of the metals have an effect on leaching behavior.

Introduction

Fly ash poses significant potential risks for the environment and human health. Fly ash contains significant amounts of metals. To assess the environmental risks associated with the emission and utilization of fly ash, the quantities of specific chemical constituents have to be taken into account, as well as the fractions of the constituents that may be mobilized into the environment.

Potentially toxic elements and compounds leached from fly ash can contaminate soil, groundwater and surface water [1-2]. Leaching studies are important in predicting the environmental impact associated with ash pond disposal techniques. Terrestrial disposal of fly ash has been regarded as a potential source of contamination due to the enrichment and surface association of trace elements in the ash particles. Much attention has been paid to leaching behavior and possible contamination, especially for the aquatic environment, when ash is in contact with water. The groundwater environment is more vulnerable than surface water due to lower velocity under low permeability and the possible accumulation of leached elements in the groundwater [3]. In this case, more soluble sublimates on the surface of the fly ash particles the dissolution of the less soluble substances in the long term are expected to influence the quality of groundwater [4].

The mobilization of trace elements from fly ash is a very slow process, and equilibrium between solid and liquid phases may not be attained even after long leaching times [5-6]. Contaminated leachates from fly ashes can pose a high toxicity problem for groundwater [7].

The dissolve of elements depends on the chemical composition of the constituents in the fly ash, and these compositions can vary depending upon the source of coal, the quality of coal, the combustion conditions, and the rate of cooling the fly ash. Non-toxic elements will dissolve first in water, but long term leaching of toxic trace elements is associated with slow mobility of elements from glass, magnetite, and related minerals [8]. Interaction of groundwater and surface water in fly ash emplacements will take a long time to remove mobile trace elements from the solid phase. Depending on the hydrogeochemical environment in which the ash is placed or used, this may result in elevated concentrations over long periods of time and create potential contamination of associated groundwater and surface water systems [9].

The elements and compounds that are adsorbed on the particle surfaces are much more easily dissolved into solution during fly ash-water interaction. The leachability of elements and compounds is closely related to the phases with which they are associated, as well as to the pH and other aspects of the leaching environment. Association with soluble phases will cause them to be leached at much higher rates. When fly ash interacts with water, the principal processes affecting the leaching process are dissolution of primary solids and precipitation of secondary solids, as well as redox, sorption and hydrolysis reactions [10].

For ash in outdoor emplacement, where the long-term interaction of potentially toxic elements with water surface water and groundwater systems may be a concern, leaching process also depends on degree of weathering and possible formation of secondary minerals [11]. The soluble salt content in fly ashes is closely related to the coal properties and pH and other environmental conditions [4].

The aims of this study are to investigate the leaching behavior of fly ash currently disposed in Turkey-Mugla and to assess the potential influence of the fly ash landfill on the environment. In the present study, therefore, it was thought pertinent to carry out a batch test to understand the behavior of some metals (Ca, Cr, Mn, Cu, Cd, Pb, Zn, Co, Ni) during leaching from fly ash. To investigate potential water pollution some metals (Ca, Cr, Mn, Cu, Cd, Pb, Zn, Co, Ni) were leached from fly ash using solutions having pHs of 2, 4 and 7. The leaching tests are used for simulation of the release of components from an ash material to a water phase. The pH values used in the test gives an accelerated leaching rate relative to actual leaching that occurs when rainwater penetrates a landfill. Due to the large amount of leachate relative to amount of solid residue, the chemical processes occurring in the laboratory tests may be different from those occurring in a deposit. However, a series of batch leaching tests provides a quick and simple means to compare the dissolution of trace metals in fly ash.

Material and Methods:

Materials

Ash samples were collected from the electrostatic precipitator of Yatağan Power Plant in Mugla, Turkey. The mineralogical, morphological, physical and chemical properties of Yatağan fly ash were determined by analyses with EDXRF [4]. Analytical results showed that about 55-80 wt % of the Yatağan fly ash less than 45 μM in size. Chemical analysis of the fly ashes showed that the Yatağan fly ash was mainly composed of CaO, SiO_2 and Al_2O_3 [12-13-14].

Total Content Experiments

A flay ash sample of 0.25 g was dried by microwave oven and digested with an acidic solution of HNO_3/HF/HCI and $HCIO_4$. The solution was diluted with 50 ml of distilled water and analyzed by ICP–AES (Opt. 2000, Perkin–Elmer).

Leaching Experiments

The ash samples were dried at 110^oC and homogenized prior to analysis. Batch leaching tests were performed on the fly ash using three different solutes to test the mobility and rate of release of particular metals (Ca, Cr, Mn, Cu, Cd, Pb, Zn, Co, Ni) from the fly ash under a range of chemical conditions. Leaching solutions with pH values of 2, 4, and 7 were prepared in the laboratory prior to the leaching tests. Bulk solutions with pH values of 2, 4, and 7 were prepared in polyethylene bottles from distilled water, adjusted to acidic conditions (pH=2 and pH=4) by adding 0.01 M HCl. The pH of the distilled water had a pH of 6.6, so the pH of the water was adjusted slightly using 0.01 M NaOH to prepare a neutral (pH=7) solution. The pH valued of the initial leaching solutions were measured *in situ* using a “Hanna” portable pH/concentration meter, calibrated against buffers of pH 2, 4 and 7 . Cross-checking with two pH meters was used to validate the pH measurements for the solutions.

15.6 g of the fly ash sample were placed into 500 ml polyethylene bottles and mixed with 250 ml of the distilled water that had been adjusted to pH values of 2 and 4. The bottles containing the fly ash and acidic solutions were sealed and shaken at room temperature (22.5– 23.5 ^oC) in a horizontal shaker at 150 rpm. Shaking periods of 1, 2, 4, 8, 16, and 24 h were used. The process was repeated three times for each of the samples.

After the required shaking time the solution in each bottle was separated from the solid phase, and the solution was filtered through 0.45 mm Millipore cellulose acetate membrane filters. These solutions were then immediately acidified, using 10 drops of analytical grade nitric acid, prior to major and trace elements determinations. The acidified samples were analyzed by ICP–AES (Opt. 2000, Perkin–Elmer).

Results and analysis:

Leaching intensity (I_i), defined below, was used to determine the leaching behavior of elements in fly ash under different pH conditions.

$$I_i = a_x V 10^3 / A_x M t$$

Where I_i is leaching intensity (h^{-1}); a_x is the concentration of element x in leached (μg/ml); V is the total volume of leached solution (ml); A_x is the concentration of element x in original sample (μg/g); M is the total weight of sample (g); and t is the leaching time (h). The concentrations of elements in the original samples in this study are shown in Table 1.

The leaching intensity (I_i) has been calculated for Cr, Mn, Co, Ni, Pb, Cd, Ca, Cu and Zn (Tables 2 and 3).

Table 1: The concentration of elements in original samples (μg/g).

	Ca	Cr	Mn	Co	Ni	Pb	Cd	Zn	Cu
The concentration in original sample (μg/g)	20	11.92	40.4	2.48	10.7	0.59	1.38	87.6	13.7

Table 2. The leaching intensity values (I_i) in leachate vary with time at pH=2 (h^{-1})

Time(h)	Cr	Mn	Co	Ni	Pb	Cd	Zn	Cu
1	265	861	316	241	558	238	125	13
2	94	428	138	122	494	133	68	5
4	49	234	60	59	179	53	33	3
8	14	71	24	20	71	17	14	0.62
16	0.08	11	4	4	17	20	0.41	0.46
24	0.02	17	5	5	15	3	2	0.92

Table 3. The leaching intensity values (I_i) of Mn, Ca, Cr in leachate at pH=4 and pH=7 (h^{-1})

	pH=4						pH=7					
Time(h)	1	2	4	8	16	24	1	2	4	8	16	24
Cr	36	28	16	8	3	4	32	18	12	6	1	2
Mn	0.091	0.039	0.019	0.009	0.003	0.002	0.082	0.034	0.016	0.009	0.003	0.002
Ca	5	3	2	0.64	0.43	0.38	1.45	1.38	0.57	0.36	0.24	0.12

Most metal oxides dissolve in acidic solutions. The pH values of the leachate from all examined fly ash samples are alkaline, ranging between 10 and 12 using distilled water. The high pH causes the precipitation of metals ions, as:

$$M^{2+} + 4OH^{-} \rightarrow M\,(OH)_2 \Swarrow\ + 2H_2O$$

in which M refers to metal ion and the symbol ⇙ indicates precipitation of the metal hydroxide as a results of the chemical reaction [15-16]. Therefore, when the pH of the fly ash is lowered due to rain or any other reason, the metal ions will not precipitate and will remain free in solution; consequently, there is some risk of contaminating surface and groundwater via leaching. The greater the acidity of the solution, i.e., the lower its pH, the larger the I_i of the metals. Therefore, the leaching intensities (I_i) of Co, Ni, Pb, Cd, Cu and Zn in fly ash are not determined for pH=4 and pH=7. The leaching intensities (I_i) of Ca, Cr and Mn with the time in leached solutions of pH 4 and 7 are shown in Table 3. The leaching of these elements from outdoor ash would be expected in regions subject to acid rain. The average pH of rainwater has been observed to be about 6.7 which were in the alkaline range in the Yatağan Basin. According to the study [17], 85% of all the measured rain samples showed the pH of rainwater to be in the alkaline range as compared to a pH 5.6 for cloud water at equilibrium with atmospheric CO_2. Therefore, the leaching of these metals may be related to rain water in the area, it is possible that under groundwater sources could be contaminated by toxic metals, such as Cr, leached from the fly ash deposited by the Thermal Power Plant.

According to average and standard deviation values, the leachability of elements under different pH conditions may be divided into four classes depending on the I_i value. Leachability would be expected to be high for $I_i \geq 200$, medium for $55 \leq I_i < 200$, weak for $0.1 \leq I_i < 55$, and very weak for $I_i < 0.1$(Table 4). The leachability of Mn is high when pH value is 2. The leaching intensity (I_i) values of Mn decrease as leaching time increases, whereas, for pH values for 4 and 7, the leachability of Mn is very weak and remains so even as leaching time increases. While there was a comparatively high concentration of Mn in the solid phase of fly ash (40 μg/g), there were the much lower Mn concentrations in the leaching solutions, which shows that the Mn in fly ash has considerably less mobility levels when pH values is 4 or 7. But, Mn is very highly mobile for pH values of 2 condition, as is clearly demonstrated in the present series of leaching tests and analyses. Paul et al., [18] indicate that Mn is leached completely from Yatağan fly ash: expect of the carbonates and simple oxides. Removal of Mn from solution is probably associated with the precipitation of $Mn(OH)_2$.

The leaching intensity (I_i) values of Ca are low, and analyses indicate that Ca should be placed in the weak leaching intensity class for pH values of 4 and 7. Yatağan fly ash exhibited high S (sulfur) concentrations and the concentrations in the solid phase increased by approximately 50%, following leaching. Ca appeared in the form of soluble $CaSO_4$, with only 18% dissolved [18]. We consider that values, leached naturally, are important for the environment. According to literature data [17-19-20], in most rains of the world, it is cations of calcium that are mainly responsible for sulfate neutralization. The source of calcium can be the dust-rich local environment and the surrounding limestone environment. This study reflects that another probable source of calcium may be the calcium remaining in the fly ash after the coal burning process in Yatağan Basin. Calcium has the highest contribution to both total ion concentration (55 %) and to total cation concentration (79 %) in rain water in this area [17].

Table 4. Leaching intensity class.

	T (hour)	***1h.***	***2 h.***	***4 h.***	***8 h.***	***16 h.***	***24 h.***
pH:2	High $I_i \geq 200$	Mn, Co, Ni, Pb, Cd, Cr	Mn, Pb	Mn			
	Medium $55 \leq I_i < 200$	Zn	Co, Ni, Cd, Zn, Cr	Pb, Co, Ni	Mn, Pb		
	Weak $0.1 \leq I_i < 55$	Cu	Cu	Cd, Cr, Zn, Cu	Cr, Co, Ni, Cd, Zn, Cu	Ni, Cu, Zn, Mn, Co, Pb, Cd	Ni, Cu, Zn, Mn, Co, Pb, Cd
	Very weak $I_i < 0.1$					Cr	Cr
pH:4	Weak $0.1 \leq I_i < 55$	Cr, Ca	Cr, Ca	Cr, Ca	Cr, Ca	Cr, Ca	Cr, Ca
	Very weak $I_i < 0.1$	Mn	Mn	Mn	Mn	Mn	Mn
pH:7	Weak$0.1 \leq I_i < 55$	Cr, Ca	Cr, Ca	Cr, Ca	Cr, Ca	Cr, Ca	Cr, Ca
	Very weak $I_i < 0.1$	Mn	Mn	Mn	Mn	Mn	Mn

The leaching intensity (I_i) values of Cr are in the weak leaching intensity class for the pH=4 and pH=7 studies, whereas, I_i values are classified in the high leaching intensity class for pH=2 studies. The I_i values for Cr in fly ash reached a maximum of 265 h^{-1} after the first hour of the leaching tests for pH=2. The increase in the leachability of the metal at the lower pH levels can be attributed to an increase in the intensity of the chemical attack on the ash mineral phases that contain most of this element [21-22-23]. The leaching intensity (I_i) values of Cr in fly ash suddenly decreased with time for pH=2. Adsorption on mineral surface is a probable reason for the low amounts of the metal released.

In general, Mn and Pb show the highest leaching intensity and Cu the lowest for pH=2. The leachability of Mn, Co, Cr, Ni, Pb, Cd and Cr are in the high leaching intensity class, whereas the leachabilities of Zn and Cu are in the medium leaching intensity class and weak intensity class, respectively, in the first hour of leaching time. The time dependence of waste-ash leaching indicates that Zn is bound at the surface of fly ash particles, rather than as a dopant [24]. Copper is found as chalcopyrite in the whole colas and may be associated with iron oxides in the fly ash [18]. The leaching intensity values of toxic metals such as Cd and Pb are high in the pH=2 tests. Therefore, greater leaching of toxic elements from outdoor fly ash can not be expected in regions subject to rain water. But fly ash can be often mixed with daily rubbish that contains a large amount of organic matter can be decomposed by microbial action into various organic acids. This would lower the pH of nearby water bodies, which would again promote leaching of toxic metals. In this regard, ash layers on the bottoms of ash ponds may continue to leach when the pH value drops in the surrounding environment.

Leaching Time

The changes of the leaching intensity values of elements from fly ash with time in solutions of pH=2.0 are listed in Table 3. The linear regression correlation (r) between the leaching intensity values of the metals and the leaching times were statistically tested and the correlation coefficients for the elements were calculated. The correlation coefficients between the leaching intensity values of the metals and the leaching time were determined to be very high. These values are given in Table 5. The correlation coefficients are in following order: Cr > Pb > Mn > Cd > Co > Cu. This order of metals may be related to leaching intensity values. Cr, Pb and Mn show the high leaching intensity values, and Cu has the lowest leaching intensity values. On the other hand, the trends for these metals can be identified as gradually descending with increasing leaching time. This phenomenon has shown that different metals may have similar trends. This situation may be explained by the solubility of metal complexes. A low pH value of the leachant always favors the formation of mobile metal species and also decreases the ability of metal ions to form surface complexes with hydrous oxides and silicate present in the residues [25].

Table5. The correlation coefficients for metals leaching intensity values and leaching time

	Cr	Mn	Co	Cu	Zn	Pb	Cd
r	0,9265	0,8302	0,7747	0,6916	0,8510	0,8896	0,8171

Different elements may have different leaching intensity classes. The difference of leaching intensity class of different elements is related mainly to chemical properties and the available concentrations of the elements. Functional oxidized group (SiO_2, Al_2O_3 and Fe_2O_3) are present on the surface of the fly ash, and there is chemical bonding between these groups and metallic ions on the surface of the fly ash (Bayat, 2002). The hydrolytic interaction of metals on the surface of a fly ash particle in the acidic solutions can be presented in an idealized manner as follows:

$$(\mathrm{Si,Al,Fe})\text{-}\mathrm{OM} + \mathrm{H_3O^+} \boxtimes (\mathrm{Si,Al,Fe})\text{-}\mathrm{OH} \ldots \mathrm{H\text{-}O\text{-}[M(OH_2)_3]^{2+}},$$

Where M represents the metal ions. The solubility of $H\text{-}O\text{-}[M(OH_2)_3]^{2+}$ varies in accordance with the type of metal. For example, in the case of a hydroxide, the solubility of Cd^{2+} and Pb^{2+} was 1.1×10^{-2} and 710 mg/l, respectively [26] .

Conclusion:

- Different elements have different leaching behaviors because of differences in elemental properties and concentrations in various samples.
- The initial pH value of the solution and the leaching time strongly influence the leaching behavior.
- The mobility of trace elements from fly ash depends not only on the metals' concentration and mode of occurrence but also on the chemical conditions associated with the leaching process, e.g., the pH of the leaching solutions used.
- It is considered that the release of metals from a particular fly ash is a fast and sometimes complex process, strongly dependent on the pH. The leaching intensity values of the metals are very high after 1 hour. The trends for these metals can be identified as gradually descending with increase leaching time.
- Fly ash disposal in the terrestrial environment possibly influences the quality of groundwater and surface water. The release of metals confirmed in the batch leaching test implies that the influence from ash disposal would pose a long-term environmental problem.
- Mn and Pb show the highest leaching intensity and Cu the lowest for pH=2.
- The order of the correlation coefficients for the leaching intensity values of the metals is Cr>Pb>Mn>Cd>Co>Cu.
- The leachabilities of toxic metals such as Cd and Pb are found to be in the high leaching intensity class in the first hour of leaching time.
- The higher the propensity for leaching, the quicker the metal gets into solution.

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PLANTS, BRYOPHYTES, EPIPHYTIC MICROORGANISMS AND FUNGI AS BIOINDICATORS OF AIR POLLUTION

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The paper presents the preliminary studies that have been carried out in the pilot area from Cişmigiu Park, Bucharest, Romania, in the framework of the Life-Environment Project LIFE02ENV/RO/000461 started in 2006. The park is treated as a complex of ecosystems. In this paper we integrated biological data. Our data will be correlated with pollution and climatic data. The initial objective of our in situ research (passive methods) is the identification of plants, bryophytes, epiphytes and macromycetes as bioindicators of air pollution from Cişmigiu Park.

We established the plant and bryophyte species highly sensitive to particular air pollutants that show specific responses to pollution effects. Bacteria, fungi and yeast had been identified on leaves as epiphytes. Taking into account fluxes of UV radiation and pollution, the most resistant are those with capsules and pigments as protectors. Yeasts are also representatives as bioindicators of pollution.

These data can show the increasing awareness of the effects of pollutants on plants, bryophytes, epiphytic microorganisms and macromycetes, and their potential as biomonitors /bioindicators of air pollutants in the terrestrial environment. Biological data are used to estimate the environmental impact and potential impact on other organisms including humans.

The response of plants to elevated concentrations of air contaminants is modified by other environmental factors and by the physiological status of the plant. Monitoring the plants directly assesses the integrated effects of these factors and contamination.

It is very important for the accumulation of air quality data for the analysis of standards, interrelating effects, source reductions and general air pollution control. All results are included in the data base of the Environmental Ministry for assessment of the impact of air pollution on human health and conservation of biodiversity. This enables the formulation of policies and regulations necessary for the protection of humans, animals and plants.

Key words: *Romania, bioindicators, air pollution, plants, bryophytes, epiphytic microorganisms*

Introduction

Air pollution from the most important emission sources (*i.e.* industrial plants, power plants, domestic heating and especially motor traffic) is a major environmental problem in cities.

Organisms, populations, biocoenoses and ecosystems are subject to biotic and abiotic stress factors: climatic fluctuation, prey-predator relationships, parasites, diseases, competition within and between species, *etc*. Such stress factors are vital at every level of biological organisation, all living organisms being adapted to a greater or lesser extent to these stressors. In recent centuries, stress factors have reached new quantitative and qualitative dimensions (Markert and Oehlmann, 1998). Entirely new substances that did not previously exist have been released into the environment by the activities of human-beings (*e.g.* heavy metals, organic compounds, gases, natural radionuclide) in quantities exceeding the tolerance limits of the organisms both in respect of adaptation and evolution. They add to the impact of natural stressors or act in combinations of their own having synergetic/antagonistic effects.

There is no single, well defined causal factor, or simple combination of one or two or even three causal factors that can explain all the changes in any ecosystem (Shütt1999).

When attempting to assess the impact of air pollutants on individual organisms/species or group of species, or whole ecosystems, the following questions are frequently posed:

1. what is the current status of the species or ecosystem?
2. what is the current trend in the status of the species or ecosystem?
3. what physical and biological methods are really available to conduct assessment?

Biological methods: any exposure to a stress by an organism or community of organisms whose presence or other easily measured attribute can be assessed either qualitatively or quantitatively (Tingey, 1989). Biological methods that include bioindicators show the presence and absence of the stress and biomonitors can provide additional information about the intensity of stress (Schütt P. 1989, Tingey D.T. 1989, Mulgrew A. & William P. 2000). Bioindicators are organisms or communities of organisms which react to environmental effects by changing their vital functions and/or their chemical composition, thus making it possible to draw conclusions on the state of their environment (Arndt *et al.* 1987). Bioindicators are grouped into accumulation indicators and response indicators. **Accumulation indicators** store pollutants without any obvious changes in their metabolisms. **Response indicators** react with visible symptoms of damage.
Accumulation indicators can react as response indicators when the amounts of harmful substances exceed their carrying capacity (Anderson R.I., 1989; Kowarik I., 1990).

Biomonitoring is divided into passive and active. **Passive (*in situ*) biomonitoring** is the use of organisms, populations, which are natural components of the ecosystem and appear there. **Active biomonitoring** includes all methods which insert organisms under controlled conditions into the site to be monitored. Environmental bioindicators, represent a complementary tool for environmental monitoring systems, and could also overcome some of the shortcomings associated with the direct measurements of pollution.

Biomonitoring (*i.e.* monitoring the state of the environment through the performance of living organisms - bioindicators) directly describes the impacts of environmental pollution on organisms, and can potentially detect the long-term exposure of a site to environmentally harmful chemicals. In addition, bioindicators also provide an overall picture of the impact of environmental factors that often cannot be detected by measuring even a wide range of physiochemical variables. Bioindicators can also be used to measure the cumulative impact of different types of environmental pressure, *e.g.* air pollution emitted from a range of emission sources (Sharpe P., 1989; Tingey D.T., 1989).

Air pollution from both local and distant sources have impacts on the environment in the form of dry and wet deposition, and the spread of pollutants is dependent on the height they reach in the atmosphere, their particle size and on climatic factors.

Leaves are colonized by bacteria, fungi and algae which are called epiphytes. Microbiology of phyllosphere is depending on plant species, age of leaves (immature, mature, senescent) season and specific natural environment (Lindow S.E., Leveau J.H.J., 2002; Papen H. et al., 2002).

Air pollution is responsible by changing conditions in phyllosphere (habitat and microbial communities). In consequences fixation of nitrogen, degradation of waxes, acceleration of senescence and producing of growth regulators are changed (Papen H. et al., 2002). In addition air pollutants make plants more sensitive to pathogens and rate of growth become lower Large fluxes of UV radiation and ozone strongly influence epiphytic microorganisms on leaves. More resistant are bacteria, yeasts and fungi because of their black, pink and orange pigments. *Pseudomonas syringae* became UV tolerant because of plasmid rulAB genes which induce DNA repair (Sundin G.W., 2002; Sundin G.W., 2002). The aim of the paper is to find if microorganisms can be used as bioindicators of air pollution in Cismigiu Park situated in the center of Bucharest in the area with heavy traffic.

Because of poikilohidry and major dependence for water, the liverworts, hornworts and mosses are very sensible to polluting substances action and from this reason the bryophytes are used as bioindicators of pollution.

The bryophytes are used for indicating the presence of heavy metals elements and their concentrations gradients for many reasons:
- The species are widely distributed and can be collected all year.
- Lack of cuticle and a root system and obtain nutrients directly from atmospheric deposition;
- They have a good heavy metals bioaccumulation ability;
- Herbarium samples from same area can by compared with fresh material.

The bryophytes technique as a means of surveying atmospheric heavy metal deposition was developed in the late 1960’s (Rühling & Taylor, 1968).

The fungi have a key role in ecosystems functioning in special in nutrient cycles and the change in community structure of fungi can have a great impact on ecosystem. It is well know that in Europe the fungi diversity decrease due to deforestation, drainage, pollution, modern rational forestry practices and replacement of native tree species by exotics.

Material and Methods

There is a shortage of distributional data for plants available for Bucharest, and hence the first step has been to establish which potential bioindicators are present searching the literature and based on field observation. Site visits, comprising transects within the sites using both qualitative and quantitative sampling (animal and vegetation) to establish the major bio-indicator groups during the first year. The sampling points have been localised using GPS Garmin e-Trex Summit, and positioned so as to include samples from the marginal zone of the green space (and thus detect any impact of major roads) and from the core zone of the green space where such impacts should be less pronounced.

The next step will start with using a pH-metre, with an electrode for soil analysis; we will correlate the pollution levels with the pollutants concentration from chemical analysis of plant, bryophytes and epiphytes samples in a specialised laboratory. In addition, we will incorporate any pollution data furnished by our partners.

We will use the statistical tools for integrated data analysis of bioindicators and physical and chemical analyses provided by the project partners.

In the pilot area, we used the inventory of taxa based on the plant species, bryophytes and epiphytes, determining the bioindicator using passive methods, *in situ* analysis of the anthropogenic ecosystem (Cişmigiu Park). We have used the species composition methods, which characterise the presence and abundance of certain species. In this phase of the study we have based our approach on knowledge about bioindicator species using the literature and field experience.

The use of plants as indicators of air pollution has been studied over the last decades, especially in forests in European and non-European country. At the vegetation level, the aerial pollutants cause injuries, such as chlorosis and decline of the trees with loss of vitality but relatively low impact on mortality. Synanthropic vegetation in town and cities is an important subject of urban ecology. In fact a great deal of ecological evaluation of urban spaces is based on vegetation which serves as an indicator of environmental conditions and ecological processes.

Based on published data, Mucina (1990) concluded that Romanian botanists (Morariu I., 1943; Spiridon L., 1973) had made contributions to the syntaxonomy of ruderal vegetation and several researchers had contributed importantly to the present knowledge of urban vegetation in Romania. All papers mentioned described studies made on the periphery of the cities and towns and on sites with ruderal vegetation inside cities, but none focussed in parks with synanthropic vegetation (plant species which occur primarily associated with human activity) comprising ruderals (plant species which occur on disturbed and waste ground), planted and stress-tolerant species (Grime et al., 1988).

We recorded the plant species, separating them into major groups (trees, shrubs and herbaceous). Following the field observations from June to November, bioindicators were noted.

For trees and shrubs, we noted the progression of the symptoms which are almost invariably the first indicators that something is wrong with the individual organism or the ecosystem in which the individuals live. Symptoms (changes in the physical appearance or the physiological function of the host organism itself) are the principal foundation for detection and diagnosis of disease and dysfunction in essentially all living organisms:

- transparency of tree crown (loss of crown density) – it occurs under a wide range of edaphic and climatic conditions

a. premature leaf-fall –in many broad-leaf trees
b. Changes in leaf size and shape – decreased leaf size, sometimes in combination with a lower leaf frequency and distortion of normal leaf form, especially close to distal ends of leading shoots.
c. Changes in leaf position and branching habit – normal, healthy tree crowns are characterised by a dense and very uniform distribution of leaves over both the peripheral and interior parts of the crown.

- Visible leaf-injuries, dust covering the leaves
- Attack by defoliating invertebrates.

For herbs, we observed species population distribution in a small area, together with vegetative or non-vegetative spread.

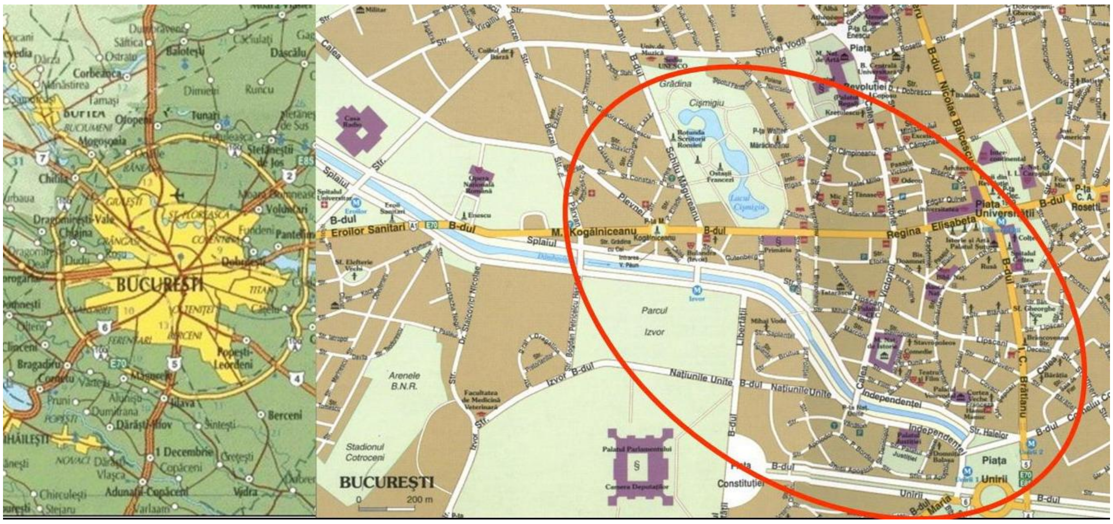

Figure 1: The pilot site map (Cişmigiu, Izvor, and Unirii Parks)

Mature leaves were cut from *Cornus mas* trees situated both at the edge of Cişmigiu Park with heavy traffic and in the area with no traffic. They were put in sealed polyethylene bags and send to microbiology laboratory. After 30 minutes leaves were washed five time with sterile distilled water to remove casual inhabitants. Then one gram of fresh weight of leaves was homogenized with sterile quartz and 9ml of sterile distilled water. The dilutions were inoculated on tryptone yeast extract agar for bacteria, potato dextrose agar with streptomycin sulfate for yeasts and filamentous fungi. After 48h respectively 10 days bacteria, yeasts and fungi were counted and identified.

Studies on bryophytes have been made as multi-element investigation and a few have been restricted to a particular metal. Because in Bucharest have been monitorised the Pb concentration in air, in last 3 years (2004-2006), we select this element for biomonitoring.

For Bucharest we chose to use in situ sampling and if in 2007 we don't have expected results we setting a new biomonitoring system with using transplanted species (table 1).

In metal deposition biomonitoring, species selection criteria include the availability of the species, its tolerance, its bioaccumulation characteristics and ease of sampling (Wolterbeek, Bode and Verburg, 1996). The use of epigeic mosses (mosses growing naturally on the ground) has been recommended in Scandinavia for assessment of heavy metal deposition on a regional scale (Steinnes et al., 1993). However, element concentrations in carpet forming mosses may be elevated by soil-blown dusts. Such contamination and possible misinterpretation of results would be particularly heightened in seasonally arid countries (Ruhling, 1995).

A small number of studies have been carried out investigating the effects of anthropogenic emission on fungi (Fellner, 1989; Pyatt, 1992; Fellner and Pešková, 1995; Adriana Pop et al., 1997; Petkovšek et al., 2003; Rudawska et al, 2003). Fruit bodies of fungi were collected from the whole area of park, from June to November every month. Only fruit bodies aboveground were considered. Reference fruit body specimens was conserved in order to be introduce, in near future, in mycological collection BUCM of the Institute of Biology Bucharest.

Results and discussions

The natural vegetation had mainly disappeared, being replaced by planted species (especially trees brought from China, Japan, America, *etc*). Remains of the natural vegetation adapted to the modified conditions of the city (either fertilisation or lack of the nutrients, changes in soil pH, increased temperature, *etc*.) because of the pollution.

Where park maintenance work (usage of fertilisers, irrigation/watering, sowing *etc*) is not applied, the vegetation cover in all three parks becomes very much degraded, with large expanses of bare ground.

In the centre of Cişmigiu Park were planted *Viola* x *wittrockiana and Calendula officinalis* and sown *Lolium perenne, Poa pratensis, Festuca arundinacea* –all introduced for the park's aesthetic. In areas by fences, under the trees, the herbaceous layer is very open with much bare ground but rich in ruderal species when compared with the sown areas where the dominant species are few, and derived from seed-mixtures used by the park administration. The herbaceous vegetation is also sparser both under the trees where the competition for light is strong and where trampling is intense.

Due to trampling, the seed dissemination of annual *Polygonum aviculare* is intense, young and small individuals covering the bare ground, offering conditions for other seed plant establishment and survival.

During the autumn, when the environmental conditions are more suitable for plantlife, late flowering and individuals with vegetative spread (clonal plants) were observed occupying the bare soil created during summer. In "hidden" less trampled areas, among trees and soil poor in nutrients had a largely ruderal vegetation: *Arctium minus, Atriplex patula, Brassica oleracea, Capsella bursa-pastoris, Chelidonium majus, Cirsium vulgare, Conyza canadensis, Lamium album, Malva neglecta, Solanum nigrum, etc.*

Alongside ruderal vegetation, some wild species with wide distribution were brought into the park by wind and birds*: Daucus carota, Typha latifolia, etc.*

Table 1: Plant species list from Cişmigiu Park

Species	**Bioindicators**
Trees and shrubs	
Acer platanoides	Field study - Visible injuries
Acer pseudoplatanus	Known bioindicator - high concentration ozone response
Acer tataricum	
Aesculus hippocastanum	Field study - Visible injuries
Ailanthus altissima	Known bioindicator - Heavy metal bioaccumulator
Amygdalus communis	
Berberis julianae	
Betula pendula	Known bioindicator - Heavy metal bioaccumulator
Buxus sempervirens	
Carpinus betulus	
Catalpa bignonioides	Field study - Visible injuries
Celtis australis	Known bioindicator - Heavy metal bioaccumulator
Cornus mas	
Cornus sanguinea	
Corylus colurna	
Cotoneaster simonsii	
Forsythia europaea	
Fraxinus americana	
Fraxinus excelsior	Known bioindicator - Heavy metal bioaccumulator
Hibiscus syriacus	
Juglans regia	
Parthenocissus tricuspidata	
Paulownia tomentosa	
Picea glauca	Known bioindicator - Heavy metal bioaccumulator
Pinus sylvestris	Known bioindicator - Heavy metal bioaccumulator
Quercus cerris	Field study - Visible injuries
Quercus robur	Field study - Visible injuries Known bioindicator - Heavy metal bioaccumulator
Quercus rubra	

Table 1: Cont.

Rosa canina	
Rubus caesius	
Salix babylonica	
Symphoricarpus albus	
Taxus baccata	
Thuja orientalis	
Tilia cordata	Field study - Visible injuries, dust accumulation on leaves Known bioindicator - Heavy metal bioaccumulator
Tilia rubra	
Tilia tomentosa	
Ulmus glabra	
Ulmus minor	
Viburnum rhytidophyllum	
Herbaceous	
Achillea millefolium	Field study – good population spread in autumn Known bioindicator - Heavy metal bioaccumulator
Agrostis stolonifera	
Arctium minus	
Atriplex patula	
Bellis perennis	
Brasica elongata	Known bioindicator - Heavy metal bioaccumulator
Brasica oleracea	
Calendula officinalis	Cultivated
Capsela bursa-pastoris	
Carduus acanthoides	
Carex polyphylla	
Carex praecox	
Carex stenophylla	
Chelidonium majus	
Chenopodium album	
Chrysanthemum leucanthemum	
Cichorium intybus	
Cirsium vulgare	
Convolvulus arvensis	
Conyza canadensis	
Crocus flavus	
Cynodon dactylon	
Dactylis glomerata	
Daucus carota	
Erigeron annuus	
Euphorbia cyparissias	
Festuca arundinacea	
Festuca rubra	Known bioindicator - Heavy metal bioaccumulator
Fragaria vesca	

Table 1: Cont.

Galium aparine	
Geranium pusillum	
Geum urbanum	
Glechoma hederacea	
Hedera helix	Field study – good spread on trees and soil
Heleborus sp.	cultivated
Hypericum perforatum	
Lactuca serriola	
Lamium album	
Lamium amplexicaule	
Linaria vulgaris	
Lolium perenne	Cultivated, Field study - good population spread in autumn
Malva neglecta	Known bioindicator - Heavy metal response
Medicago sativa	Known bioindicator - Heavy metal response
Myosotis arvensis	
Oxalis corniculata	Field study - good population spread in autumn
Plantago lanceolata	
Plantago major	
Plantago media	
Poa annua	
Polygonum aviculare	Field study - good population spread in autumn
Potentilla reptans	Field study - good population spread in autumn
Prunella vulgaris	
Ranunculus repens	Field study - good population spread in autumn in irrigated areas
Rorippa pyrenaica	
Rumex crispus	
Rumex obtusifolius	
Setaria pumila	
Setaria viridis	
Silene vulgaris	
Solanum nigrum	
Stellaria media	
Taraxacum officinale	Field study - good population spread in autumn
Tragopogon orientalis	
Trifolium pratense	Field study - good population spread in autumn Known bioindicator - Heavy metal response
Trifolium repens	Field study - good population spread in autumn
Typha latifolia	Field study – few wild individuals
Verbena officinalis	
Veronica arvensis	
Viola arvensis	
Viola x wittrockiana	

Photo 1: Cismigiu Park: dry herbaceous layer (up left), *Aesculus hippocastanum* injuries (up right), bare soil (down left), specialist taking samples (down right)

Photo 2: Defoliators attack (upper photos) on *Quercus* (left down) and dust on *Tilia* (right down) species

The total number of heterotrophic bacteria, yeasts and filamentous fungi were decreased on leaves belong to trees situated near the road with heavy traffic (table 2). More sensitive were yeasts and less sensitive were filamentous fungi.

Table 2. Total number of microorganisms on *Cornus mas* leaves(CFU/g fresh weight)

Type of microorganism	*CFU/g fresh weight*	
	Not polluted area	Polluted area
Heterotrophyc bacteria	$2{,}4x10^6$	$1{,}8x10^4$
Yeasts	$4{,}2x10^5$	$1{,}0x10^2$
Filamentous fungi	$1{,}4x10^4$	$1{,}9x10^3$

The decreasing of total microbial number is a consequence of the fact that leaves absorbed high quantities of heavy metals like lead, cadmium and copper. Yeast and some bacteria are sensitive to lead but depositions of all metals increase microbial sensitivity.

Even number of fungi is not very much decreased it was noticed change in fungal population structure (table 3)

Table 3. Fungal and yeasts populations on *Cornus mas* leaves (CFU/g fresh weight)

Fungal/yeast	*CFU/g fresh weight*	
	Not polluted area	Polluted area
Acremonium sp.	12	2
Alternaria alternata	55	54
Aureobasidium sp.	18	19
Botrytis sp	18	16
Cladosporium cladosporioides	28	28
Cladosporium herbarum	32	32
Cryptococcus sp.	10	0
Penicillium sp.	18	16
Rhodotorula sp.	12	1
Stemphylium sp.	10	2
Torula sp	14	3
Trichoderma viride	10	0
Ulocladium sp	7	3

It was noticed a strong decrease of the following fungal genera: *Acremonium, Rhodotorula, Torula, Stemphylium Ulocladium*; *Cryptococcus and Trichoderma* had been not identified. Most resistant fungi in polluted area are: *Alternaria alternata, Aureobasidium sp., Botrytis sp., Cladosporium cladosporioides, Cladosporium herbarum and Penicillium sp.* Reducing population of fungi which colonize *Cornus mas* leaves could be explained by sulfur dioxide antifungal activities as also noticed Yang et al (2001).

More then one century ago, for Cişmigiu area is indicated *Marchantia polymorpha* subsp. *ruderalis* Bischl. et Boisselier. The research activities concerning liverworts of Bucharest were made since 1998 to present.

Fruit bodies of 18 species of macromycetes were found in studied area. The most abundant species found in Cismigiu is *Coprinus micaceus* (Bull.: Fr.) Fr. and *Ganoderma applanatum* (Pers.) Pat.

The number of species and the number of fruit bodies of mycorrhiza forming fungi found was very low. From 18 species only three species was mycorrhiza-forming fungi and for each species was found only one fruit body. According to Fellner and Pešková (1995) one of the myco-bioindication methods, myco-indication through mycocoenoses, use the ratio of mycorrhiza-forming fungi to all macromycetes within the study area to evaluate the degree of pauperization of ectomycorrhizal mycocoenoses. In order to correctly estimate the ratio of mycorrhiza forming fungi and the other fungi further investigation are needed, because the formation of fruit bodies depend on the abiotic factors, especially on soil humidity and temperature, and because the fruit bodies for some species last just several hours or days. For this reason the number of mycorrhiza-forming fungi collected in this short period can depend of soil humidity and temperature more than of atmospheric pollution.

Several of fungus species can be considerate as potential bioindicators, but for confirmation heavy metal concentration analysis need to be done: *Ganoderma applanatum* (Pers.) Pat. which can long-term monitor/accumulate atmospheric pollutants according with the research of F. B. Pyatt (1992). The high abundance of *Coprinus micaceus* (Bull.: Fr.) Fr. fruit bodies can have as a cause the fact that this species is tolerant of pollution. In support of this fact are the occurrences of this species in other places in Bucharest and other towns near streets. One of the reasons can be that this species can accumulate heavy metals.

Conclusions

Humans affect the city by introducing species for aesthetic and amenity reasons. Many other plant bryophytes, epiphytic microorganisms and fungi species “creep” into the city. Whether they survive from the former forests that once covered the same place instead of concrete buildings and streets, or they spread into an environment created by human beings for themselves.

The combination of natural stress factors over-intensified in the city (higher temperature because of heat-reflecting asphalt and concrete, less precipitation, *etc.*) and intensification of pollution cause the decrease of plant resistance to the stress factors and their eventual death. The specific richness clearly decreases and plant populations further reduce their distribution areas already affected by fragmentation (due to trampled trails made by humans as short-cuts to the engineered asphalt paths).

Marchantia polymorpha *L. subsp.* ruderalis *Bischl. et Boisselier can by used starting with 2007 to metal deposition biomonitoring, especially Pb (♂ - Cişmigiu Park, 3.IV.2004, leg. & det. Ştefănuţ S. [BUCA B2937], ♂ - 6.VII.2005, leg. & det. Ştefănuţ S. [BUCA B317]).*

On polluted area take place a reduction of the microorganisms’ populations which colonize *Cornus mas* leaves. Yeast and fungal diversity is reduced in polluted area and we can consider yeasts as bioindicators of air pollution in urban area. Most resistant fungi to air pollution in urban area are: *Alternaria alternate, Cladosporium cladosporioides, Cladosporium herbarum* and *Penicillium sp*

Treating Cişmigiu Park as a complex of ecosystems, it is a manmade simplified complex for aesthetic and amenity reasons. The density of plants, bryophytes, epiphytic microorganisms and fungi is decreasing with the increasing of the density of human beings. Wildlife (plants and animals) in the cities is governed by human activity.

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IMPORTANCE OF RAPID MIXING TIME ON SLUDGE DEWATERING PROPERTIES

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The effect of rapid mixing duration on floc growth, breakage and regrowth and dewaterability in the flocculation of a highly turbid (1000 NTU) kaolin suspension with aluminium sulfate and a polyaluminium chloride coagulant was investigated using a dynamic monitoring device (PDA 2000). Nine different rapid mixing durations (0-300 s) at 400 rpm were applied to the model suspension, followed by slow stirring at 40 rpm for 10 min. Flocs were broken at 400 rpm for 10 s, then the mixing rate was reduced to 40 rpm for another 10 min to allow the regrowth of ruptured flocs. For both coagulants it was observed that floc size decreased with increasing rapid mixing time, leading to worsening turbidity removal. The break-up of flocs were irriversible. Floc strengths increased to some certain rapid mixing time, for longer rapid mixing times no significant change was observed in floc strengths. Dewaterability, in terms of CST, was found to be improved with increasing rapid mixing duration (decreasing floc size).

Keywords: dewatering; flocculation; hydrolysing coagulant; rapid mix; capillary suction time

Introduction

Mixing is an essential process in particle aggregation when a rather rapid growth rate (than Brownian diffusion) is desired. Uniform dispersion of the coagulant in order to provide contact with as many particles necessiates some form of intense agitation. Then the destabilised particles are allowed to collide and grow into aggregates by applying a slower mixing rate. Rapid and slow mixing can either be achieved in stirred tanks or through hydraulic structures.

Rapid mixing conditions have been shown to influence floc growth and structure. When the flocculation occurs via charge neutralisation mechanism, inadequate mixing may cause local overdosing of coagulant leading to local particle restabilisation. In sweep flocculation regime raw water solids gain a positively charged coating from the nucleation of positively charged hydrolysis products, which only exist for a very short time (~ 1 s) before transforming to the amorphous precipitate (Amirtharajah and Tambo, 1991). In this short time interval they must be dispersed throughout the suspension prior to arriving as neutrally charged $Al(OH)_3$.

It was claimed (Amirtharajah and Mills, 1982) that initial mixing conditions are not so important in the case of sweep flocculation, but this is not well established. On the contrary, recent studies have shown that rapid mixing is crucial to floc growth for sweep flocculation (Bache et al., 1999; Yukselen and Gregory, 2004b). Bache et al. (1999) claimed that the conclusion of Amirtharajah and Mills (1982) was a misconception, stemming from a focus on the quality of the settled water rather than on the nature of the floc (e.g. floc strength). They investigated the effect of rapid mixing on floc strength. To do this, they added the colloids 5 min after coagulation (simulating an extreme case of poor mixing) and concluded that the floc strength is significantly reduced compared with addition of the coagulant into the suspension with good rapid mixing. Yukselen and Gregory (2004b) studied the effect of rapid mixing time on growth, breakage and regrowth of kaolin flocs with alum and PACl coagulants. They found that floc size decreased and as a result residual turbidity increased as rapid mixing time increased.

Francois and Van Haute (1984) reported that the diameter of ruptured and regrown flocs decreases as the duration of rapid mixing increases. Francois (1988) reported that a rapid mixing time longer than the critical mixing time lead to a longer floc build-up time because of temporary decrease in floc growth. A rapid mixing time shorter than the minimum time required to build up flocculi (i.e., so called building units of flocs) also resulted in the same way.

There are also some other studies (Rossini et al., 1998; Kan et al., 2002a, 2002b) which concluded the same way that floc size decreases with increasing rapid mixing time.

Since mixing parameters have crucial effects on floc strength, size and structure they are closely related to sludge dewatering.

As a measure of ease for sludge dewatering (by means of water release) the CST test has been widely used since the method is cheap, easy to apply, and consist of a portable apparatus. Its application field is generally found in sludge conditioning with polyelectrolytes, and especially determination of optimum polyelectrolyte dose. General practice is that conditioning of metal hydroxide sludges with polyelectrolytes enhance dewaterability, mainly due to loss of intrafloc water (Knocke et al., 1993). A dose giving the lowest CST is taken as the optimum dose, and generally further polyelectrolyte dosing is found to give no significant improvement or worsening in dewatering (Lee and Liu, 2000, 2001; Wu et al., 2003). However, the situation might be different with metal hydroxide flocs due to the chemical nature of flocs and difference in flocculation mechanisms compared to polyelectrolyte conditioning.

In some cases it appears that flocs with more open structure are more readily dewatered (Waite, 1999). Lower density, porous flocs may be permeable to water for flocs of given mass, and significant flow could occur through floc as well as around floc. This suggests that better dewaterability may be observed as floc size increases (which is in the case with polyelectrolytes). On the other hand, this ignores the possibility that higher density structures may give faster dewaterability because of smaller floc size and reduced drag. Diminishing CST values with decreasing floc size were reported by Turchiuli and Fargues (2004). It is thought that larger size flocs consist of a package of solid particles and some water entrapped in the solid structure (intrafloc water). However, this water component may disappear or be significantly reduced when the size of flocs are smaller, which may give lower CST values as a sign of better dewatering.

There are many studies focusing on polyelectrolyte conditioning of sludges. However, very few studies on the dewaterability of sludges formed with only hydrolysing coagulants are present. It may be very useful to keep in mind that sludges conditioned with polyelectrolytes are priorly formed with hydrolysing coagulants which can be evaluated as building stones of polyelectrolyte flocs. Thus, dewaterability of polyelectrolyte conditioned sludges may be significantly affected by the properties of flocs formed with hydrolysing coagulants. This study aims to investigate the effect of rapid mixing duration on dewatering of sludges from the flocculation of highly turbid kaolin suspensions with alum and a PACl coagulant.

Materials and Methods

Suspension

Kaolin clay (Merck, Bole White) with a small amount of commercial humic acid (Aldrich) added to prevent destabilisation and slow coagulation of the kaolin particles due to Ca^{2+} in tap water was used as stock suspension. The kaolin+HA stock suspension was prepared as described by Yukselen and Gregory (2002a). For the flocculation tests, the stock suspension was added into 1-L jars filled with 800 mL tap water. The turbidity of suspensions used in all of the flocculation experiments was adjusted to give about 1000 NTU which was determined by WTW Turb 550 model turbidimeter.

Coagulants

Aluminium sulfate octadeca hydrate ($Al_2(SO)_4 \,.\, 18H_2O$; Merck) ‘alum’ was used. The salt was dried in oven at 103-105°C and dissolved in deionized water at a concentration of M/10. This alum stock solution was kept in refrigerator at 4-5°C.

A commercial polyaluminium chloride (PACl) product (Kemira Kemi AB, Helsingborg, Sweden) was used. This PACl coagulant, which was named as PAX-216 had a density of 1.35 g/cm^3, was supplied as an 8.1 wt % Al solution. This solution was used without any dilution.

Apparatus

The procedure of floc formation experiments was similar to those described before in a number of works (Gregory and Duan, 2001; Yukselen and Gregory, 2002a, 2002b, 2004a, 2004b) employing an on-line optical flocculation monitoring device (Photometric Dispersion Analyser – PDA 2000, Rank Brothers Ltd., Cambridge, UK) in modified jar-tests.

800 mL of synthetic suspensions were included in 1-L jars, each stirred with mixing units connected to a Flocculator 90 semiautomatic jar-test device (Kemira Kemwater, Helsingborg, Sweden). Sample from one jar was circulated at a flow rate of 25 mL/min. for dynamic monitoring of the state of aggregation through transparent plastic tubing (3 mm i.d.) via a peristaltic pump.

The PDA 2000 gives a useful Flocculation Index on the state of aggregation. The FI value is not an exact measure of the floc sizes, it can only be used as comperative information on floc properties under different aggregation conditions such as different mixing intensities and times, different coagulant types and doses, etc. However, the FI value was shown to be in good correlation with mean floc size and residual turbidity after sedimentation (McCurdy *et al*., 2004).

A capillary suction time device (Capillary Suction Timer, Type 304M, Triton Electronics Ltd.) was employed to measure the dewaterability of sludges.

Procedure

Standart jar tests were performed for flocculation. To determine the effect of rapid mixing duration; nine different rapid mixing times (0 – 300 s) at 400 rpm (G = 518 s^{-1}) were studied. After rapid mixing slow stirring was performed at 40 rpm (G = 16 s^{-1}) for 10 min for floc growth followed by a 10 s-400 rpm mixing to achieve the breakage of full grown flocs. Then, the stirring speed was reduced to its previous lower value for another 10 min to allow regrowth ruptured flocs. The G values were calculated following Mejia and Cisneros (2000), who used a similar jar test device, and represent average shear rates in the stirred suspensions

The state of aggregation was monitored dynamically with the PDA 2000 optical monitoring device in each set of jar test experiments.

At the end of each jar test the flocculated suspension was transferred into an Imhoff cone for settling. Volume of the settled sludge and residual turbidity of the supernatant were measured after 30 min and 2 hr settling periods. At the end of 2 hr settling, CST test was performed with the sludge samples.

All of the experiments repeated three times for reproducibility of data.

Results

The alum dosage giving the lowest residual turbidity and CST was taken as the optimum dose (6.75 mg/L as Al).

Floc formation, breakage and re-formation with alum and PACl

Nine different rapid mixing durations (0-300 s) at 400 rpm were applied to the model suspension to investigate the effect of rapid mixing time on floc formation, breakage and reformation, followed by slow stirring at 40 rpm for 10 min to allow the aggregation of destabilised particles. The full grown flocs were ruptured at a stirring rate of 400 rpm for 10 s, the mixing rate was then restored back to its value before breakage for another 10 min in order to achieve the regrowth of broken flocs. The results of dynamic monitoring is presented in Fig.1.

From Fig.1. it is seen that the plateau value is considerably higher for shorter rapid mixing durations; the largest flocs are formed with ‘no rapid mixing case’. Flocs formed after 5 s rapid mixing are larger than flocs formed after 10 s rapid mixing, however, all three rapid mixing conditions give nearly the same FI value for regrown flocs. Floc size gradually decreases for full grown, ruptured and regrown flocs with increasing rapid mixing duration; the longest rapid mixing duration, 5 min, always gives the smallest floc size. Floc break-up process was found to be irriversible for flocculation with alum.

Following Francois (1987), for the breakage and regrowth of flocs under cycled shear conditions Yukselen and Gregory (2002a) quantified a “strength factor”, a “recovery factor” and a “breakage factor” in terms of Flocculation Index. These can be written as:

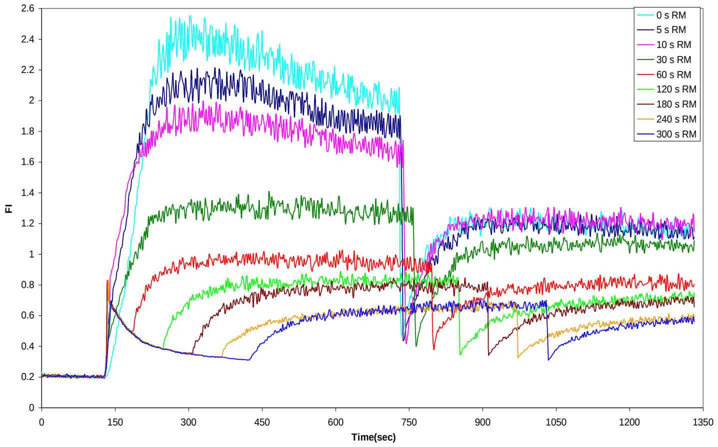

Fig.1. Floc formation, breakage and re-formation for different rapid mixing durations with alum.

Strength factor = $(FI_2 / FI_1) * 100$

Recovery factor = $[(FI_3 - FI_2) / (FI_1 - FI_2)] * 100$

Breakage factor = $(FI_1 - FI_2) / FI_1 * 100$

where FI_1 is the flocculation index for fully grown flocs, FI_2 is the value after breakage, and FI_3 is the value for regrown flocs.

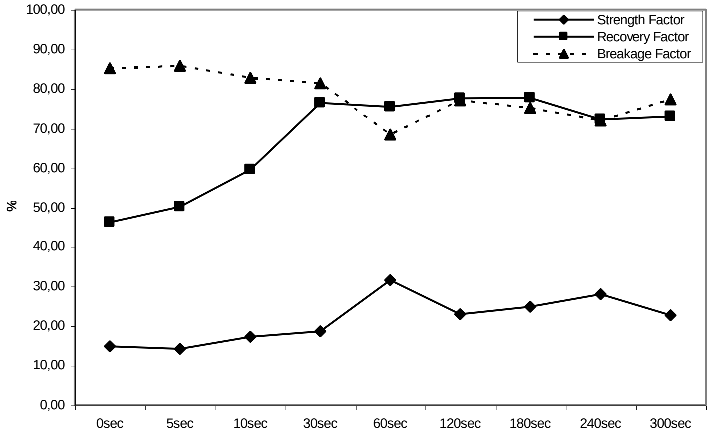

Fig.2. Strength, Recovery and Breakage Factors; investigation of the effect of breakage time with alum.

By examining Fig.2 it can be said that both floc strength and recovery factor gradually increase until 60 s rapid mixing, for prolonged rapid mixing no significant change is observed. Longer rapid mixing obviously does not improve floc strength and size recovery.

The relative flocs sizes are consistent with the residual turbidity measurement results, as presented in Fig.3. Broken flocs has the worst settlability and give the highest residual turbidity whereas unruptured flocs give the lowest in each case. Especially after 0 s, residual turbidity continuously increases as the rapid mixing time increases. A very interesting point is that the lowest residual turbidities were obtained with ‘no rapid mixing condition’ at formation, breakage and re-formation. This is likely related to the solids concentration in the suspension; e.g. the suspension is very concentrated that contact between particles and coagulant species readily occurs. This may not be observed with more dilute suspensions. It may seem that there are two optimum rapid mixing durations. A similar behaviour of two optimum rapid mixing durations were observed by Rossini et al. (1998) in their study with highly turbid suspensions flocculated with alum and ferric chloride. However, from Fig.1 a delay to reach the maximum floc size can be seen with ‘no rapid mixing case’. This delay is probably the time for surface charge neutralisation. Although flocs formed without rapid mixing are larger than flocs formed with 10 s rapid mixing, the former are not thought to be denser than the latter but looser in structure because it is known that lower agitation intensity causes larger and looser flocs and size effects overcome density effects (Gregory, 1997). An increase in residual turbidity is observed with 5 s rapid mixing, then a decrease with 10 s rapid mixing though the latter generally gives greater residual turbidity than ‘no rapid mixing case’.

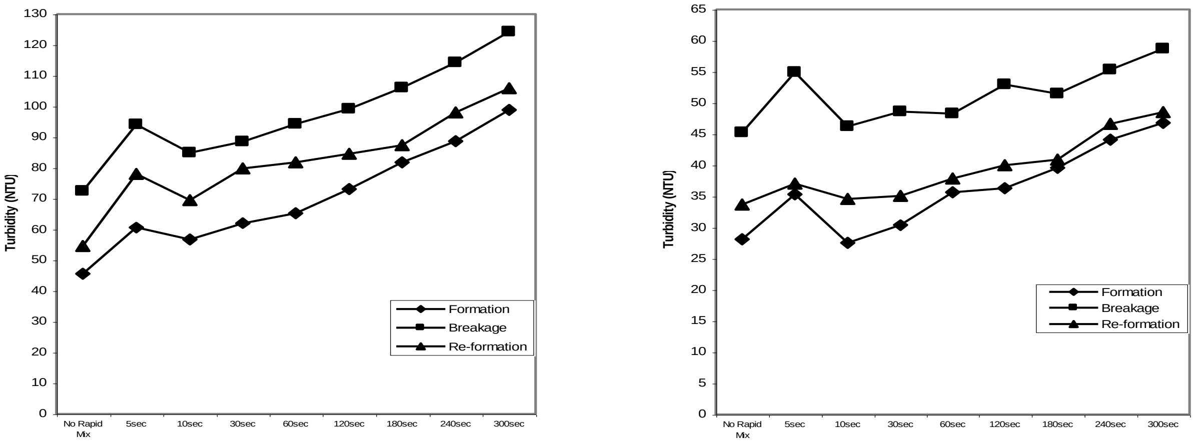

Fig.3. Residual turbidity at formation, breakage and re-formation after 30 min (left) and 2 hr (right) settling with alum.

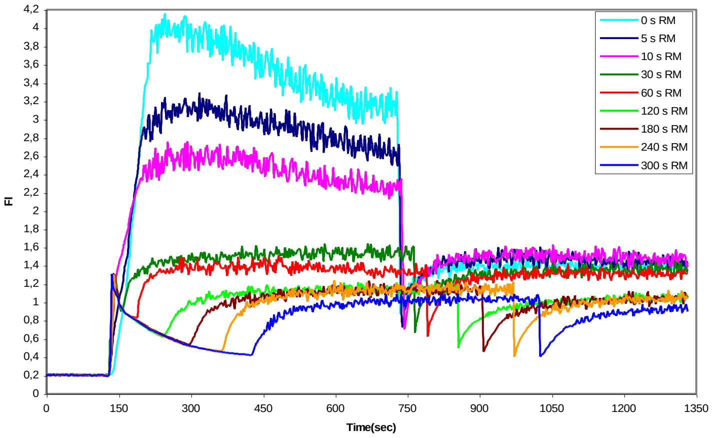

Fig.4. Floc formation, breakage and re-formation for different rapid mixing durations with PACl.

5 s rapid mixing gives larger flocs than 10 s, the latter gives the lower residual turbidities than the former. This shows that 10 s rapid mixing is the optimum; shorter durations (5 s) give poor mixing, longer durations seem to result in poorly settlable flocs and worsened turbidity removal.

When the same experiments were carried out with PACl very similar results to those with alum were found. Formation, breakage and re-formation curves under different rapid mixing conditions are shown in Fig.4.

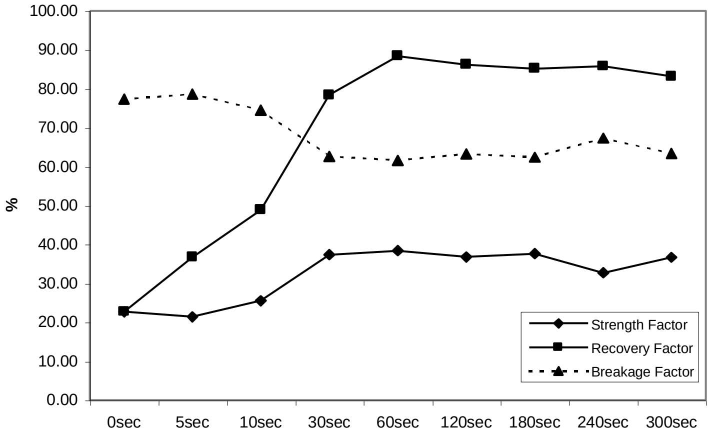

Fig.5. Strength, Recovery and Breakage Factors; investigation of the effect of breakage time with PACl.

As seen in Fig.4, similar to the results with alum, the largest flocs are formed without rapid mixing. Larger flocs formed with 5 s rapid mixing than with 10 s rapid mixing. On the other hand, with these three different rapid mixing durations floc sizes are reduced to nearly the same value through breakage process and after breakage flocs regrow to nearly the same size. As the rapid mixing duration increases floc size diminishes significantly, almost 3-fold reduction is observed when FI values of full grown flocs are compared for the shortest and the longest rapid mixing times.

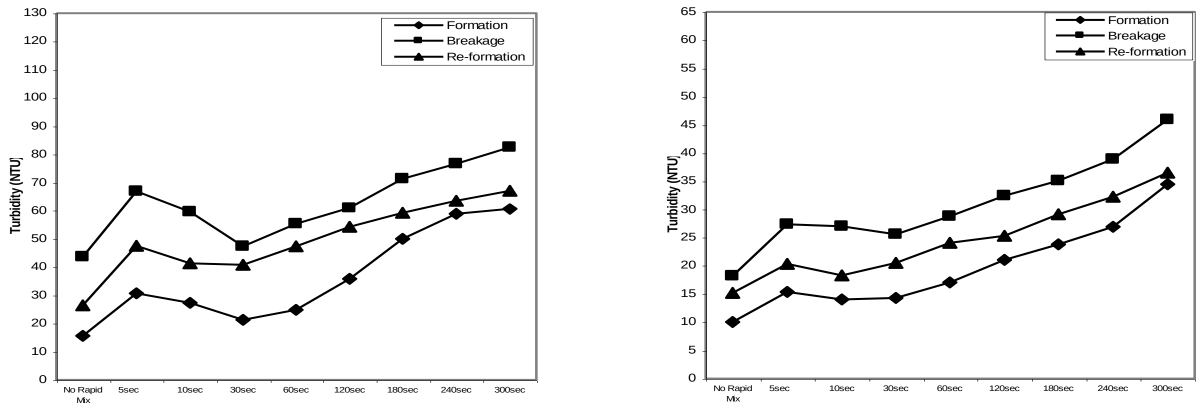

Fig.6. Residual turbidity at formation, breakage and re-formation after 30 min (left) and 2 hr (right) settling with PACl.

Again, as with alum, strength and recovery factors rise gradually with increasing rapid mixing time up to 60 s rapid mixing, however, longer rapid mixing does not significantly effect floc strength and size recovery (Fig.5). Obviously, as the rapid mixing time is increased and floc size is diminished as a result, the ratio of size reduction keeps the same value after some certain rapid mixing time. This is also valid for the size recovery.

The residual turbidity data in Fig.6 clearly show turbidity removal efficiency is significantly worsened after breakage and regrowth and also the rapid mixing duration is increased. Evidently, this indicates the irriversibility of floc breakage. Different from the case with alum, greater turbidity removal was observed with PACl, which is consistent with the finding that larger flocs were formed with PACl.

Dewatering of alum and PACl sludges

In Fig.7 a decreasing trend in CST with increasing rapid mixing duration is seen. The CST values of sludges of full grown and regrown flocs are closer to each other, which is probably due to the fact that as the time of rapid mixing increases the size difference between these two type of flocs decreases.

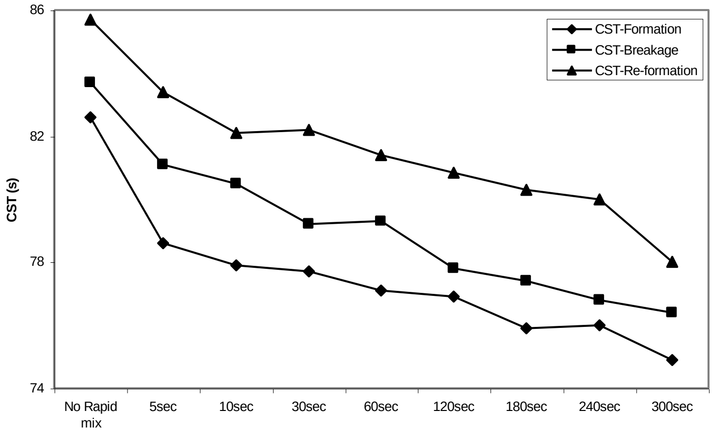

Fig.7. CST at formation, breakage and re-formation for different rapid mixing times after 2 hr settling with alum.

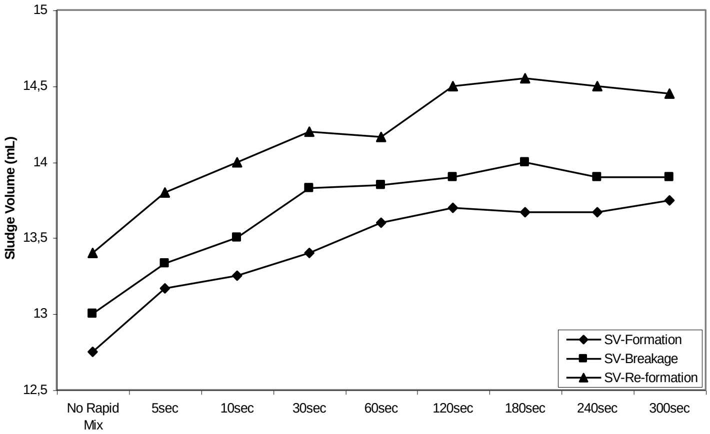

Fig.8. Sludge volume for different durations of rapid mixing after 2 hr settling with alum.

As seen in Fig.8 sludges volume after 2 hr settling exhibit an increasing trend with increasing rapid mixing time. Since residual turbidity and sludge volume after 2 hr settling increase with increasing rapid mixing duration it can be interpreted that settlability decreases with increasing rapid mixing time. As a result, a gradual decrease in sludge solids content should be expected, which is obviously seen in Fig.9.

It is more convenient to interpret all the data presented in Fig.7, 8 and 9 together. For each rapid mixing time condition the full grown flocs sludge shows the least volume whereas the regrown flocs sludge gives the highest volume. This must be linked to floc size. The full grown flocs have the greatest size (probably looser in structure) as presented in Fig.1. These flocs may be compressed and compacted and the sludge consolidates to give the least volume (the highest sludge volume reduction during 2 hr settling period is observed with these flocs). On the other hand, broken flocs have the smallest size in each case. These flocs show worst settling (as seen by the residual turbid-

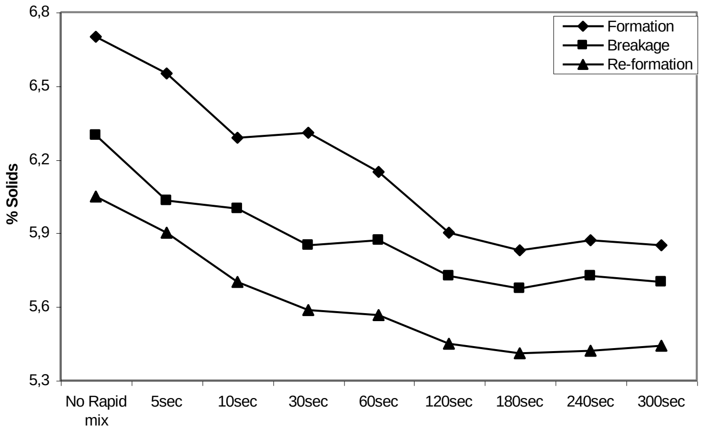

Fig.9. Alum sludge content; % solids (wt./wt.).

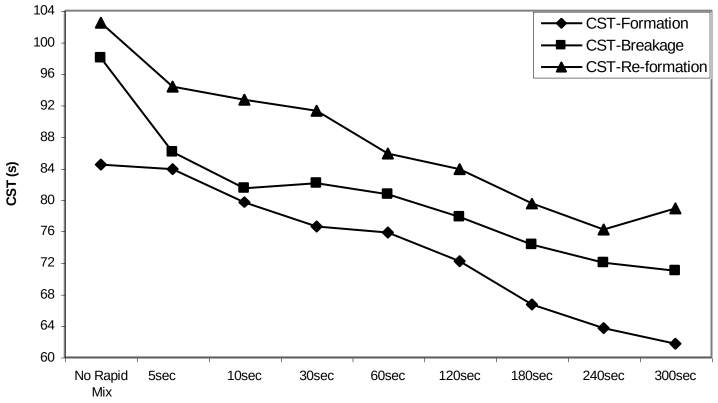

Fig.10. CST at formation, breakage and re-formation for different rapid mixing times after 2 hr settling with PACl. ity values in Fig.3) together with the fact that these small flocs occupy less volume when settled. The regrown flocs are somewhere between; they show better settling than broken flocs thus more amount of sludge is expected but they are smaller than full grown flocs thus weaker compaction and consolidation is observed when compared to full grown flocs and sludges. The regrown flocs are thought to have highest amount of intrafloc water because they have the least amount of solids content (Fig.9) and highest CST values (Fig.7) in each rapid mixing time case.

The interpretaion above is also valid for dewatering of PACl sludges (Fig.10).

As seen, CST values of PACl sludges for shorter rapid mixing times are higher than those of alum sludges; for prolonged rapid mixing times PACl exhibits better dewatering. For rapid mixing times longer than 10 s (good mixing), CSTs of PACl sludges are shorter, this suggests that poor mixing causes worsened dewatering. Data is also convenient with the finding that CST decreases with decreasing floc size (due to increasing rapid mixing time); since alum flocs are much smaller than PACl flocs for shorter rapid mixing durations alum sludges give lower CST values, as the rapid mixing time is increased the sizes of alum and PACl flocs get closer and as a result the CST values of alum and PACl sludges also get closer.

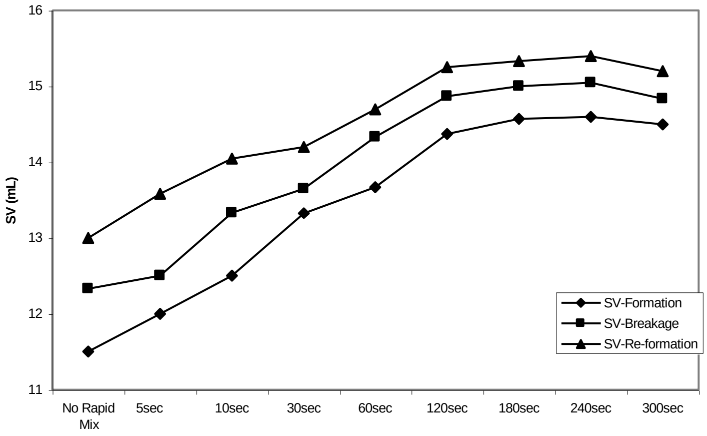

Fig.11. Sludge volume for different durations of rapid mixing after 2 hr settling with PACl.

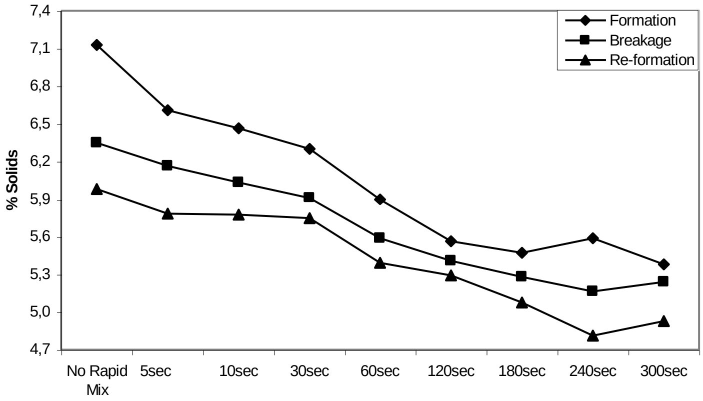

Fig.12. PACl sludge content; % solids (wt./wt.).

According to the sludge volume data for PACl sludge presented in Fig.11, with shorter rapid mixing times less amount of sludge is settled with PACl. This may be a result of the fact that larger flocs form with PACl and compaction of these flocs in settled sludge thus sludge consolidation is more significant with PACl than alum.

Solids content values of alum sludges were found to be higher than those of PACl sludges nearly for all rapid mixing time conditions. This is not unusual when the fact that larger flocs form with PACl is considered and actually indicates that mechanism of flocculation and the structure of flocs formed with both alum and PACl are similar.

Conclusion

The findings of the present study highlighted that the duration of rapid mixing has crucial effects on the floc growth, breakage and regrowth with hydrolysing metal coagulants and dewatering of their sludges. As a detrimental effect for particle removal efficiency, prolonged rapid mixing was observed to cause smaller floc formation and worsened settlability, which resulted in increasing residual turbidity with increasing rapid mixing time.

Due to the high particle concentration of the model suspension, the onset of flocculation is very rapid. Relatively much larger flocs are formed without any rapid mixing, which may lead to a misinterpretation that rapid mixing may seem unnecessary. However, this may not be observed with rather dilute suspensions. The purpose of rapid mixing application is to provide as many contacts as possible between coagulant species and particles before reaching into the amorphous precipitate, the fact is, the model suspension is such concentrated that contact readily occurs, but with a delay which is thought to be time for charge neutralisation. Much larger flocs are formed with PACl coagulant, especially after shorter rapid mixing times. This leads to significantly better turbidity removal efficiency compared to alum. Also, PACl flocs exhibit more durability against increased shear. Alum flocs show higher size recovery after breakage than PACl flocs for shorter rapid mixing times (may be considered as poor mixing), which suggests that flocculation with PACl necessiates a little longer rapid mixing than flocculation with alum.

For shorter rapid mixing times alum sludges show better dewatering than PACl sludges, whereas CST values of PACl sludges are lower for prolonged rapid mixing times. Good mixing (rapid mixing times longer than 10 s) leads to PACl sludges showing shorter CSTs indicating that poor mixing causes worsened dewatering. A general trend of decreasing CST values with increasing rapid mixing durations was observed, which is unusual when effects such as surface drag losses and cake blinding are considered; dewatering is improved as floc size decreases. This is thought to be related to intrafloc water ratio; when flocs are smaller they have less water/solid ratio in their floc package thus free water content of sludge, which can rather easily be removed increases. Similar results were reported by Turchiuli and Fargues (2004).

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TOLUENE INHIBITION OF AN ANAEROBIC REACTOR SLUDGE IN TERMS OF ACTIVITY AND COMPOSITION OF ACETOCLASTIC METHANOGENS

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In this study; it is aimed to determine the effect of toluene on an anaerobic sludge taken from a full-scale upflow anaerobic sludge blanket (UASB) reactor in terms of potential activity and composition of acetoclastic methanogens. Specific methanogenic activity (SMA) test results showed that 5%, 9.5%, 14%, 24%, 29%, 38% and 62 % inhibition occurred in the potential methane production (PMP) rate of the sludge at toluene concentrations of 0.1mM, 0.2mM, 0.3mM, 0.4mM, 0.5mM, 0.6mM and 1mM, respectively. Fluorescence *in situ* hybridization (FISH) results showed that relative abundance of archaeal cells was approx. 19% throughout the SMA tests. The anaerobic sludge was dominated by acetoclastic genus *Methanosaeta.* The other acetoclastic genus *Methanosarcina* was not observed within the sludge. It was found out that increasing toluene concentrations do not have any effect on relative abundance of *Methanosaeta* spp. which was between 73% ± 1.6 and 68% ± 2.1 of the archaeal population.

***Keywords** : Methanosaeta* spp., acetoclastic methanogenic activity, FISH, toluene, inhibition,.

INTRODUCTION

Treatment of industrial wastewaters such as pharmaceutical, alcohol distillery, dairy and brewery effluents in anaerobic bioreactors has gained importance since the introduction of high rate anaerobic reactors (Lettinga *et al.*, 1980). The major drawback for application of anaerobic treatment processes is complex, interdependent microbial community which reacts highly sensitive to sudden changes in environmental conditions. Changes in numbers and activities of methanogens in anaerobic sludges can not be determined by measurement of parameters conventionally used to monitor anaerobic treatment reactors which can only provide information about the current conditions inside the reactor (Ince *et al.*, 2005). This can be done using fluorescence *in situ* hybridization (FISH) and specific methanogenic activity (SMA) test (Pind *et al.*, 2003; Jawed and Tare, 1999). The SMA test allows determination of potential activity of methanogens. Therefore, changes in sludge activities due to fluctuation in characteristics of wastewaters, inhibitory substances etc. can be followed by using the SMA test. Fluorescent *in situ* Hybridization (FISH) is a molecular tool which gives an opportunity for determination of active microbial cells within their natural habitats (Wagner *et al.*, 2003). Combining these two methods provide valuable data used for better understanding and operation of the anaerobic treatment systems.

Pharmaceutical industry wastewaters may contain significant concentrations of a wide variety of priority pollutants including organic solvents and chemicals which may adversely affect performance of biological treatment processes. The solvents may contain methylene chloride, toluene, isopropyl alcohol, chloroform, chlorobenzene, chloromethane, cyanide, phenol and benzene (EPA, 1997). These solvents are generally removed from the wastewater using recovery processes; however, wastewaters of some pharmaceutical industries may still contain some solvents at relatively high concentrations. A portion of these solvents may be relatively biodegradable, but there might have been specific compounds in the chemical synthesis-based pharmaceutical wastewaters which may be difficult to biodegrade by the microbial population. Improvement of anaerobic systems especially for treatment of wastewaters containing these solvents needs determination of inhibitory effects on microorganisms' vitality and activity. Although there are valuable studies investigating the effects of some aromatic hydrocarbons such as benzene, toluene, ethyl acetate on pure or binary cultures, little attempt has been made to assess effects of particular solvents on anaerobic wastewater treatment reactor sludges in terms of qualitative and quantitative measures of methanogenic species and their activities (Meckenstock *et al.*, 2004; Alagappan and Cowan, 2003; Hwang *et al.*, 2003; Alagappan and Cowan, 2001; Rogers *et al.*, 2000). Therefore, in this study; it is aimed to determine the effect of toluene on an anaerobic sludge taken from a full-scale upflow anaerobic sludge blanket (UASB) reactor in terms of potential activity and composition of acetoclastic methanogens. The SMA tests had been carried out to determine the effect of different toluene concentrations on the potential acetoclastic methanogenic activity of the anaerobic sludge. The microbial community structure of the SMA samples was also characterized using fluorescent rRNA targeted oligonucleotide probes specific for Archaea, acetoclastic genus *Methanosarcina* and *Methanosaeta*.

MATERIALS&METHODS

Analytical methods

Hewlet Packard 6850 gas chromatograph (GC) with a thermal conductivity detector (HP Plot Q column 30 m x 530 µm) was used to determine gas compositions for SMA tests. Due to granular characteristics of reactor sludge, total solids and total volatile solids (TS/TVS) were measured. All analyses were carried out according to Standard Methods (APHA, 1998).

Description of SMA test equipment

The specific methanogenic activity (SMA) test unit was used to determine acetoclastic methanogenic activity. The fully computerized test unit was originally developed by Monteggia (1991) and modified by Ince (1995). The schematic diagram is shown in Figure 1. The SMA test unit consisted of eight 1 L digestion flasks. Temperature stability in the flasks is controlled by a water bath. Mixing is provided by magnetic stirrers. Gas measurement system contains a manometer and tubing for interconnection between the anaerobic reactor and the other units. Gas metering system has an eight channel analog input board model DAS 800 (supplied by Metrabyte Corporation, U.K.) which was used to simultaneously monitor the gas production of the eight independent digesters. A PC was connected to the gas metering system. Details and the experimental procedure of the SMA test were given in a subsequent paper (Ince et. al., 1995).

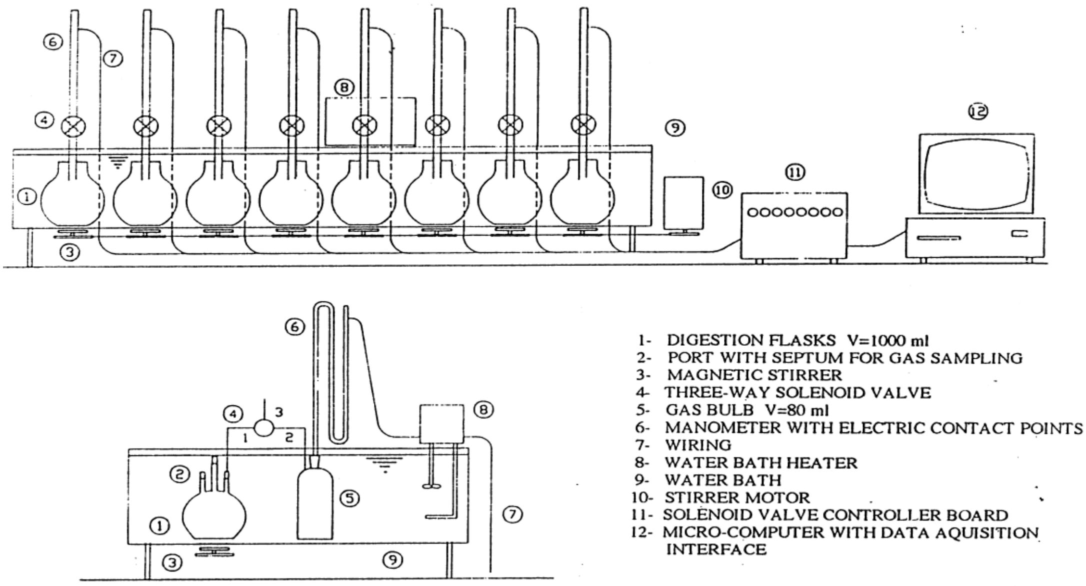


Figure 1. Experimental set-up for SMA test unit

Feed and Seed Sludge for SMA Test

Seed sludge was taken from 143 m^3 full-scale mesophilic UASB reactor which is used in the anaerobic stage of the two-stage anaerobic-aerobic biological treatment system at a local alcohol distillery, Istanbul, Turkey.

It is known that approximately two-thirds of the methane produced in an anaerobic bioreactor is derived from acetate (Zinder, 1993). For this reason, acetate was used as feed during SMA tests. Acetate concentrations in a range of 1000-4000 mg dm^{-3} were initially tested in order to reach maximum potential methane production (PMP) rate during the SMA tests. Among those 2000 mg dm^{-3} acetate concentration was found to be optimum. Toluene concentrations in the range of 0.1mM, 0.2mM, 0.3mM, 0.4mM, 0.5mM, 0.6mM and 1mM were maintained within the SMA reactors for inhibition studies. TS and TVS concentrations of the the UASB reactor sludge were 150000 mg dm^{-3} and 140000 mg dm^{-3} respectively.

FISH Technique

Fixation and Dehydration. Duplicate samples taken from each SMA reactor were immediately fixed using standard paraformaldehyde fixation method at least 4 hours at +4^{0}C. Samples were washed with phosphate buffered saline (PBS) and stored in PBS-absolute ethanol (1:1, v/v) at -20^{0}C (Harmsen *et al.*, 1996). Fixed samples are dehydrated by successive amount of ethanol (60, 80, 100%).

Total cell counts: Total cell counts of the sludges were obtained by using SYBR Green I (10,000× in dimethyl sulfoxide; Molecular Probes) (Weinbauer and Beckmann, 1998). Counts were obtained by using an Olympus BX 50 Epifluorescence Microscope equipped with a 100 W high-pressure mercury lamp, U-MWIB and U-MWG filter cubes. Dilutions that resulted in between about 50 and 300 cells per field of view were used.

Hybridization. 16S rRNA-targeted oligonucleotide probes used in hybridization step were MS821 (Raskin et al., 1994) for determination of *Methanosarcina* spp., MX825 (Raskin et al., 1994) for *Methanosaeta* spp., ARC915 (Stahl et al., 1988) for Archaea, and UNIV1392 (Pace *et al*., 1986) for the whole microbial community in the anaerobic sludge. All probes were obtained commercially (Qiagen Corp., Germany). Hybridizations were carried out at 46^{0}C for at least 4 hours according to the procedure of Amann *et al.* (1990). Hybridization buffers for all probes were prepared with 20% formamide.

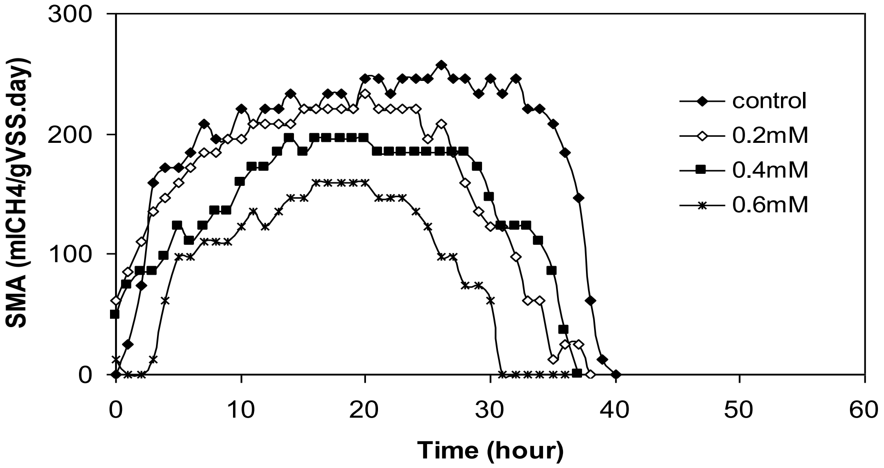
Washing. Hybridized cells were washed twice in a wash buffer described by Lathe (1985) for 15 min at 48˚C before a final wash with deionized water to remove the excess and unbound probes.

Observation. Samples were examined using Olympus BX 50 Epifluorescence Microscope equipped with a 100 W high-pressure mercury lamp. A cooled CCD camera and Spot Advanced software were used to capture the images. The images were processed and analyzed using Image-Pro Plus version 5.1 image analysis software (Media Cybernetics, U.S.A.). Duplicate samples were subdivided into two parts, counts for 10 random fields of view were obtained for each sample, and the average cell count was calculated.

RESULTS AND DISCUSSION

SMA Test Results

SMA tests had been carried out to determine the effect of different toluene concentrations on the potential acetoclastic methanogenic activity of the anaerobic sludge. As seen in the Figure 2 and 3, PMP rates of sludge at toluene concentrations of 0, 0.1mM, 0.2mM, 0.3mM, 0.4mM, 0.5mM, 0.6mM and 1mM were 258, 245, 233, 221, 196, 184, 160 and 98 ml CH_4 $gVSS^{-1}day^{-1}$ respectively.



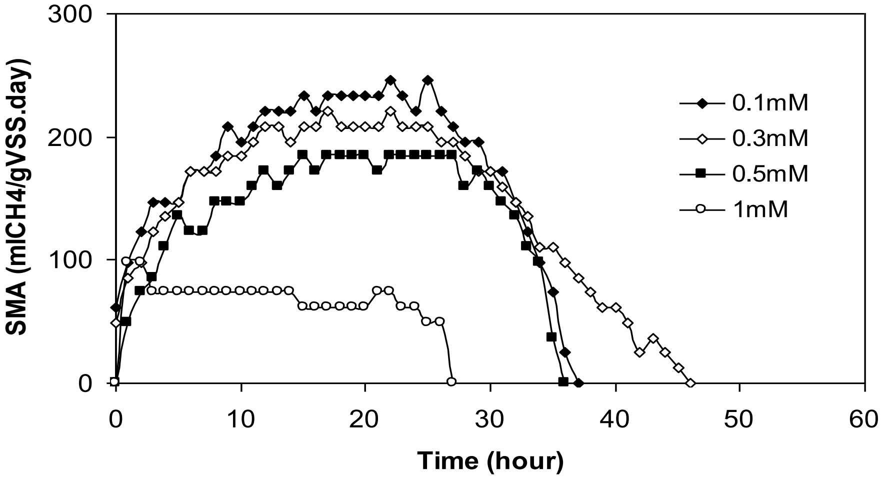


Figure 2. SMA test results at various toluene concentrations

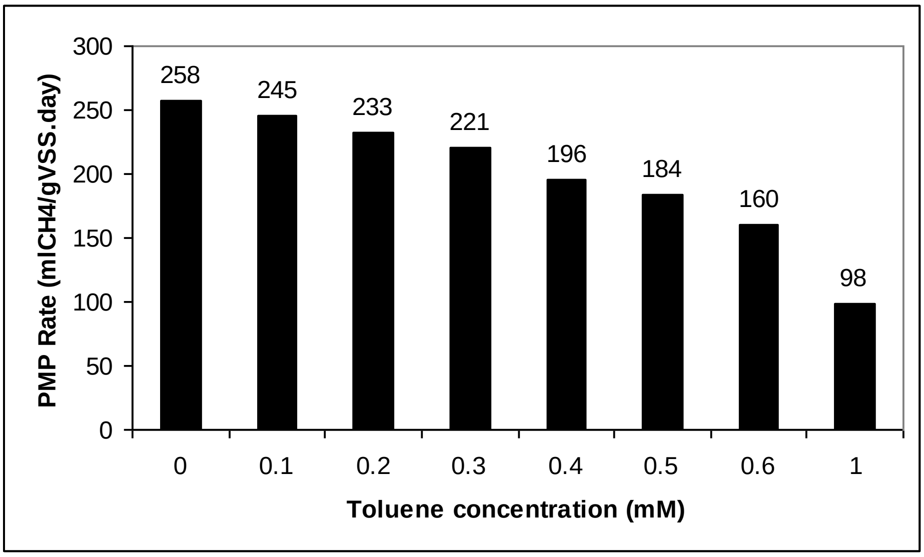


Figure 3. PMP rates at various toluene concentrations

When PMP rates of the sludge at various toluene concentrations were compared with the PMP rate of the sludge without toluene, it was seen that 5%, 9.5%, 14%, 24%, 29%, 38% and 62 % inhibition occurred in the PMP rate of the sludge at toluene concentrations of 0.1mM, 0.2mM, 0.3mM, 0.4mM, 0.5mM, 0.6mM and 1mM respectively (Figure 4).

There are plenty of studies assessing the effect of different amendments of toluene on anaerobic reactor sludges under sulfate reducing, nitrate reducing and methanogenic conditions (Cattony et. al., 2005; Martinez et. al., 2006; Mrowiec et. al., 2005; Grbic-Galic and Vogel,1987). It was reported that different toluene concentrations up to 100 mM can be degraded in anaerobic reactors and did not have a negative effect on the organic matter removal of the reactor sludges. However, effect of toluene on potential methanogenic activity was not assessed in those studies.

Our study first to report that toluene addition up to 1 mM causes serious losses in potential acetoclastic methanogenic activity of the anaerobic sludge. From the operational stand point of anaerobic reactors, such activity losses may not be reflected in the reactor performance if an anaerobic reactor is under loaded compared to its maximum loading capacity. However, if longer exposure of the anaerobic sludge to toluene occurs, the reactor may not achieve desired organic matter removal due to significant losses in the potential activity of acetoclastic methanogens.

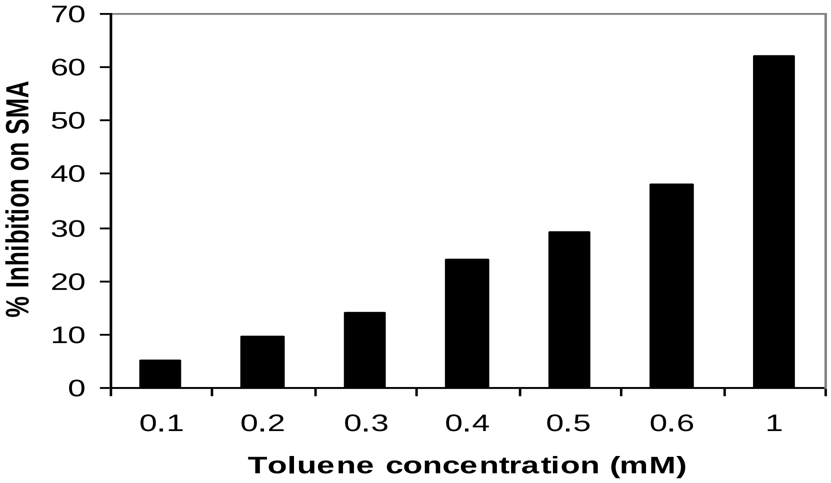


Figure 4. % Inhibition on SMA at various toluene concentrations

FISH Results

The microbial community structure of the SMA samples was characterized using fluorescent rRNA targeted oligonucleotide probes specific for Archaea, genus *Methanosarcina* and *Methanosaeta*. Epifluorescence micrograph examples of the hybridized sludge samples were shown in Figure 5. Relative abundances of Archaea and acetoclastic genus *Methanosaeta* were given in Table 1. The other acetoclastic genus *Methanosarcina* was not observed within the sludge under any condition. The results showed that relative abundance of archaeal cells was approx. 19% throughout the SMA tests. The archaeal population in the anaerobic sludge was dominated by acetoclastic genus *Methanosaeta.* It is generally assumed that dominance of *Methanosaeta* spp. results in more stable reactor performance (Wiegant, 1988; MacLeod, 1990). Numerical dominance of the genus *Methanosaeta* compared to other methanogens in anaerobic reactors has been reported previously (Ficker *et al.* 1999; Merkel *et al.*, 1999; Sekiguchi *et al.*, 1999; Zheng *et al.*, 2000; Plumb *et al.* 2001).

In this study, it was found out that increasing toluene concentrations do not have any effect on relative abundance of *Methanosaeta* spp. which was between 73% ± 1.6 and 68% ± 2.1 of the archaeal population. This is consistent with a previous report that diversity of archaea remained unaltered during the different phases of an experiment assessing effect of toluene concentrations between 20 mM and 100 mM on a horizontal-flow anaerobic immobilized biomass (HAIB) reactor (Cattony et. al., 2005).

However, microscopic characterization of HAIB reactor biomass revealed a diversity of microbial morphologies and denaturant gradient gel electrophoresis (DGGE) profiling showed a variation of bacterial and sulfate reducing bacteria (SRB) populations, which were significantly associated with toluene amendments.

Table 1 Changes in number and composition within the archaeal population

Toluene Concentration (mM)	[a]Detectable cells (%)	[b]Archaeal Population (%)	[c]*Methanosaeta* spp. in the archaeal population (%)
0	94 ± 3.4	18.8 ± 1.6	73 ± 2.8
0.1	89 ± 4.6	19.3 ± 1.9	71 ± 2.9
0.2	99 ± 5.6	18.7 ± 1.1	68 ± 4.1
0.3	93 ± 3.1	19.2 ± 2.2	69 ± 5.2
0.4	93 ± 4.7	19.1 ± 2.1	72 ± 5.3
0.5	96 ± 4.5	18.5 ± 1.3	72 ± 2.7
0.6	88 ± 5.3	18.9 ± 0.9	70 ± 4.4
1	98 ± 5.2	19.6 ± 1.2	68% ± 2.1

[a] (The number of cells detected with UNIV1392)/(Total cell count using SYBR Green)

[b] (The number of cells detected with ARC915)/(The number of cells detected with UNIV1392)

[c] (The number of cells detected with MX825)/(The number of cells detected with ARC915)

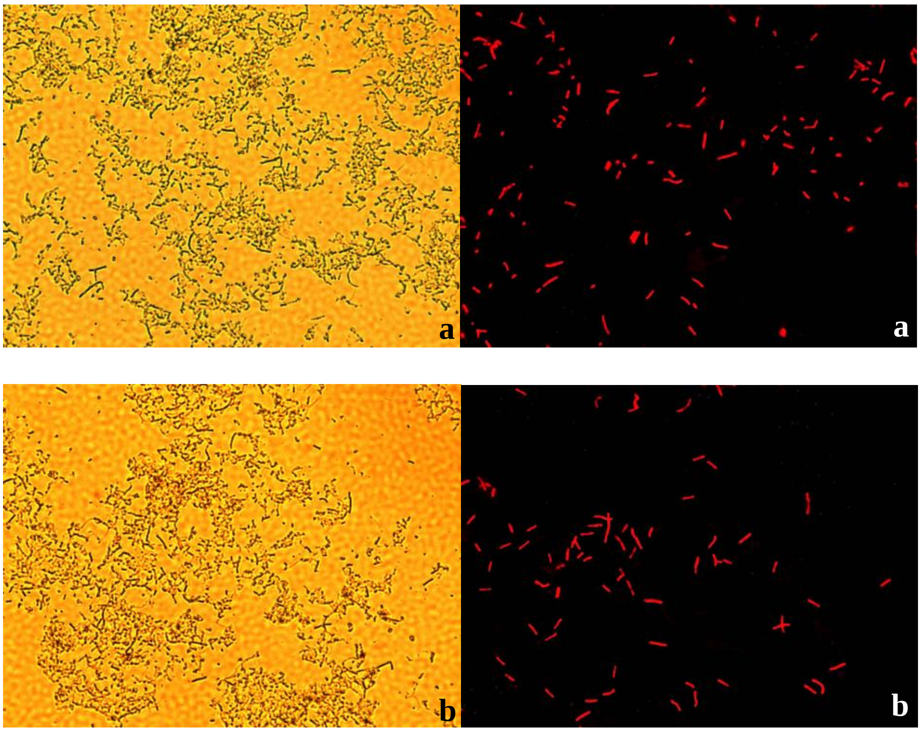


Figure 5. Epifluorescence micrographs of the hybridized sludge samples. Light and fluorescent images are in the same field. Cells were detected with probe (a) ARC915 (Archaea), (b) MX825 (*Methanosaeta* spp.). The images were processed using Image-Pro Plus version 5 image analysis software (Media Cybernetics, U.S.A.).

Only two methanogenic genera, *Methanosaeta* and *Methanosarcina*, are known to produce methane from acetate (Zinder, 1993). Therefore, it can be said as a possible explanation that 62 % loss in the potential acetoclastic methanogenic capacity of the seed sludge at 1mM toluene concentration could be attributed to change in the physiological state, and/or the relative numbers and composition of *Methanosaeta* spp. in the archaeal population. However change in the relative numbers of *Methanosaeta* spp. in the sludge could not be observed. Instead, a possible change in the physiological state of the *Methanosaeta* spp. has caused potential acetoclastic methanogenic capacity loss. Besides, change in the *Methanosaeta* spp. may occured at species level which could not be determined by the genus specific hybridization probes used in this study.

CONCLUSION

Effect of toluene on archaeal composition in an anaerobic sludge was determined and interpreted with the specific methanogenic activities of the sludge of interest. Results revealed that there is a negative impact of increasing toluene concentrations on methanogenic activity whereas it was not seen any effect on archaeal population in genus level. This study states the importance of toluene on the efficiency of the anaerobic treatment plant. FISH results also showed that further study is necessary to find out the effect of toluene on the composition of acetoclastic methanogens using other culture-dependent methods such as cloning and sequencing of 16S rDNA sequences, DGGE or FISH using species specific hybridization probes.

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CLEAN DYEING TECHNOLOGY WITH BASIC NATURAL DYE ON COTTON FABRICS USING ULTRASONIC TECHNIQUE

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In order to address environmental issue, clean textile dyeing technology is today interested to natural dyes, owing to their Eco-preservation and the growing awareness of their non-hazardous nature. Synthetic dyes involve many carcinogenic chemicals and the effluents, which are discharged in the river or emitted in the atmosphere result in pollution. Synthetic basic dyes remarked high acute and chronic toxicity on human beings, carcinogenic effect on animals, in addition to a hazardous effect on aquatic marines. These factors have brightened the scope to carry out this research, by making a comparative dyeing study by ultrasonic and conventional heating techniques on cotton fabrics with the only known natural basic dye; Berberine. Cotton fabrics are characterized by their low dye affinity and poor fastness properties to washing and light when using basic dyes. The present study remarked the optimum dyeing condition of cotton fabrics dyed with Berberine dye, and evaluated the different fastness properties.

1- Introduction

Nowadays, a revival interest in the use of natural dyes in textile colouration has been growing, due to the stringent environmental standards imposed by several countries in a response to the toxic and allergic reactions associated with synthetic dyes. [1] Considerable researches works are being undertaken around the world on the application of these dyes in textile colouration. [2-15]

Basic dyes comprise compounds varying widely in chemical composition; they produce attractive, bright, and highly intensive dyeing. Nowadays, they are less often used due to their significant high toxicity denoted by The Ecological and Toxicological Association of Dyes and Organic Pigment Manufactures (ETAD). [16]
Berberine, the dye pigment present in the roots of barberry, is the only example of natural basic or cationic dye, as a dye, barberry has been mentioned since the 14th century in the records of Christian monasteries [17-21].,

Consumer surveys have shown that garments made from cotton fabrics are generally preferred for their natural feel and drape. [22] Cotton has a negligible affinity to basic dyes, although the use of these dyes would enhance cotton appearance. [23] Only mordanted cotton can be dyed with basic dyes.[24] Cotton fabric was modified by different methods to enhance its dye-ability towards basic dyes. [25-28]

Power ultrasonic can enhance a wide variety of chemical and physical processes, mainly due to the phenomenon known as cavitations in a liquid medium. [1, 29-30] The usefulness of ultrasonic as a novel dyeing accelerant, and its efficiency in increasing the dye uptake on different fabrics has been demonstrated. [1, 15, 31-34]

We conducted the present study to investigate the dyeing and fastness properties of cotton fabrics dyed with the only natural basic dye; Berberine, whereas cotton was modified by H-acid to enhance its dye-ability. Different factors affecting the dye-ability and fastness properties were thoroughly investigated. Comparative results of the dyeings using both ultrasonic and conventional techniques are also presented.

2- Experimental

2-1- Material

Mill, scoured and bleached plain-weave cotton fabric (poplin) was used for this study. The fabric was purified in the laboratory by a mild treatment with a solution containing 5 g/l sodium carbonate and 2 g/l non-ionic detergent (Hostapal CV, Clariant). The fabric was then thoroughly washed and air dried.[35] Commercial crushed berberine roots was used, its properties were listed in Table1, and its chemical structure was represented in Fig. 1a. H-acid was obtained from local commercial source; its chemical structure was represented in Fig.1b. Alum and stannous chloride were used as environmentally friendly mordants, sodium carbonate, and glacial acetic acid used to adjust the pH values.

2-2- Methods

2-2-1-Conventional and Ultrasonic Extractions

Conventional and ultrasonic extractions were carried out in 100 ml distilled water using varying amounts of the dye materials (2-15%) for different time intervals (20-120 min). The conventional extraction was carried out at boiling whereas the ultrasonic one was carried out at different temperatures (50-80^0 C) using different sonic powers (100-500 W). After filtration and certain dilution, the optical density of the dye liquor 420 nm was measured. [36, 37] Ultrasonic extraction and dyeing were conducted in thermo-stated CREST bench-top 575 HT ultrasonic cleaner of capacity 5.75 L, frequency 38.5 kHz and with a maximum 500W output. The output levels are from 100-500 W.

2-2-2-Treatment of Cotton [38]

Each 1g of cotton fabric was immersed for 24 hours at room temperature in a solution containing 2g H-acid in 100 ml distilled water, containing 6 drops of glacial acetic acid. The fabric then removed from the H-acid solution pressed well to a constant weight then dyed with the Berberine bath.

2-2-3- Dyeing Procedure

The treated cotton was dyed in a bath containing (0-30 g/l) sodium chloride, 10 % berberine dye with liquor ratio 50:1, , at pH values (2-9) for (20-120 min.), and at (40-80^o C) using conventional heating (CH). For comparison, the same condition of dyeing was carried out using ultrasonic technique (US) with sonic power of 500 W. The pH values were recorded with Hanna pH meter and adjusted with dilute solutions of sodium carbonate and acetic acid as the dye extract was 5.6. The dyed samples were rinsed with cold water, washed in a bath of liquor ratio 40:1, using 3g/l non ionic detergent(Hostapal CV, Clariant), at 60^o C, for 30 min, then rinsed and finally dried at ambient temperature. The reflectance of the soaped samples was measured on the Ultrascan XE spectrophotometer. Relative colour strengths (K/S) were determined using the Kubelka-munk equation.[39]

2-2-4- Mordanting Methods

Treated cotton was mordanted by i) pre-mordanting, and ii) post-mordanting methods. Alum, and stannous chloride mordants with concentration of 10 g/l were used. In the premordanting method, the treated cotton samples were first immersed in aqueous solutions of mordants for 45 min. at 30°C. The mordanted samples were then dyed by the Berberine dyeing bath. In the post-mordanting method, dyeing was carried out on the treated cotton samples in absence of mordant, followed by mordanting in a separate baths with the mordants for 45 min. at 30° C. [3]

2-3- UV/ Vis Absorption Spectra

The uv/ vis absorption spectra in water were recorded using a shimatzu uv/ vis spectrophotometer. The quantity of dye up-take was estimated using

$$\mathbf{Q= (C_o - C_f)\ V/W} \qquad \mathbf{(1)}$$

Where Q is the quantity of dye- uptake (mg/g), C_o and C_f are the initial and the final concentrations of dye in solution (mg/l), respectively, V is the volume of dye bath (ml), and W is the weight of fibre (g). The concentration of dye solutions was determined after reference to the respective calibration curve of berberine dye using Lambert- Beer Law.

2-4- Fastness Testing

Colourfastness to washing, rubbing, perspiration, and light were tested according to AATCC technical manual. [40]

3-Results and Discussion

Power ultrasonic has great potential for application in a wide variety of industrial processes. It offers potential cost saving in time, chemicals, energy, and reduced effluent, [41-43] in this context, applying ultrasonic technique (US) in compared with the conventional heating (CH) one in dyeing cotton fabrics using Berberine dye as a natural basic dye was of interest.

3-1- Dye Extraction

3-1-1- Effect of Dye Amount

Comparative extraction of Berberine dye using (US) and (CH) techniques was done at 80° C, the extent of extractability was monitored spectro-photometrically at λ_{max} 420 nm. Fig. 2 shows that as the percentage of the dye amount increases, the absorption of the dye extract also increases whether using (US) or (CH) techniques with much higher values at all points in the (US). The maximum extractability was attained with 15 %. The 10 % was selected in this study because there was a slight difference in the absorbency between (10-15) % as shown in Fig. 2.

3-1-2- Effect of Extraction Time

(US) and (CH) extractions of Berberine (10%) were carried out for (20-120 min.). Fig. 3 shows that, the rate of dye extraction by (US) is higher than that of (CH) to reveal maximum dye extraction after 40 min. for the (US). It is worth noting that the absorption of the extract using (US) was 1.76 mg g^{-1} after 40 min., whereas on using (CH) it was only 0.95 mg g^{-1} after 100 min. Prolonged extraction time using (US) however may lead to dye degradation as revealed by decreasing the absorbance of the extract.

3-1-3- Effect of Extraction Temperature

Extraction of Berberine dye is temperature dependant and directly proportional with temperature to conclude effective extraction at 80^o C. Expectedly, the extractability was found to increase as the temperature increases. On using (US) the absorbency is 1.76 mg g^{-1} at 80^o C whereas it was only 0.67 mg g^{-1} on using (CH) at the same temperature as shown in Fig. 4. This behavior reflects the additional enhancing effect due to power ultrasonic that provides easy, efficient route for dye extraction without the need to boil the water as heating may lower the brightness of the extracted dye. [1, 44]

3-1-4- Effect of Ultrasonic Power

The effect of ultrasonic power on the extractability of Berberine was conducted at different power levels (100-500 W). As shown in Fig. 5, the absorption of the extract increases with increasing power level up to 300 W at which the maximum extraction was attained. Power ultrasonic helps much dye extraction from Berberine by virtue of its dispersion, degassing and diffusion capability.

3-2- H- acid Treatment

Fig. 6: represents the efficiency of H-acid treatment on the colour strength of the dyed cotton samples with Berberine dye, using (CH) and (US) techniques in compared with the untreated (control) sample. It was denoted that H-acid treatment increases the dye-uptake of the dyed samples. This can be explained by the adsorption of H-acid on cotton fibres by virtue of hydrogen bond formation between its hydroxyl and the amino groups and the hydroxyl groups of cellulose.[38]

3-3- Effect of Dye Bath pH

The pH values of the dye bath have a considerable effect on the dyeability of the treated cotton samples with berberine dye under both (US) and (CH) techniques as shown in Fig. 7. It is clear that both (CH) and (US) have improved the dyeability of the samples at pH 7, with much higher values at all points in the (US). The adsorption of H-acid molecules overcomes the presence of hydroxyl groups of cellulose due to the amino groups of H-acid. At pH 7, the cationic natural dye is ionic-ally bonded with the treated cellulose fibres.

3-4- Effect of Salt Addition

Fig. 8 shows the effect of salt concentration on the colour strength obtained for the dyed samples under both (US) and (CH) techniques. It is clearly indicated that the colour strength increases with the increase of salt concentration in the (US) and (CH) techniques with pronounced increase in the (US) than the (CH). In case of (US), a plateau is attained at 15 g/l salt and then started to decline slightly with excess concentrations, whereas on using (CH) the maximum colour strength was attained at 20 g/l salt, then remains nearly stable with excess concentrations. Sodium chloride salt enhances the adsorption and diffusion of the dye molecules towards the treated cotton surface. In case of (US) technique, there is a decline in the colour strength with salt concentrations up to 15g/l; this may be explained by the interference of the cationic and anionic charges in the dye bath.

3-5- Effect of Dyeing Temperature

As shown in Fig. 9, it is clear that the colour strength increases with increase in dyeing temperature in both cases of (US) and (CH) techniques with pronounced increase in the (US) case than the (CH) one. The increase in dye-uptake can be explained by fibre swelling that enhanced the dye diffusion. On the other hand, the ultrasonic power provides de-aggregation of dye molecules which leads to further enhancement of dye diffusion and thus, better dye-ability compared with (CH) technique.

3-6- Effect of Dyeing Time

As shown in Fig. 10, the colour strength increased as the time increased in both (US) and (CH) techniques with much higher values at all points in the (US) case. In case of (US) technique, a plateau is attained after 60 up to 80 min. and then started to decline slightly with prolonged time. Whereas in case of (CH) technique, the decline in colour strength began after 100 min. The decline in the colour strength may be due to the degradation of the dye molecules because of the prolong dyeing time.

3-7- Effect of Ultrasonic Power

As shown in Fig. 11, when using different power levels (100-500 W); the colour strength of the dyed samples seemed to be directly proportional with the supplied power. This behavior investigates the assisting effect of ultrasonic power on the dye-ability of treated cotton samples with Berberine dye. This assistance is due to: i) break up of micelles and high molecular weight aggregates into uniform dispersions in the dye bath (dispersion). ii) the expulsing of dissolved or entrapped gas or air molecules from fibre into liquid and removal by cavitations that facilitates the dye-fibre contact (degassing), and iii) accelerating both; the interaction or chemical reaction between dye and fibre**,** and the rate of dye diffusion inside the fibre by piercing the insulating layer covering it (diffusion) [45, 46]

3-8- Kienetics of Dyeing

Time-dye-uptake isotherms of cotton samples dyed ultrasonically and conventionally with Berberine dye are shown in Fig. 12. It was denoted that the dye-uptake values of ultrasonically dyed samples are generally better than those of the conventionally one. The isotherms of both techniques started to be differentiated from each other to show better dye-uptake for Berberine dye under ultrasonic technique in comparison with the conventional heating. Data in Fig. 12 can be analysed by using the derivable general form of the first order rate Equation (2) (1, 47-49). Fig. 13 evaluated the dye up-take versus time of dyeing with Berberine dye under conventional and ultrasonic techniques.

$$\frac{A_t - A_f}{A_0 - A_f} = e^{-kt} \qquad \textbf{(2)}$$

A_t is the absorbance at time t, A_0 is the initial absorbance, A_f is the final absorbance, t is the reaction time and k is the reaction rate. Since the absorbance of solution is directly related to the concentration by Lambert-Beer law, therefore, equation (2) can be rewritten in terms of dye-uptake to give equation (3):

$$\frac{Q_t - Q_f}{Q_0 - Q_f} = e^{-kt} \qquad \textbf{(3)}$$

Q_t is the dye-uptake at time t, Q_0 is the dye-uptake at zero time, and Q_f is the final dye-uptake, t is the dyeing time and k is the dyeing rate. Taking the logarithm of equation (3) would lead to equation (4) and since Q_f is known, Q_t-Q_f can be calculated.

$$\ln\left|Q_t - Q_f\right| = \ln\left|Q_0 - Q_f\right| - kt \qquad \textbf{(4)}$$

A plot of $\ln\left|Q_t - Q_f\right|$ vs. time is expected to be linear with a slope of –k and an intercept of $\ln\left|Q_0 - Q_f\right|$ if the reaction is first order. Figure 13 shows the plot of $\ln\left|Q_t - Q_f\right|$ as a function of time for dyeing of cotton samples with Berberine dye using both ultrasonic and conventional heating techniques. As can be seen in this figure the linear fitting of equation (4) holds indeed and the values of dyeing rate constants could be obtained as listed in Table 2.

The time of half dyeing $t_{1/2}$, which is the time required for the samples to take up half of the amount of dye taken at equilibrium, is estimated either from each isotherm directly (Figure 12) and/or from the following equation:

$$\mathbf{t_{1/2} = \ln 2/k} \qquad \textbf{(5)}$$

The values of half dyeing $t_{1/2}$ are given in Table III. The rate constant of dyeing cotton with berberine dye is clearly increased with ultrasonic technique in comparison with conventional heating one. In addition, the values of $t_{1/2}$ of dyeing are clearly short for those samples dyed with ultrasonic in comparison with those dyed conventionally.

3-9- Standard affinity

The data for dyeing equilibrium are generally reported as the standard affinity of dyeing, -Δμ,.[1,51] It has been reported that the dyeing of cotton fibers using natural dyes follows the same mechanism as that of disperse dyes, i.e. via partition mechanism [1,7] Therefore, the standard affinity can be calculated using equation (6):

$$-\Delta\mu = RT \ln \frac{[C]_f}{[C]_s} \qquad \textbf{(6)}$$

R is the gas constant, T is the absolute temperature (K), $[C]_f$ and $[C]_s$ are dye concentrations in the fibre and the dye bath, respectively. From Table III it can be seen that the standard affinity of cotton fiber in the case of US is higher than the case of CH. This is another evidence for the enhancement effect of ultrasonic power, increasing the affinity of Berberine dye toward cotton fibers in comparison with conventional heating technique.

3-10- Ultrasonic efficiency

Ultrasonic efficiency ($\Delta k\,\%$) in accelerating, the dyeing rate was examined by introducing the following equation:

$$\Delta k\,\% = \frac{\left(k_{US} - k_{CH}\right)}{k_{CH}} 100 \qquad \textbf{(7)}$$

k_{US} and k_{CH} are the rate constants of dyeing with ultrasonic and conventional heating techniques, respectively. As shown in Table 2, the value of ultrasonic efficiency is positive indicating a favorable effect of ultrasonic power on the dyeing process. [1, 50]

3-8- Fastness Properties

The different fastness properties of the treated cotton samples dyed with Berberine dye in absence and presence of mordant using conventional and ultrasonic techniques were evaluated in Table 3 (a and b) respectively. In general mordanting increases the value of fastness properties [51-53], in our case this is not been clear. This holds true in case of ultrasonic and conventional dyeing techniques. Poor washing fastness is due to the weak dye- fibre bond between the dye and the fibre, and the ionization of the (OH) groups of the dye during washing under the alkaline condition. [53] On the other hand, the poor light fastness is due to the inherent susceptibility of the chromophore to the photochemical degradation. [18] Metal mordanting forms a complex dye which aggregates dye molecule into a large particles insoluble in water, and protects, both by steric and electronic effects, the weak point of the dye structure from attack by means of the reactive species during photochemical reaction, in addition to promotes aggregation of the dye. (54, 55) resulted in an improvement in the washing and light fastness respectively.

Conclusion

Treated cotton fabric with H-acid enhances its dye-ability towards natural basic dye; Berberine. Ultrasonic proved effectiveness in the dye extraction and dye-uptake of treated cotton fabric dyed with Berberine. This technique in addition to its advantage of saving the processing time and energy offers better environmental impact as it saves much dye-uptake.

Table 1: Characteristics of Berberine Dye Used

Botanical name	**C.I. Name**	**Class**	**Part used**	**λmax.$^{(nm)}$ in water**
Berberies aristata	Natural yellow 18	Alkaloids	Root	420

Table 2: Dyeing rate constant k, efficiency of ultrasonic Δk, times of half dyeing $t_{1/2}$, standard affinity -Δμ, and amount of final dye uptake by treated cotton fabric using berberine dye.

K x 100 (min^{-1})		**ΔK (%)**	**-Δμ (kJ/mol)**		**$t_{1/2}$ (min)**		**Q_f (mg/g)**	
US	CH		US	CH	US	CH	US	CH
11	8	37%	13.9	11.8	6.2	8.62	116.6	54.15

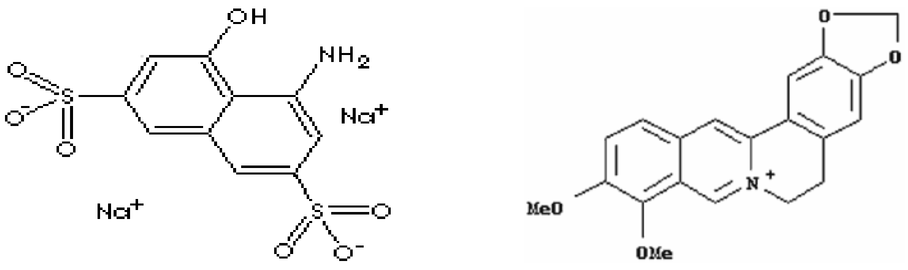
Table 3a: Fastness properties of treated dyed cotton under conventional heating technique

Samples	**Rubbing**		**Washing**			**Perspiration**						**Light**
						Acidic			**Alkaline**			
	Dry	**Wet**	**Alt.**	**St. ***	**St. ****	**Alt.**	**St. ***	**St. ****	**Alt.**	**St. ***	**St. ****	
Control	**4**	**3-4**	**3-4**	**3**	**3**	**2-3**	**3-4**	**3**	**3**	**4**	**3-4**	**3**
(I)												
Alum	**4-5**	**4**	**3-4**	**3-4**	**3-4**	**3**	**4**	**3**	**3**	**4**	**3-4**	**5**
Tin	**4-5**	**3-4**	**3-4**	**3-4**	**3-4**	**2-3**	**4**	**3**	**2-3**	**3**	**3**	**5-6**
(II)												
Alum	**4-5**	**4**	**3-4**	**3**	**3-4**	**3**	**4**	**3-4**	**3-4**	**4-5**	**4**	**5**
Tin	**4**	**3-4**	**4**	**4**	**4**	**3-4**	**4**	**4**	**3-4**	**4**	**4**	**5**

Table 3b: Fastness properties of treated dyed cotton under ultrasonic technique

Samples	Rubbing		Washing			Perspiration						Light
						Acidic			Alkaline			
	Dry	Wet	Alt.	St. *	St. **	Alt.	St. *	St. **	Alt.	St. *	St. **	
Control	4-5	3-4	4	3-4	3-4	3-4	3-4	4	3	3	3	3
(I)												
Alum	4-5	3-4	3-4	3-4	3-4	3-4	3	4	3-4	3	4	5-6
Tin	4	3-4	3	3	3	3-4	3	3-4	3-4	2-3	4	5-6
(II)												
Alum	4-5	3-4	3	3-4	4	4	3	4	4	3-4	4	5
Tin	4	3-4	3	4	4	4	3-4	4	4	3-4	4	5-6

Control: H-acid treated sample **(I) Pre-mordanting** **(II): Post-mordanting**
Alt.: alteration **St.*: staining on cotton** **St. ** staining on wool**



Berberine Structure H-acid (1-amino, 8-napthol, 3, 6-
disulphonic acid)

a **b**

Fig. 1: Chemical structure of berberine and H-acid

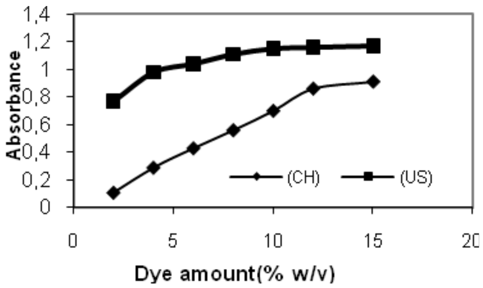


Fig. 2: Plots of dye extraction versus dye amount By (US) and (CH) 1hr. at 80° C. For (US) 500W

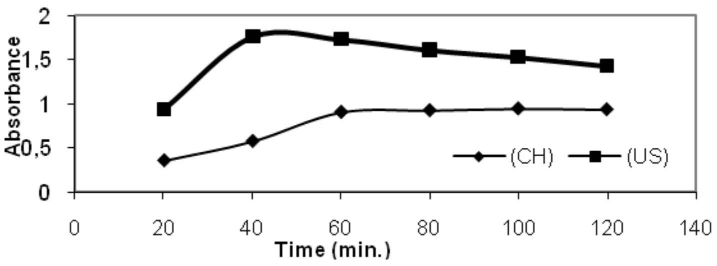


Fig. 3: Effect of time on the extent of dye extraction using (CH) and (CH) techniques: at 80° C, 10 % w/v dye amount; for US, 500 W,

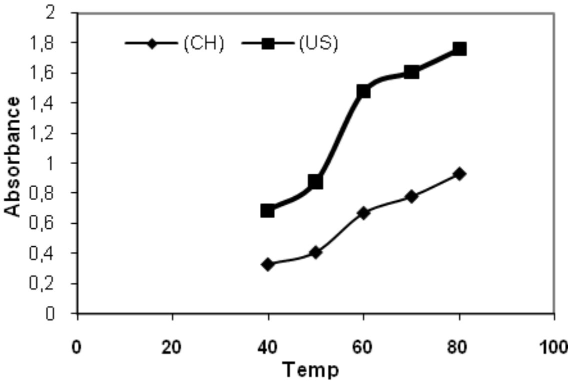


Fig. 4: Effect of temperature on the extent of dye extraction using (CH)and (US) techniques. 10 % w/v dye amount ,for (US); 500 W, 40 min; for (CH), for 60 min.

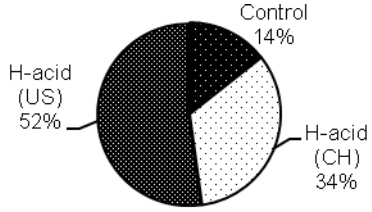


Fig. 6: Effect of H-acid treatment on the dyeability of cotton with Berberine dye using (CH) and (US) techniques

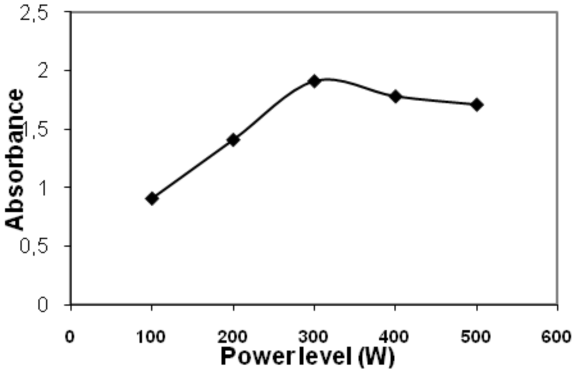


Fig. 5: Effect of ultrasonic power level on the extent of dye extraction. 10% w/v dye amount, at 80^o C, for 40 min.

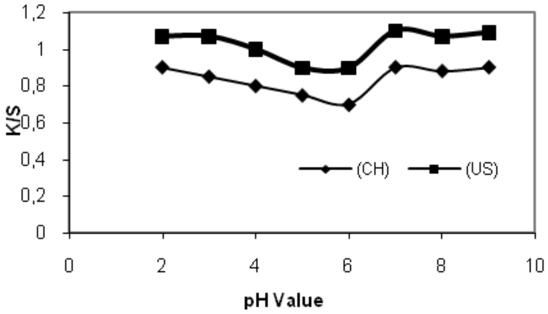


Fig. 7: Effect of dye bath pH on the colour strength of treated cotton. 500 W, L:R 50:1, 25 ml aqueous dye extract (10%) 1hr., at 80^o C

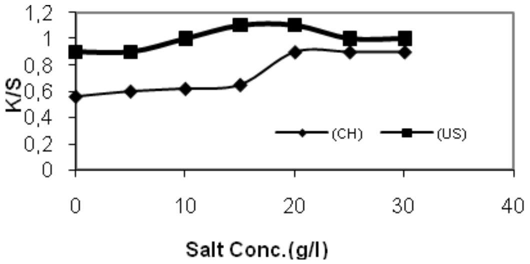


Fig. 8: Effect of salt concentration of the dye bath on the colour strength of treated cotton.500W, L:R 50:1, 25 ml aqueous dye extract (10% w/v), 1hr., at 80° C, at pH 7

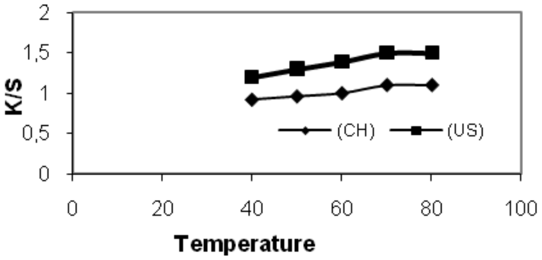


Fig. 9: Effect of the dye bath temperature on the colour strength of treated cotton. 500W, L:R 50:1, 25 ml aqueous dye extract (10% w/v), 1hr., at pH 7, 15g/l and 20g/l salt for (US) and (CH) techniques respectively

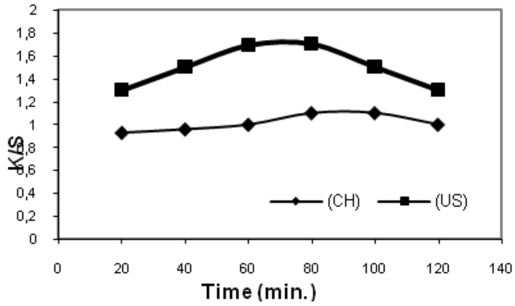


Fig. 10: Effect of the dye bath time on the colour strength of treated cotton.500W, L:R 50:1, 25 ml aqueous dye extract (10% w/v), at 80° C, at pH 7, 15g/l and 20g/l salt for (US) and (CH) techniques respectively

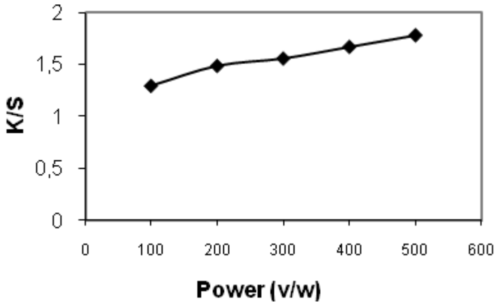


Fig. 11: Effect of the dye bath power level on
the colour strength of treated cotton, 500W,
L:R 50:1, 25 ml aqueous dye extract

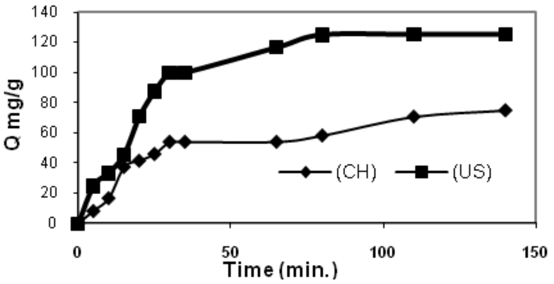


Fig. 12: Ultrasonic and conventional dyeing rates of treated cotton fabrics

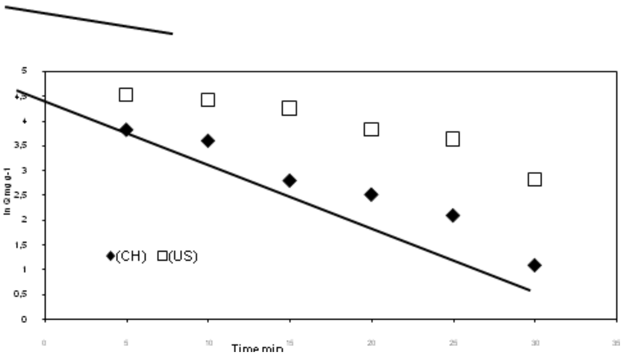


Fig. 13: Plots of In ($Q_t - Q_f$) versus time of dyeing with Berberine dye under conventional and ultrasonic techniques

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ADDRESSING SYNERGIES BETWEEN CHEMICAL SAFETY AND SUSTAINABLE PRODUCTION AND USE OF CHEMICALS

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Natural circulation of chemicals with their transformation and disposal into environmental streams follows fixed pathways. Many chemicals are indispensable in regulating most vital processes, in adequate quantities/concentrations. These steady natural ways are more and more interrupted and changed by human activities, either by the uncontrolled accumulation of existing chemicals or by the production of new chemicals. The ever increasing trend of "*chemicalisation*" with its known and unknown implications on human health, biota, genetic structures, regeneration processes and environmental media still proceeds in many regions of the world. Modern society is at the crossroads, being challenged to find the right balance between the benefits and the risks of chemicals. The recognition of the wide-ranging consequences of pollution, reaching many fundamental physical and chemical processes in biosphere, has quite recently resulted in some internationally harmonised activities in the field of chemical safety. Generally, legislation for the control of chemicals in the EU falls under two extensive headings: monitoring the releases of chemicals into different environmental media, and on the other hand controls over the manufacture, import, export, marketing, use and finally management of waste chemicals. While previously confined to particular countries, innovative and more effective Europe-wide policies to support sustainable production and use of chemicals are now in progress. Since the very beginning of the popularization of the concept of sustainability the chemical industry for its part - as the driving force in the "*chemicalisation*" of every aspect of our society - has progressively started out to prove its willingness in being a partner of sustainable development with different voluntary programmes. Indicators that reflect endeavours in achieving chemical safety and sustainability in practice must therefore provide us with crucial information that highlights this turning point. This paper discusses some facts and trends on the state of chemicals management in Slovenia and the EU. The paper tries also to present some chemicals-related information problems including the current situation regarding the development of chemical indicators of special interest.

Keywords: *chemicals, chemical safety, sustainability, environment*

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[1] The views of the author do not necessarily reflect those of the Statistical Office of the Republic of Slovenia.

1.1 Introduction

Man-made chemicals are an integral part of the contemporary way of life, being unimaginable without chemicals that are incorporated in almost all the materials and articles we use at work and at home, from building materials to cosmetics. Although a zero-risk and a pollution-free subsistence had never been recorded in any period of human history, our living environment has changed radically since the very emergence of the chemical industry. Chemicals are widespread in all media of environment following the production of enormous number of chemicals, their marketing, their transportation and storage, their use patterns, and finally their discharge and degradation processes. Humans and ecosystems have been exposed to chemicals in different ways, at all stages of their life-cycle, originating from more manageable point sources as well as from less discoverable diffuse ones.

The Chemical Abstract Service Registry (CAS Registry), which is the world's largest substance database with millions of structures and chemical names, contains more than 30 million organic and inorganic substances, of which 12 million are commercially available chemicals.

The present EU System concerning general industrial chemicals distinguishes between so-called »existing chemicals« and so-called »new chemicals«.

The European Inventory of Existing Commercial Chemical Substances (EINECS) contains a list of more than 100,000 "*existing*" substances that ware deemed to be on the European market on or before September 1981. It has been estimated that there are 30,000 existing chemicals on the European market at volumes of 1 tonne per year per producer/importer or more that are largely not covered by regulations requiring positive approval and which we therefore cannot consider safe. Only a very small portion of these substances are subject to a comprehensive risk assessment carried out by Member States authorities.

These existing substances dominate the European market over "*new*" chemicals by a high factor. The European List of Notified Chemical Substances (ELINCS) currently contains over 3,800 substances, tending to be an ever expanding list following notification to competent authorities of the placing of new substances on the market. In contrast to existing substances, they are required to be subject to more comprehensive testing and assessing procedures as to their risks to human health and the environment, according to Directive 67/548 and its amendments respectively, before marketing.

It seems that no area of environmental concern creates more anxiety among people than the risk from known and unknown hazardous substances. It is largely caused by general lack of knowledge about the properties and uses of chemicals, particularly about existing chemicals.

The accessible information on chemicals in the scientific literature and from existing toxicity and ecotoxicity tests tends to focus more on acute effects, while much less information is available on the effects of long-term low-dose exposure, let alone on the mixtures of certain substances that may interact in the environment differently.

1.2 Chemical safety and regulatory system context

Any good policy guidance on chemicals and consumer products essentially depends on reliable and due information on the occurrence of chemicals in the environment, and the exposure to humans and wildlife. It is chemicals producers, importers and users who should be responsible for providing reliable information, but in practise they are mostly weak partners to competent authorities across the European countries in their endeavour to compile reliable and recognizable information about impacts of hazardous chemicals and major routes of exposure. So the current allocation of responsibility is not appropriate and the most burden of risk assessing falls on public authorities.

Ever increasing numbers of chemicals in use required stringent surveillance to track out hazardous substances turning up in environmental media and human tissues as well as tissues of other living organisms.

The present EU legislative framework for chemical substances is a compilation of many different Directives, Regulations, Decisions and Recommendations, which have been developed over many years, relating to chemicals and consumer products, occupational health, environment protection, process and transport safety, and sustainable management. Thus legislation for the control of substances is allocated into two comprehensive headings: surveillances over emissions of chemicals into air, water and land, as well as over food contaminants and residues and surveillances over the production, import, marketing and use of chemicals before being put into waste streams. The first heading is commonly known as environment pollution control and has been developed over a very long period. The second heading has been developed more recently and is often referred to as chemicals control or chemicals policy. The Community's various contributions have begun with some ad-hoc instruments. The development of a harmonised system for classification, packaging and labelling of dangerous substances began with adoption of Directive 67/548/EEC, followed by a number of its amendments, being the basic instrument in any risk assessment process.

All these rules, together with those at national level and those from international agreements, treaties and conventions, constitute the legal basis of the chemicals management system. Safety requirements have to be met throughout the Community. Their implementation corresponds with two essential objectives: high level protection of public health and the environment, and prevention of barriers to free movement of goods within a single market.

Although rather uneven by scope, national environmental policies in European countries have developed steady environmental regulations. Historical evolution of European chemicals management efforts has been reflected through dynamic and rapid changes in the chemicals policy. An integrated chemicals policy has been actively promoted over the past decade, by introducing various mandatory and voluntary mechanisms. Since environmental conditions are different between Member States, some of them may wish to employ national rules expanding beyond the EU legislation. Besides regulatory measures, countries adopted voluntary measures (e.g. education programmes, priority lists of undesirable chemicals, green procurement orders (GPO), research and development programmes on safer alternatives, and phase-out requirements of most problematic chemicals designed to signal and stimulate businesses using chemicals to reduce emissions and to develop safer substitutes), particularly Nordic countries, pointed to achieve more stringent, sound and long-term and prevention-oriented sustainable production and use of chemicals. To stimulate companies from chemical and other industries to give up environment polluting, governments can introduce economic tools, e.g. levy taxes directly linked to pollution or provide other incentives. The "*polluter pays*" principle is another means in the struggle against polluting processes.

While previously more effective in particular countries, these innovative and ever harmonising Europe-wide policies to promote sustainable chemicals management are now exhibiting progressive trends.

Actually, many environment and consumer protection standards (such as those on air and water quality, food additives, waste management, especially hazardous, etc.) in these countries dominate by extensiveness over those in other regions of the world. Environmental protection has become integrated into all policy fields with the general aim to ensure sustainable development.

Slovenia like other Member States follows Community's objectives and trends to be in line with European integrating processes and to be able to create as harmonised and integrated national chemicals policy as possible and thus achieve the high level of chemical safety.

The history of safety regulations in Slovenia can be traced back to many years ago. The existing chemical safety legislation is not self-dependent, it is highly affected by requirements and rules set by the EU, OECD and international levels.

The National Chemicals Bureau (NCB) provides scientific, administrative and technical support to the conception, development, implementation and monitoring of national policies related to chemical safety. It represents the focal point for collecting information on new and existing chemicals and the assessments of risks to consumers, workers and the environment. It supports the transposition of EU Directives and Regulations into national legislation as well as their updating and harmonization.

In order to facilitate and enhance interinstitutional synergies concerning the implementation of national policies and the programmes and measures based on the provisions of the Chemicals Act as well as to support expertise developed under other legislative pieces closely related to the Act, the Government of the Republic of Slovenia has established an intersectoral committee on chemical safety according to Article 56 of the Chemicals Act. The committee coordinates the work of the responsible ministries and assures a sound and integral development of chemical safety at the level of the whole country. The intersectoral committee on chemical safety also provides for the exchange of information concerning the broad area of chemical safety among sectors and internationally, discusses the problems in the chemical safety area, suggests and harmonizes common intersectoral solutions and cooperates in the preparation of the national programme on chemical safety as well as of the action plans. The governmental sectors, economy, social activities, non-governmental organizations (NGO) and other interest groups which work or have responsibilities in whichever area of the chemicals life-cycle are represented in the committee.

As a strategic document in the area of chemical safety, the National Programme on Chemical Safety (NPCS) for the period 2006-2010 covers national priority fields which are recorded as follows[1)]:

- Integrated intersectoral chemical safety legislation
- Integrated chemical inspection
- Health and safety at work with chemicals
- Chemicals waste
- Chemical accidents
- Integrated monitoring of chemicals pollution

The NPCS also emphasises some general measures to be considered:

- Chemical safety has to be ranged as the key aspect of national safety.
- Incorporation of the precaution principle as defined in the EU documents should be an integral part of chemicals management and decision-making processes
- Hazardous chemicals should be substituted with those less or non hazardous and use of chemicals in general should be reduced as much as possible.

The more relevant changes expected in the near future to affect the whole Slovenian system of chemicals management, including the chemical industry and other stakeholders, concern the implementing of the new EU chemicals strategy, i.e. the REACH system, the Globally Harmonised System of Classification and Labelling of Chemicals (GHS) as well as the implementation in praxis of principles and approaches of sustainable development and chemicals management embodied in the Declaration on a Strategic Approach to International Chemicals Management (SAICM) to achieve toxics-free future by the year 2020.

1.3 The new EU system on the area of chemical safety

Besides so many good facts about effectiveness of policies leading to decreasing concentrations of some harmful chemicals in the environmental compartments there remain a number of unresolved problems, e.g. insufficient characterization, management and communication of risks and as a consequence the possible hazards of chemicals as well as deficient exposure-response assessment. This led to a situation in which there are very little toxicity data on the great majority of 100,000 plus chemicals currently used industry-wide and nearly nothing is known about their potential environmental and human health impacts.

Since the current EU regulatory system of chemicals production and use proved to be weak, impeditive and ineffective, hampering even research and innovation of safer substances and processes, and thus provoking the EU chemical industry to lag behind its rivals in the US and Japan in this regard, the European Commission is currently developing a new policy on chemicals, based on the objectives and priority areas for action on the environment and health laid down in the 6th Environmental Action Programme, the headline targets of the EU Strategy for Sustainable Development and the White Paper for a future Chemicals Policy.

The White Paper strategy outlines the major objectives needed to be balanced within the overall framework of sustainable development. The two most relevant aims of the new EU chemicals strategy are protection of human health and environment from the risks of chemicals while enhancing the competitiveness of the EU chemical industry. A high level of chemical safety and a competitive chemical industry will be ensured through a system for Registration, Evaluation and Authorization of Chemicals – the REACH system.

The REACH system is based on the idea that the chemical industry itself is the most competent partner - given the industry's unique expertise as to chemical products and processes - to ensure that the chemicals it produces and puts on the market do not inflict upon human health and the environment. The new system is one of the most comprehensive and the most complex European legislative projects related to chemicals in general and to chemical safety in particular.

Introducing a new approach of control over production, marketing and use of chemicals and chemicals containing products, the REACH framework will enter into force in the form of the so-called REACH Regulation, meaning that its transposition into national legislation is mandatory to be met throughout the Community.

Unlike the existing EU legislation which has introduced two separate regimes for assessing chemicals, one relating to existing chemicals and one to new chemicals, the forthcoming REACH framework will create a single system of assessing for both of them, to bridge the knowledge and management gap between new (usually more thoroughly tested and managed) and existing chemicals by eliminating this distinction. Substances are now described as "*non-phase-in substances"* (i.e. those not produced or marketed prior to entry into force of REACH) and "*phase-in substances"* (those substances listed in the EINECS or those that have been manufactured in the Community but not placed on the Community market in the last 15 years or the so called "*no longer polymers"* of Directive 67/548). The REACH based new European chemicals policy will require basic data on all chemicals in commerce, information on risk assessment throughout chemicals life-cycles, rapid evaluation of chemicals risks and substitution of chemicals of highest concern with safer alternatives.

The communication requirements of the REACH framework establish a more balanced allocation of information ensuring that not only the producers and importers but also their customers, i.e. downstream users and distributors, have the information they need to use chemicals safely. Information relating to health, safety and environmental properties, risks and risk management measures is required to be passed both down and up the supply chain. Commercially sensitive information is not required to be exchanged.

All this will be sufficient to provide fundamental restructuring of chemicals management policies and to create integrated chemicals policy embodied in REACH.

Having been developed, to a great extent, by obligations resulting from international treaties, agreements and conventions, it will be likely to set the standards to be useful for global chemicals management. The REACH system as well as several Member States' policies and international treaties are guided by the concept of the Generational Goal – which implies the elimination of dangerous chemicals within one generation.

1.4 Need for an Integrated European Chemicals Information System

The ever greater emphasis placed on the attainability of toxics-free society and sustainable development over the last two decades raised a number of practical and methodological issues. The Commission White Paper on a Strategy for a Future Chemicals Policy highlighted a general lack of knowledge on the exposure to the existing substances under review under the existing substances regulation 793/93. It was recommended that an information system should be established on environmental concentrations and releases. It was pointed out that monitoring data ascertained by the Member States or by industry should be made available in an easily accessible form2).

Similar shortcomings regarding data availability, accessibility and comparability were recorded by some expert groups participating in the integrated monitoring programmes as well as by others from broader health and the environment protection community, noting the inconsistencies and the different interpretations about what the data mean, so that the general need for a better organised data and information exchange was broadly recognised.

The operation of efficient and successful chemical safety - being a complex of management principles and systems applied to the identification, understanding and control of hazards involved in the manufacture or use of chemicals - to protect the interests of the whole European population requires the establishment of a well developed Integrated European Chemicals Information System. Available data could be derived from the variety of sources, though very scattered, ranging from real time measurement records of the pollutants concentrations in environmental compartments, contaminants levels in animal and human tissue samples, food samples – mostly as a result of systematic monitoring programmes – to the annual production and trade statistics on chemicals. Therefore the development of a system that could improve the availability of information on concentrations, exposure and effects of chemicals in different natural and urban systems is of high priority. In that way data from scattered sources will be systematically structured to convey adequate information to different users. Type and detail of information depend on the user’s request. Some of them need primary, more detailed data, such as risk assessors, inspectors, indicator developers and research community, while others like governments, decision-makers, politicians, media, NGOs and the general public prefer aggregated information, such as indicators, where, depending on the intended use, the level of aggregation should be different.

1.4.1 Indicators as a tool in communication process

The concept of indicators in communication process is not a new one. Indicators present just a way of information packaging in a simple and straight manner helping to convey a momentous message to target audiences.

The OECD defines an indicator as a parameter, or a value derived from a set of parameters, that points to, provides information about/or describes the state of a phenomenon. It has significance beyond that directly associated with the parameter value.

From a policy-making point of view the use of environmental indicators is indispensable to show the degree of progress and success of policies using a range of approaches and frameworks. The development and use of indicators was popularized particularly as a tool for assessing progress with sustainable development objectives and has been used in this regard at international, national, regional and local levels. National and local governments and international organizations use a wide variety of environmental indicators.

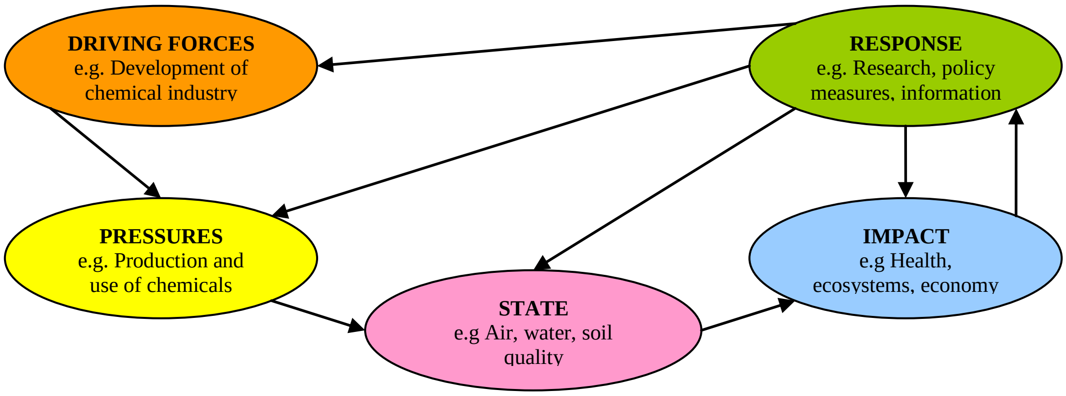
Considering the work done by governments, industry and the public to stimulate changes in chemical safety, it is anticipated that there will be indicators that can exactly measure trends in chemical safety. For better understanding and presenting problems as well as the level of sustainability in the production and use of chemicals, a system of corresponding indicators is required.

The critical component for the development of chemical indicators is identification of data that are useful for determining the status of chemical safety. A seriously selective approach is needed to determine what in fact presents a relevant indicator in a given context. The reasonable selection of chemical indicators requires a connection with political objectives, the capability of monitoring pressures, state and impacts related to chemicals and even the resulting societal response. Indicator-based information has been highly stated by the most important European policy initiatives: 6th Environment Action Programme, the EU Sustainable Development Strategy and will become an integral part of the new EU chemicals strategy, i.e. a new chemicals reporting system, presently under development (REACH-IT).

There are many initiatives to determine complex interdependences between phenomena that reflect all elements of the cause-consequence chain that link human activities to their ultimate environmental, social and economic impacts. The majority of these initiatives prefer the use of the framework developed by the OECD to promote standardisation of environmental indicators; this was given the acronym **DPSIR-*Driving forces, Pressure, State, Impact, Response***. The essence of this model is a system analysis view of the relations between the environment and human systems, for reporting environmental issues. The DPSIR framework demonstrates that social and economic development *(Driving forces)* exerts *Pressure* on the environment and, as consequence, the *State* of environment changes. Finally this becomes evident as *Impact* on human health, ecosystems and the environment, which may trigger a societal *Response* as feed-back or reprisal on *Driving forces*. This model has been used throughout Europe for indicator based reporting.

Indicators which present driving forces, environment pressures and societal response are considered policy levers, i.e. those reflecting the points that can be affected by policy and at which the policy is aimed. Although rather politically relevant some state and impact indicators, however, do not present areas that could be significantly affected by policy actions. Consequently, their relevance for policy is reflected indirectly, mostly by rising public awareness.

Figure 1. The DPSIR framework for reporting on environmental issues



The question what is that should be presented with the chemical indicators, e.g. consequences of toxics on humans and the environment or policy performance, is cleared in the sense that in principle all types of indicators from the DPSIR framework are needed. Chemical indicators – existing and those foreseen to be developed in the EU – are allocated as an integral part of different groups with different names, e.g. *"Headline indicators", "Pressure indicators", "Environmental indicators", "Sustainable development indicators",* etc.

In order to convey the massage about complex phenomena related to "*chemicalisation"* of our society and the environment and to simplify communication process to target groups of users, there was an idea of combining the information contained in a set of indicators into an aggregated index, presenting more condensed information. To develop an *"Index of toxic chemicals"*, a set of proxy indicators is required, targeting at different social/economic sectors. This set of proxy indicators proposed would be the basis for the index on toxic chemicals. The problem is that the contribution of each indicator (the weighting factor) can only be derived by modelling and expert judgement. Work on the development of indicators requires statistical data on produced, imported and consumed volumes of chemicals, industrial and private usage and consumption patterns (the latter being a bit problematic), intrinsic properties of chemicals and toxicity data. This includes good interpretation of measured and modelled data, usually required for risk assessments processes. In this case a breakdown by Member States is not feasible for the total index; some indicators are strictly based on EU level data collection, measures and tools3).

Generally aggregated indices should first satisfy the same criteria as other indicators: policy relevance, timeliness, analytical soundness and measurability, including transparency and ease of understanding and comparability across Member States.

Taking into account the present state of data availability, the EU Statistical Office (Eurostat) initiated in 2001 a 3-year project to develop a set of chemical indicators. Three types of indicators were proposed: "*Source", "Impact"* and "*Policy performance indicators"*.

The index ***(CHEMSIX-CHEMical Source Index)*** has been developed, based on the available produced and traded volumes of certain hazardous substances (production minus export plus import - Source data), combined with a model for weighting the intrinsic properties of and the potential exposure to these chemicals$^{4)}$.

Policy performance indicators are the outcome of an in-depth policy analysis of the White Paper and the REACH proposal. The proposed indicators are designed to monitor the progress in setting up the new REACH system. These indicators are presented as: a) number of substances evaluated, b) quantitative volume of new and existing substances and c) share of assessed substances, compared to the total volume of chemicals produced and imported.

Policy performance indicators will not be available at national level as the European Chemicals Policy (REACH) is a common effort of all Member States, managed by a central Chemicals Agency$^{4)}$.

Impact indicators are more complex, constituting different populations and environments on the one hand and risk types on the other. In essence chemicals are assigned to the matrix according to their toxic properties, the population, the estimated doses and other parameters. After ending the project further work on these indicators is required.

1.5 Chemical industry – Chemicals from production to waste streams

Social, economic and environmental aspects of chemicals issues should be considered in all parts of their life-cycle, from "*cradle to grave*". Producers, importers and downstream users have to be collectively responsible for local, regional and global environmental and social impacts of their actions. However, the production and use of chemicals as the source and starting point of chemicals released to society or the environment towards their complex final fate are the core factors of the sustainability concept.

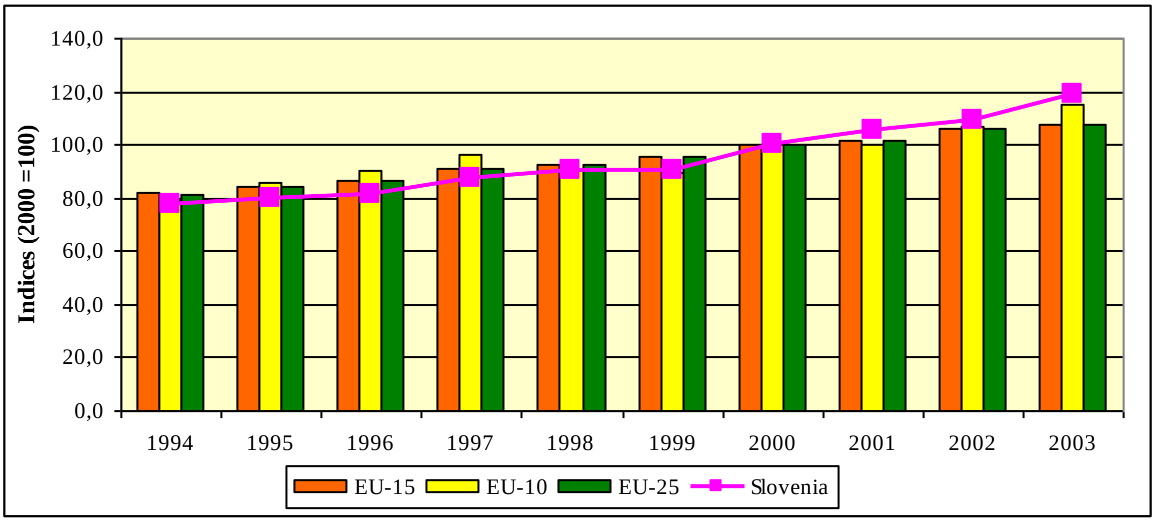
The chemical industry as a global industry is considered to be very heterogeneous in its character. Transforming materials as inputs by chemical processes into a variety of new substances/products with different chemical and physical properties is its major activity.

The chemical industry comprises activities that can be classified differently, depending on the classifications used. According to the Standard Classification of Activities (NACE Rev. 1), the European chemical industry is assigned into three major sections: Manufacture of coke, petroleum products and nuclear fuel (DF), Manufacture of chemicals, chemical products and man-made fibres (DG) and Manufacture of rubber and plastic products (DH).

The European chemical industry as a whole is the EU's third largest manufacturing industry, just behind food, beverages and tobacco, in terms of production, and electrical engineering in terms of value added. The EU is considered to be the world's most important producer of chemicals, being rather ahead of the USA and even further ahead of Japan.

The Slovenian chemical industry is one of the country's few industrial sectors that are expanding. Striving for being competitive on the global market, the pharmaceutical industry plays an important role. Among other important areas of the chemical industry are the production of paints and dyestuffs.

Figure 2. Chemical industry production indices, 1994-2003



Source: SORS, Statistical Yearbook 2005; CEFIC,
http://www.cefic.org/factsandfigures/level02/downloads_index.html

Figure 2 illustrates production trends of the European chemical industry over the period 1994-2003 expressed through production indices (2000 = reference year), broken down by different EU levels. Compared to the reference year 2000, the Slovenian chemical industry proved constant production growth in subsequent period observed. It was even greater than the average production growth of observed EU-15, EU-10 and EU-25 levels.

The changes facing the EU chemical industry are reflected in its self proclamation towards sustainability. To this end, its objective is to supply its customers worldwide with the highest quality products, at the lowest competitive cost, in a healthy and environmentally sustainable way and on a long-term basis.

Despite the fact that the chemical industry is one of the most highly regulated industrial sectors, ensuring that its products can be used safely, producing products which affect everybody's life is to a large extent the reason why there are so many concerns expressed by the general public and health authorities.

Besides government regulations, the chemical industry has taken a proactive role by leading programmes designed and launched to improve chemical safety. Among them the most recognizable are "*Responsible Care*", "*Product Stewardship*" and "*Chemical Industry Sustainable Economical and Ecological Development*" *(CHEMISEED)*, which tend to be vital to instil public confidence and maintain good business performance. For example, through the Responsible Care programme, member companies are committed to support a continuing programme to improve the industry's responsible management of chemicals. The principles of *"Green" or "sustainable"* chemistry and "*green*" engineering are becoming basic guidance in production processes of many world-wide distinguished companies. The Slovenian chemical industry is actively included in programmes being carried out across Europe by means of the Slovenian Association of Chemical Industry.

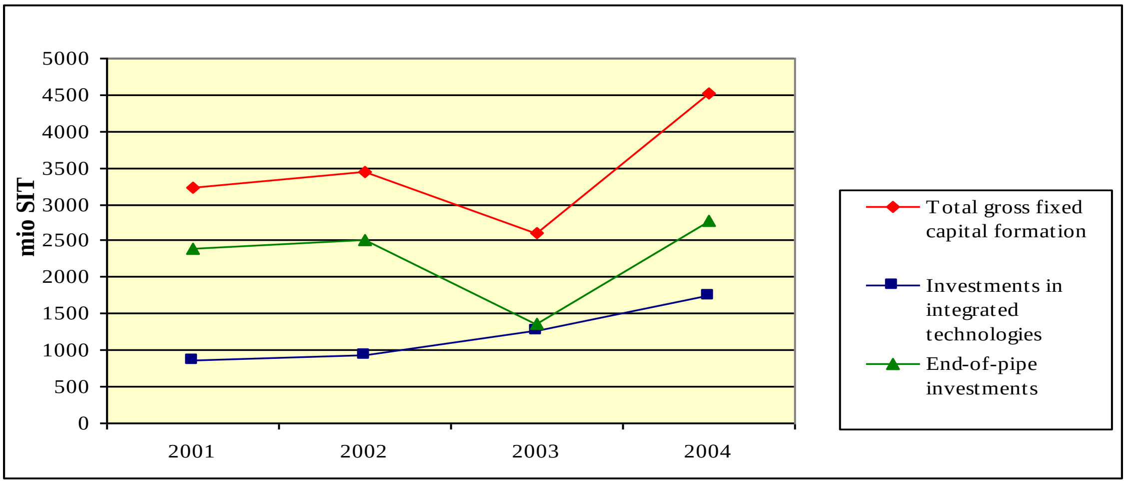
For better understanding and presenting the environmental problems, some special economic indices are required. Among them data on expenditure for the environmental protection are very important. Environmental protection expenditure is the response to the pressure and the state of the environment; it shows the preparedness for preserving the quality of the environment while avoiding, preventing, removing and reducing the harmful impacts to the environment. Data based on annual statistical surveys show that current environment expenditures in the Slovenian chemical industry in 2004 amounted to 20.6% of the total environment expenditures in the manufacturing industry5).

Gross fixed capital formation for environmental protection is distinguished by the purpose and nature to the end-of-pipe investment and investment in integrated technologies. From data in Figure 3 it is evident that in the period 2001-2004 total gross fixed capital formation for environmental protection in the chemical industry in Slovenia was greatest in 2004 (SIT 4,522 million), compared to previous year it increased by 73%. 38.7% of the total sum was investment in integrated technologies, while the rest was end-of-pipe investment.

Investments in integrated technologies in the chemical industry show constant growth since 2001, their share amounted to 31% of total investments in integrated technologies in the manufacturing industry. These investments cover investments for new or adaptation of existing methods, practices, technologies, processes or equipment designed to prevent or reduce the amount of pollution created at the source, thereby reducing the environmental impacts associated with the release of pollutants and/or polluting activities (reducing the impact to the environment). Pollution prevention can comprise different measures such as adaptation of equipment and technology, changes in production with the new improved technology, change of raw materials for cleaner products and/or changes in environmental management5).

End-of-pipe investments in the chemical industry over the same period observed were the greatest in 2004, in comparison to the previous year they increased by 104%, while their portion in total end-of-pipe investments in the whole manufacturing industry amounted to 30%. This comprises the investments that cover investments for the new methods, practices, technologies, processes or equipment designed to collect and remove the pollution and pollutants after their creation. They are intended also to treat and dispose the pollutants and to monitor and measure the level of pollution (mainly end-of-pipe methods, techniques or equipment, e.g. air emissions filters, wastewater treatment plants, waste collection and treatment activities)5).

Figure 3. Gross fixed capital formation for environmental protection in chemical industry, Slovenia,
2001-2004

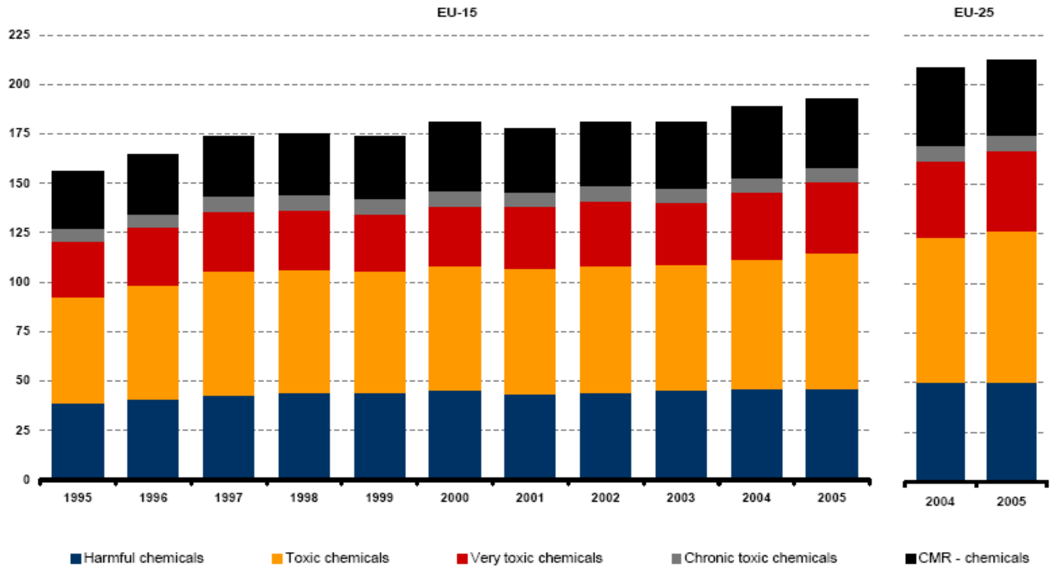


Source: SORS, Rapid information, No 209, 2006

Despite all new approaches and efforts to produce safer products, the chemical industry in general keeps being seen as the driving force behind the pressure to society and wildlife. The real risk can only be estimated when we consider the complex life-cycle of chemicals, their environmental fate and the effects of the impacts side.

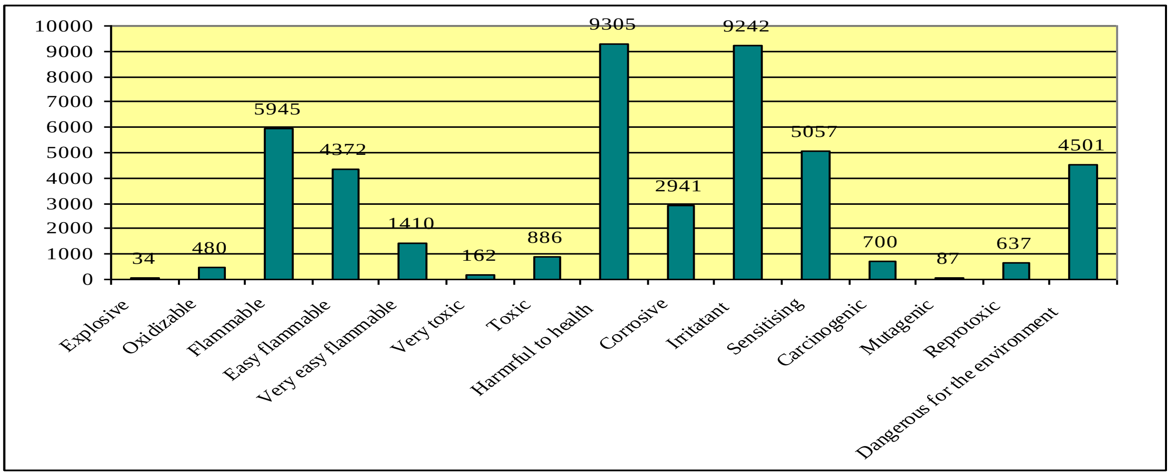
Data in Figure 4 present the trend in aggregated production volumes of toxic chemicals, broken down into five toxicity classes, which present one of the Eurostat's sustainable development indicators assigned to the theme "*Human health protection and lifestyles*". These classes are derived from the Risk Phrases assigned to the individual substances in Annex 6 of the Dangerous Substance Directive 67/548/EEC. The chemicals are grouped into five classes: Carcinogenic, mutagenic and reprotoxic (CMR) chemicals; Chronic toxic chemicals; Very toxic chemicals; Toxic chemicals and Harmful chemicals. Expressed in tonnage volumes, total amount of these dangerous substances for EU-15 shows constant upward trend over the period taken into account. The time series for EU-25 is too short to estimate the real trend.

Figure 4. EU production of toxic chemicals, by toxicity classes
(Mio tonnes)



Source: Eurostat, PRODCOM base

Figure 5. The number of dangerous chemicals on the Slovenian market, by class of dangerousness, 2005

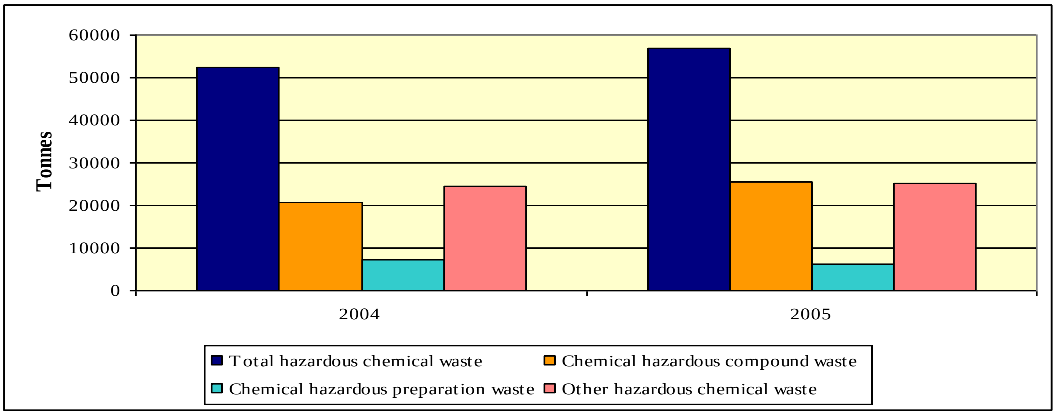


Source: Slovenian Chemicals Bureau, Chemicals database

Among dangerous chemicals which were registered on the Slovenian market in 2005 in terms of the number those harmful to health dominate, followed by irritant, flammable and dangerous to the environment chemicals (Figure 5). The share of individual chemicals can not be precisely expressed because some chemicals may occur in two or more groups simultaneously. Approximately 85% of the total number of dangerous chemicals registered on the domestic market in 2004 was imported to Slovenia. The majority of them are used by industry and service businesses.

Industrial waste generation is one of the most revealing indicators of production and consumption patterns of business entities. Environmental impacts of increasing hazardous waste volumes reflect the management practices of its generators, which in case of hazardous chemical waste are strongly related to the area of integrated management of chemicals.

Figure 6. Hazardous chemicals waste generated, Slovenia, 2004-2005



Source: SORS, Statistical Yearbook, 2006

Data in Figure 6 illustrate quantities of hazardous chemical waste generated in Slovenia in the period 2004-2005. Total amount of hazardous industrial waste generated in 2005 in Slovenia amounted to 122,161 tonnes, of which hazardous chemical waste presents 56,810 tonnes (47%). Compared to the previous year the amount of hazardous chemical waste increased by 8.2%. The greatest increase was recorded with chemical compound waste (22%), followed by the increase of other chemical waste (4%), while the amount of chemical preparation waste decreased by 18%. The amount of total hazardous chemical waste which was subject to internal recovery processes by waste generators is estimated at 3.2%, which is 2.6% less than in the previous year. 23.3% of this type of waste was internally disposed while the rest was delivered to other specialised entities for further recovery or disposal handling.

Conclusion

We need a proper mechanism to implement the global vision of sustainability in practice. Based on historical experience, we would expect the rate of harmful impacts of chemicals to fall less effectively than desired by the Generational Goal. An approximately ideal state of chemical safety is very difficult to realize under present conditions of awareness of different actors influencing the way of performing the principles set by most important European and international strategies. This will be a process with many alternating blind alleys and successes. But if we are to live in a healthy environment, we have to persevere with the task.

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ACUTE TOXICITY OF MERCURIC CHLORIDE ON RAINBOW TROUTS AND CHUBS

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Acute toxicity of mercury-II chloride ($HgCl_2$), one of most toxic pollutants for aquatic ecosystems, in chub (*Alburnoides bipunctatus*) and rainbow trout (*Onchorhynchus mykiss*) was investigated in the present study. Actual concentration of $HgCl_2$ was ranged from 0.10 to 8.00 mg/L. Concentrations of $HgCl_2$ that killed 50% of the chub and rainbow trout within 96 h (96-h LC_{50}) were estimated as 0.205 and 0.814 mg/L, respectively. Acute toxicity tests were evaluated by the Finney's Probit Analysis. Chub (*Alburnoides bipunctatus*) was appeared to be more sensitive than trouts (*Onchorhynchus mykiss*) to $HgCl_2$.

Keywords: *Mercury-II-cloride, Acute toxicity, European chub, Alburnoides bipunctatus*

Introduction

The determination of toxic compounds present in the aquatic environment and its effect on fish is a basic issue in aquatic toxicology (Bolis et al. 2001, Datta and Kaviraj 2003). Toxic substances may be determined with chemical analysis of water but its effects on fish and ecological risks for aquatic ecosystem could not be determined by chemical analysis. That's why, the preferred way to evaluate the ecological influence of toxic compounds is mortality or bioassay experiments in general (Başer et al. 2003, Svobodova et al. 2003).

Mercury compounds are very toxic and all forms of mercury are possible human carcinogens (ATSDR, 1999). Mercuric chloride has been used in agriculture as fungicide, in medicine as a topical antiseptic and disinfectant. Mercury-II-clorur is commonly used both for industrial, scientifically and agricultural purposes around the world as well as in Turkey.

In this work, mercury-II-clorur was selected for the bioassay experiment. The aim of this study was to determine the acute toxicity (96-h LC_{50}) of mercury-II-clorur formulation on rainbow trouts (*Onchorhynchus mykiss*) and chubs (*Alburnoides bipunctatus*) and variation of toxicity of mercuric chloride between two species.

Chub is (Eurasia) widely distributed in the basins of Biscay Bay, the North, Baltic Sea, Black, Caspian and Aral seas, in Vardar and Struma rivers of the Aegean basin, in the Tigris-Euphrates river system, in the Reza'iyeh Lake basin, and in some other localities in Iran. This species is a member of protected fauna according to Appendix III of the Bern Convention (URL 1**)**. Trouts is a common culture fish for aquaculture in the world.

The toxicity of many metal compounds to the rainbow trout, *Oncorhynchus mykiss*, was first studied in detail and chosen a widely available species, amenable to life in the laboratory, a fish of considerable commercial importance and sensitive to most toxic pollutants and reacts more quickly than most species to adverse environmental conditions (Abel, 1996).

Materials and Methods

Two species; rainbow trouts (*Onchorhynchus mykiss*) and chubs (*Alburnoides bipunctatus*) were selected for the bioassay test study. Chubs (*Alburnoides bipunctatus*) (weights:18.14±4.53 g, lengths:12.43±1.06 cm) were obtained from Iyidere stream in Rize. Fish were caught by electrofishing and brought to the laboratory within 20 min in plastic buckets with sufficient air. Trouts (*Oncorhynchus mykiss*) (weights:28.02±9.23 g, lengths:12.75±1.53 cm) were taken from a local trout breeding farm near laboratory. After 15 days acclimatization, the fish were placed into the maintenance tanks 250-L capacity. Temperature was regulated at 20±1°C by using heaters for chubs and at 15±1°C for trouts. Except for the dosing instance, all tanks were aerated. Test tanks were filled with 200 L of tap water. Some characteristics of these tanks water were dissolved oxygen 7.35-7.86 mg/L, pH 7.3-7.5, conductivity 158 - 182 μS and total hardness 61-65 mg $CaCO_3$/L (Table 1).

Table 1. Physicochemical properties of test water

Parameter	*Onchorhynchus mykiss*	*Alburnoides bipunctatus*
Tempetature (°C)	15±1	20±1
pH	7.3-7.5	7.3-7.5
Dissolved oxygen (mg/L)	7.2-8.6	5.7-6.9
Conductivity (μS/cm)	158-182	158-182
Total hardness (as $CaCO_3$)	61-65	61-65

Following the preliminary experiments, all determinations were repeated three times. Groups of experimental animals, each consisting of 10 individuals were selected at random and placed into aerated tank. After 48 h of adaptation, different concentrations of mercury-II-clorur were added to the experimental tanks. Mercury-II-clorur was prepared by diluting it in pure water to give the stock material. Dosing solutions were prepared from this stock by diluting with pure water to give the dosing concentrations of 0.000, 0.100, 0.125, 0.150, 0.175, 0.200, 0.400 mg/L for chubs. For trouts, the dosing concentrations are 0.000, 0.280, 0.400, 0.560, 0.840, 1.000, 1.120, 1.400, 2.000, 4.000 and 8.000 mg/L. During the last 24 h of adaptation, and throughout the duration of the experiment, animals were not fed. Mortality was controlled at 24, 48, 72, and 96 h after the start of the tests. Dead individuals were removed immediately. Behavioral changes were recorded in detail at 1-6 hours and every 12 h during tests.

The bioassay system was as described in standardized methods (APHA, AWWA, WEF, 1998) and the national regulation (Turkish Official Gazette, 1991). The LC_{50} and 95% confidence limits were calculated by a computer program (US EPA, 1999, Finney, 1971).

Results

The physicochemical characteristics of test water are listed in Table 2. Temperature ranged from 14 to 16 °C during experimentation. The pH of the water ranged from 7.3-7.5 and Dissolved oxygen ranged from 7.2 to 8.6 mg/L for rainbow trout, from 5.7 to 6.9 mg/L for chubs. The calculated 96-h acute LC_{50} value (95% confidence limits) of mercury-II-clorur using a static bioassay system to chub (*Alburnoides bipunctatus*) and rainbow trout (*Onchorhynchus mykiss*) were 0.205 and 0.814 mg/L, respectively. Control mortality was zero. The results show that mercury-II-clorur is very toxic to fish. Results appear in Table 2.

Table 2. LC_{50} values (with 95% confidence limit) of $HgCl_2$ (in mg/L) estimated by Finney for *O.mykiss* and *A.bipunctatus*

Species	LC_{50} value	95% confidence limit	Slope
Onchorhynchus mykiss	0.814	0.695-0.906	10.402
Alburnoides bipunctatus	0.205	0.185-0.346	12.095

Fish behaviour in Mercuric chloride bioassay test on Oncohynchus mykiss;

The control group showed normal behavior during the test period. The changes in behavioral response started 3 h after dosing mercury-II-clorur concentrations of 0.28, 0.40 and 0.56 mg/L concentrations had close to normal behavior. But there was 100% mortality at 1.40, 2.00, 4.00, 8.00 mg/L concentrations within the first 30 min after dosing. At 0.84 mg/L concentration, less general activity was recorded when compared with the control group and loss of equilibrium was observed. The responses of loss of equilibrium and hanging vertically in the water were observed above 0.84 mg/L concentration. 1.12, 1.40, 2.00, 4.00 and 8.00 mg/L showed all responses at high levels and the onset was within the first hour after dosing with mercury-II-clorur. Rapid gill movement, erratic swimming, swimming at the water surface and gulping for air and prolonged and motionless laying down on the aquarium bottom were other responses observed at all concentrations above 0.84 mg/L concentration.

Table 3. Cumulative mortality of fry rainbow trout (n=10, each concentration)

Concentrations (mgL^{-1})	Number of dead fry rainbow trout			
	24 h	48 h	72 h	96 h
Control	-	-	-	-
0.28	-	-	-	-
0.40	-	-	-	-
0.56	-	1	1	1
0.84	1	4	4	4
1.00	4	8	8	8
1.12	7	10	10	10
1.40	10	10	10	10
2.00	10	10	10	10
4.00	10	10	10	10
8.00	10	10	10	10

The mortality of rainbow trout for mercuric chloride doses 0.280, 0.400, 0.560, 0.840, 1.000, 1.120, 1.400, 2.000, 4.000, 8.000 mg/L were examined during the exposure times at (24, 48, 72 and 96 h) (Table 3) (Figure 1). The lowest concentrations of mercuric chloride (0.20, 0.40 and 0.56 mg/L) showed the lowest fish mortality at 96 h. The fish exposed during the period 24-96 h had significantly increased number of dead rainbow trout with increasing concentrations. There were significant differences in number of dead fish between the durations 24-48 h in each concentrations but no differences in 72-96 h. The highest concentrations of 1.12-8.00 mg/L showed the the highest fish mortality (Table 3) (Figure 1). The calculated 24, 48, 72 and 96 h LC50 values (95% confidence limits) using a static bioassay system for fry rainbow trouts were determined as 1.028 (0.945-1.118), 0.814 (0.695-0.906), 0.814 (0.695-0.906), 0.814 (0.695-0.906) mg/L, respectively (Table 4). There were not significant differences between LC1-99 values obtained different time of exposure (Table 4).

Table 4. Letal concentrations (LC $_{1\text{-}99}$) of mercuric chloride depending on time (24-96 h) for fry

rainbow trout

Point	Concentration (mgL^{-1}) (95% confidence limits)							
	24 h		48 h		72 h		96 h	
LC_1	0.738	(0.488-0.841)	0.487	(0.279-0.602)	0.487	(0.279-0.602)	0.487	(0.279-0.602)
LC_5	0.813	(0.602-0.900)	0.566	(0.369-0.671)	0.566	(0.369-0.671)	0.566	(0.369-0.671)
LC_{10}	0.857	(0.671-0.935)	0.613	(0.427-0.713)	0.613	(0.427-0.713)	0.613	(0.427-0.713)
LC_{15}	0.887	(0.722-0.960)	0.647	(0.471-0.743)	0.647	(0.471-0.743)	0.647	(0.471-0.743)
LC_{50}	1.028	(0.945-1.118)	0.814	(0.695-0.906)	0.814	(0.695-0.906)	0.814	(0.695-0.906)
LC_{85}	1.191	(1.100-1.462)	1.024	(0.920-1.232)	1.024	(0.920-1.232)	1.024	(0.920-1.232)
LC_{90}	1.233	(1.130-1.572)	1.081	(0.966-1.348)	1.081	(0.966-1.348)	1.081	(0.966-1.348)
LC_{95}	1.299	(1.174-1.754)	1.172	(1.033-1.550)	1.172	(1.033-1.550)	1.172	(1.033-1.550)
LC_{99}	1.431	(1.256-2.162)	1.363	(1.159-2.034)	1.363	(1.159-2.034)	1.363	(1.159-2.034)

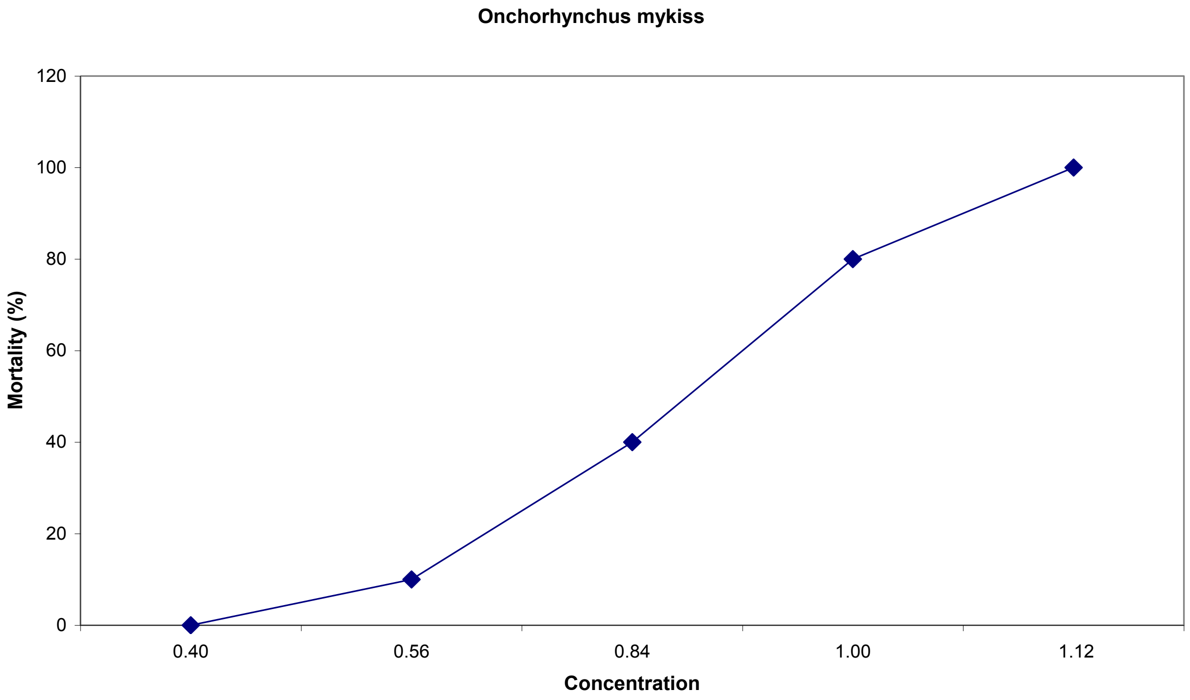

Figure 1. Percentage of mortality of *O.mykiss* after 96 h exposure to different concentrations of mercuric chloride

Fish behaviour in Mercuric chloride bioassay test on Alburnoides bipunctatus;

The control group showed normal behavior during the test period. The changes in behavioral response started 3 h after dosing mercury-II-clorur concentrations of 0.100, 0.125 and 0.150 mg/L concentrations had close to normal behavior. But there were 100% mortality at 0.400 mg/L and 50% mortality at 0.200 mg/L concentrations within the first 6 hours after dosing. At 0.175 mg/L concentration, less general activity was recorded when compared with the control group and loss of equilibrium was observed. The responses of loss of equilibrium and hanging vertically in the water were observed above 0.175 mg/L concentration. 0.200 and 0.400 mg/L showed all responses at high levels and the onset was within the first 6 hours after dosing with mercury-II-clorur. Rapid gill movement, erratic swimming, swimming at the water surface and gulping for air and prolonged and motionless laying down on the aquarium bottom were other responses observed at all concentrations above 0.175 mg/L concentration.

Table 5. Cumulative mortality of Chub (n=10, each concentration)

Concentrations (mgL^{-1})	Number of dead chub			
	24 h	48 h	72 h	96 h
Control	-	-	-	-
0.100	-	-	-	-
0.125	-	-	-	-
0.150	-	-	-	1
0.175	1	1	1	1
0.200	5	5	5	5
0.400	10	10	10	10

The mortality of chub for mercuric chloride doses 0.100, 0.125, 0.150, 0.175, 0.200 and 0.400 mg/L were examined during the exposure times at (24, 48, 72 and 96 h) (Table 5) (Figure 2). The lowest concentrations of mercuric chloride (0.100, 0.125 and 0.150 mg/L) showed the lowest fish mortality at 96 h. The fish exposed during the period 24-96 h had significantly increased number of dead chub with increasing concentrations. There were not significant differences in number of dead fish between the durations 24-96 h in each concentrations. The highest concentration of 0.400 mg/L showed the the highest fish mortality (Table 5) (Figure 2). The calculated 24, 48, 72 and 96 h LC50 values (95% confidence limits) using a static bioassay system for chub were determined as 0.200 (0.187-0.290), 0.200 (0.187-0.290), 0.200 (0.187-0.290), 0.205 (0.185-0.346) mg/L, respectively (Table 5). There were not significant differences between LC_{1-99} values obtained different time of exposure (Table 6).

Table 6. Letal concentrations (LC $_{1\text{-}99}$) of mercuric chloride depending on time (24-96 h) for chub

Point	Concentration (mgL^{-1}) (95% confidence limits)							
	24 h		48 h		72 h		96 h	
LC_1	0.158	(0.045-0.175)	0.158	(0.045-0.175)	0.158	(0.045-0.175)	0.132	(0.041-0.154)
LC_5	0.169	(0.076-0.182)	0.169	(0.076-0.182)	0.169	(0.076-0.182)	0.150	(0.075-0.168)
LC_{10}	0.176	(0.100-0.187)	0.176	(0.100-0.187)	0.176	(0.100-0.187)	0.161	(0.101-0.178)
LC_{15}	0.180	(0.120-0.192)	0.180	(0.120-0.192)	0.180	(0.120-0.192)	0.168	(0.123-0.187)
LC_{50}	0.200	(0.187-0.290)	0.200	(0.187-0.290)	0.200	(0.187-0.290)	0.205	(0.185-0.346)
LC_{85}	0.222	(0.203-0.632)	0.222	(0.203-0.632)	0.222	(0.203-0.632)	0.250	(0.212-1.841)
LC_{90}	0.227	(0.206-0.763)	0.227	(0.206-0.763)	0.227	(0.206-0.763)	0.262	(0.218-1.042)
LC_{95}	0.235	(0.211-1.009)	0.235	(0.211-1.009)	0.235	(0.211-1.009)	0.280	(0.227-1.433)
LC_{99}	0.252	(0.219-1.708)	0.252	(0.219-1.708)	0.252	(0.219-1.708)	0.319	(0.245-2.607)

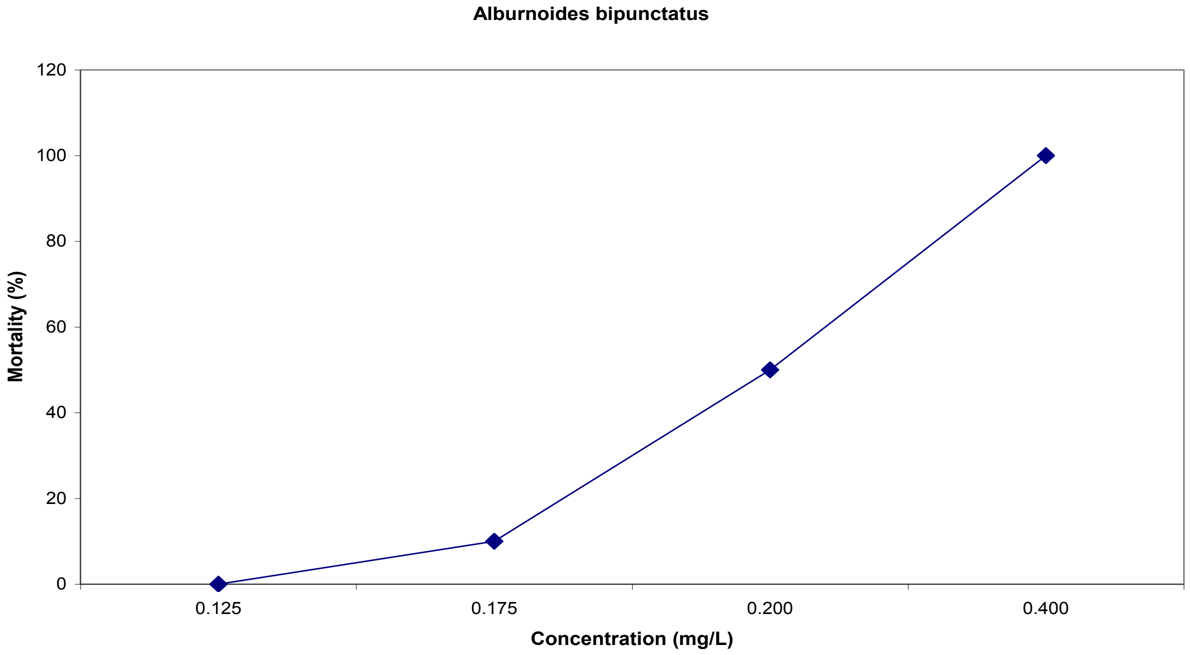

Figure 2. Percentage of mortality of *A.bipunctatus* after 96 h exposure to different concentrations of mercuric chloride

Discussions and Conclusions

The 96-h LC_{50} value of mercury-II-clorur in chubs was found as 0.205 mg/L and 96-h LC_{50} for fry rainbow trout was 0.814 mg/L in the present work. In aquatic toxicology, if LC_{50} (mg/L) concentration is smaller than 1 mg/L, the chemical is highly toxic and if between 1-10 mg/L, then it is considered to be a moderately toxic (Louis et al., 1996). Therefore we report mercury-II-clorur to be highly toxic to fish species used. According to FAO/UNEP (1991), The 96 h LC_{50} values for $HgCl_2$ are for catfish, 0.35 mg/L; rainbow trout, 0.22 mg/L; striped bass, 0.09 mg/L; brook trout, 0.075 mg/L and mummichog, 2.0 mg/L.

The LC_{50} value of mercury-II-clorur in other aquatic organisms was reported as 0.037 mg/L for fathead minnow, 0.16 mg/L (96-h EC_{50}) for bluegill sunfish (size:0.6 g) and 0.903 mg/L for rainbow trout (URL 2). The 96-h LC_{50} values of inorganic mercury was reported as 0.002 mg/L (30d) for crayfish (*Orconectes limosus*), 0.005 mg/L for cladoceran (*Daphia magna*), 0.01 mg/L for scud (*Gammarus pseudolimnaeus*), 0.2 mg/L for juvenile rainbow trout, 0.44 mg/L for *Notopterus notopterus*, 0.0073 mg/L for leopard frog (*Rana pipiens*), 0.107 mg/L for marbled salamander (*Ambystoma opacum*), 0,0058 mg/L for blue mussel (*Mytilus edulis*), 0.33mg/L for adult slipper limpet (*Crepidula fornicata*), 0.089 mg/L for bay scallop (*Argopecten irradiance*), 0.0035 mg/L for juvenile mysid shrimp (*Mysidopsis bohia*), 0.015mg/L for adult copepod (*Acartia tonsa*), 0.0153 mg/L for prawn (*Penaeus indicus*), 0.014 mg/L for polychaete larva (*Capitella capitata*), 0.098 mg/L for haddock (*Melanogrammus aeglifinus*) (Eisler, 1987).

Sastry and Gupta (1978) reported the mercury (LC_{50}: 1.8 mg/L) inhibits the activities of phosphates in the liver but no significant effect on the digestive enzymes within the experimental period of 96 hours. According to present study, chubs (*Alburnoides bipunctatus*) are more sensitive than rainbow trout (*Oncorhynchus mykiss*).

Mercury-II-clorur has slightly toxicity to fish and other aquatic organisms as is common with many metalloids, pesticides and other chemicals. However, because of lack of tight controls during marketing in many countries, there may be unexpected potential risks on the environment. Special consideration should be given to residues in food and bioaccumulation in non-target organisms including man.

Acknowledgement

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REMOVAL OF COLOUR FROM INDUSTRIAL WASTEWATER

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This experimental study is related to the garment and carpet manufacturing industries located in and around the city of Varanasi. The ancient city of Varanasi is also termed as the cultural and religious capital of India. The city has been famous for its Banarasi Saree and carpet industries, which are based on silk, wool and cotton fabrics. These industries use acid and direct dyes for colouring of their fabrics. Reactive dyes are also used on account of their brighter colours and ease in application. However, acid dyes are more frequently used in high quantity as compared to the other two varieties. Acid Red 94 is one of the important dyes, applied in these industries and therefore, it has been identified for this study.

The study has been conducted to determine and subsequently, compare the removal efficiencies of this dye by using commercially available alum and water treatment plant sludge. The sludge was collected from the water treatment plant located at Bhelupur in Varanasi city.

1. INTRODUCTION

Dyes are coloured chemicals consisting of ionizing, aromatic organic compounds. These are based fundamentally on the structure of benzene. Dyes are broadly classified as natural or synthetic. Synthetic colouring agents are harmful to human beings and animals because of their toxicity, carcinogenicity, mutagenicity, tetarogenicity and other such characteristics, which inflict adverse effects on human health. Anthropogenic sources like certain industries and mainly dyeing units discharge dyes in their wastewater streams, which finally find their ways into the water bodies.

Sludge obtained from various industrial operations has been reported for dye removal by many researchers. Martin *et al*. (2003) have compared the removal of three anionic dyes from aqueous solutions using commercially available activated carbon and activated carbon obtained from surplus biological sludge of wastewater treatment plants. Golder, Samanta and Ray (2006) have investigated the potential of electro-coagulated metals hydroxide **sludge**, generated during **removal** of Cr^{3+} using Al electrode, for adsorption of Congo Red from aqueous solution. Netpradit, Thiravetyan and Towprayoon (2003) studied the capacity and mechanism of metal hydroxide **sludge** in removing three anionic reactive **dyes** from aqueous solution. Kargi and Ozmihci (2004) have studied the biosorption performance of powdered activated sludge for removal of different dyestuffs.

Sponza and Isik (2004) have studied the de-colourization of Direct Black 38 with granulated anaerobic sludge. Rozada *et al*. (2003) have studied the removal of Methylene Blue and Saphranine from solution using activated carbon obtained from chemical activation and pyrolysis of sewage sludges in batch and fixed-bed systems. Chu (2001) has studied the removal of dyes from textile dying wastewater by recycled alum sludge generated by the coagulation process. Li *et al*. (*article in press*) have employed Fenton's process to treat synthetic **dye** wastewater with supply of Fe (II) electrolytically generated from iron-containing **sludge,** which was recycled and reused. Santos *et al*. (2004) investigated the impact of different redox mediators on colour removal of azo dye model compounds and textile wastewater by thermophilic anaerobic granular sludge (55°C) in batch assays. Otero *et al*. (2003) have carried out the kinetic and equilibrium modelling of the removal of Methylene Blue from solution by adsorbent materials produced from sewage sludges. Fu *et al*. (2002) have studied **the removal** of a Copper-Phthalocyanine **dye** (Reactive Turquoise Blue KN-G, RTB) from wastewater under anaerobic and aerobic conditions using acclimated **sludge.** Sirianuntapiboon and Srisornsak (2007) have studied the removal of disperse dyes from textile wastewater using bio-sludge. Chu and Chen (2002) have studied the removal of basic dyes from wastewater using activated sludge biomass as an adsorbent. Gulnaz, Kaya and Dincer (2006) have studied the removal of reactive dye by dried activated sludge in a batch system. Annadurai *et al*. (2003) have examined the capacity of adsorbent recycled from microwave thermal treatment to remove Rhodamine 6G from wastewater.

In this paper, the results of an experimental study conducted for the removal of Acid Red 94 from industrial wastewaters using commercial alum and water treatment plant sludge has been presented. First of all, removal has been studied using commercial alum, as this material is used for treatment of coloured wastewater by most of the textile-dyeing industries in and around Varanasi city. Removal of the same dye using water treatment plant sludge, obtained from Bhelupur Water Treatment Plant, Varanasi, has also been carried out. The results obtained in case of the materials mentioned above have been compared for the identification of an efficient, economic and environmentally sustainable removal methodology for treatment of coloured industrial wastewaters.

2. Sieve Analysis of Water Treatment Plant Sludge

Sieve analysis of the water treatment plant sludge has been done and the weight (%) of sludge of every sieve size is presented in tabular form in Table 1.

Table 1: Results of Sieve Analysis Conducted on Water Treatment Plant Sludge

Sieve Size (micrometers)	**Weight of Sludge after Sieving (grams)**	**Weight (%)**
Greater than 500	44.5	12.71
500 - 355	23.3	6.66
355 – 125	32.4	9.26
125 – 90	49.8	14.23
90 – 75	37.9	10.83
Less than 75	159.2	48.58

3. EXPERIMENTAL RESULTS FOR THE DYE ACID RED 94

3.1 Determination of Wavelength Corresponding to the Maximum Absorption

Wavelength for the maximum absorption (λ_{max}) for this dye has been determined by varying the wavelength scale by 10 nanometers (nm) and subsequently recording the absorption of the particular wavelengths. For getting more accurate result, wavelength for the maximum absorption has been determined by varying the wavelength in a narrow range of 2 nm afterwards. The results obtained are presented in the graphical form below in Figures 1 and 2.

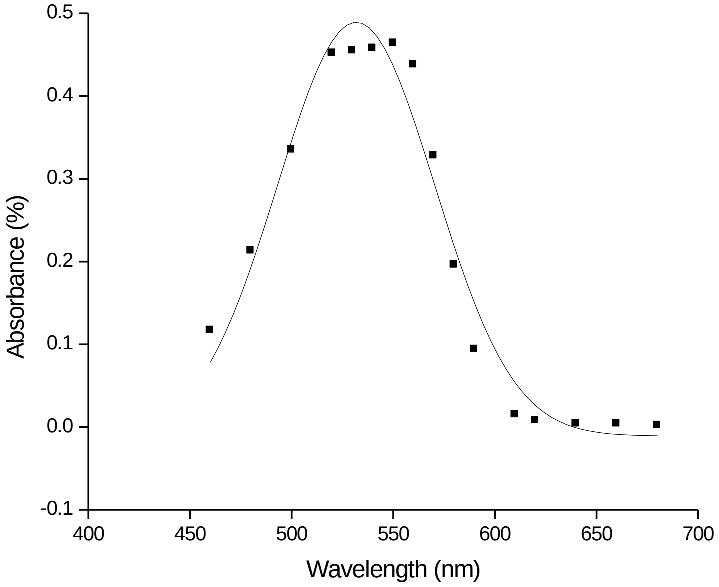

Figure 1: Determination of λ_{max} (Variation Interval = 20 nm)

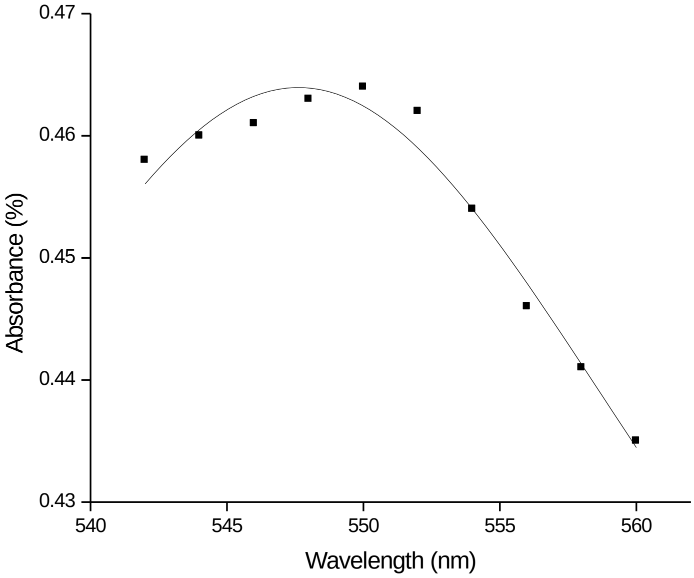

Figure 2: Determination of λ_{max} (Variation Interval = 2 nm)

3.2 Preparation of Calibration Curve

Calibration curve has been drawn for the dye (Acid Red 94) for concentration range of 0-100 mg/L against percentage absorbance and it is found to be a straight line as shown in Figure 3.

3.3 Determination of Upper Concentration Limit

To determine the maximum dye concentration after which the coagulation is not required for removal process (because the dye starts coagulating automatically), Jar test has been carried out without adding any coagulant. After concentration of 70 mg/L, settlement of dye starts. The result in the graphical form is presented in Figure 4.

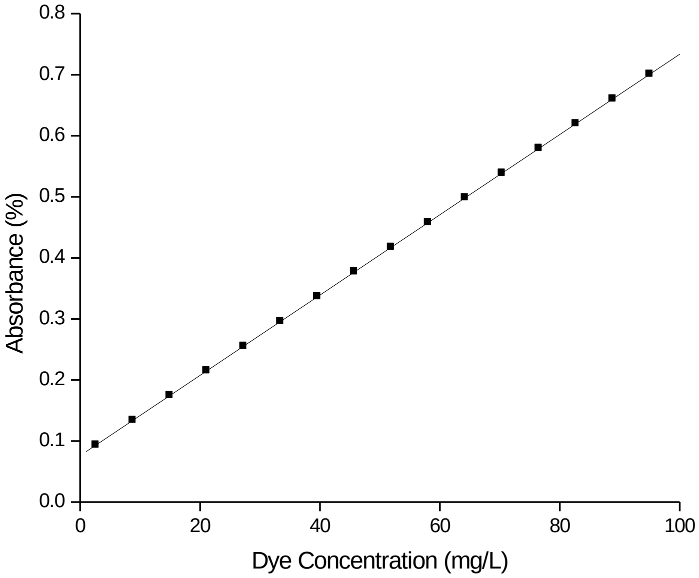

Figure 3: Calibration Curve

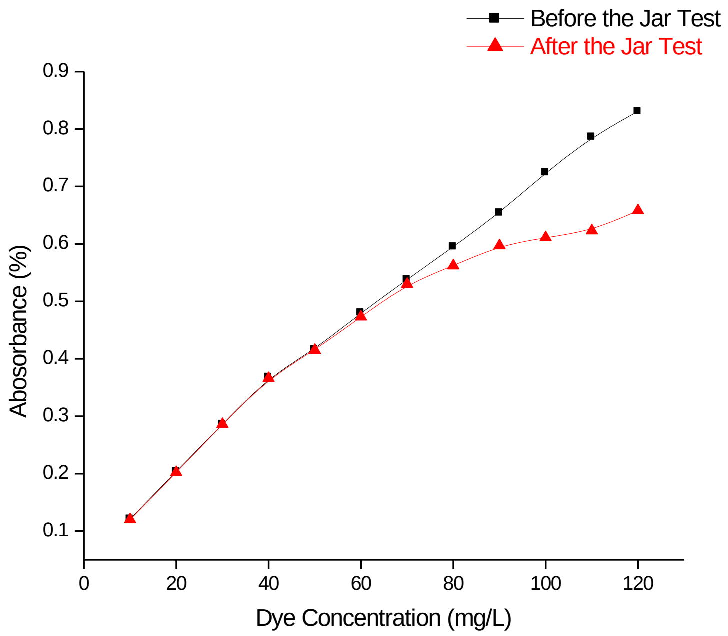

Figure 4: Determination of the Maximum Concentration Limit (Acid Red 94)

3.4 Removal at Varying Concentration

The percentage removal has been studied for this dye by varying its concentration with an interval of 10 mg/L. The coagulant dosage has been kept constant at 100 mg/L. The result in the graphical form is shown in Figure 5. The maximum removal occurs at the concentration of 20 mg/L of the dye.

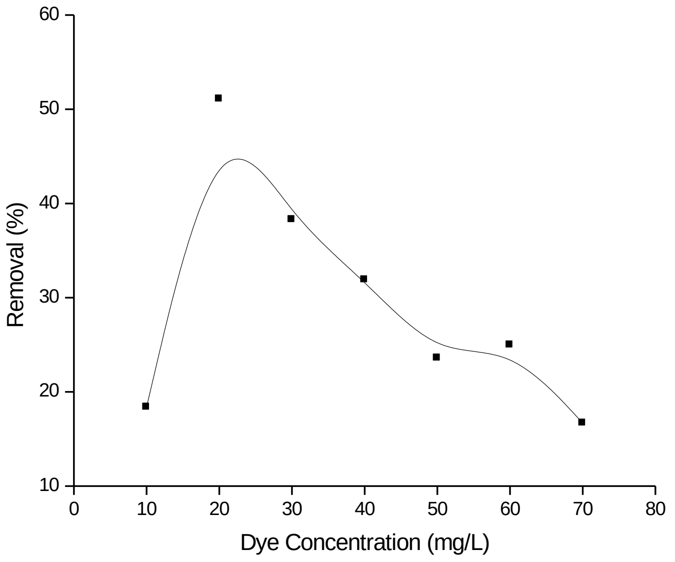

Figure 5: Removal at Varying Dye Concentration (Alum Dosage 100 mg/L)

3.5 Removal with Varying Coagulant Dosage

Percentage removal with varying coagulant dosage has been studied for dye concentrations of 10 mg/L, 20 mg/L and 30 mg/L. The results are presented in graphical form in Figures 6, 7 and 8 respectively. From these figures, optimum coagulant dosage can be determined for different concentrations of the dye.

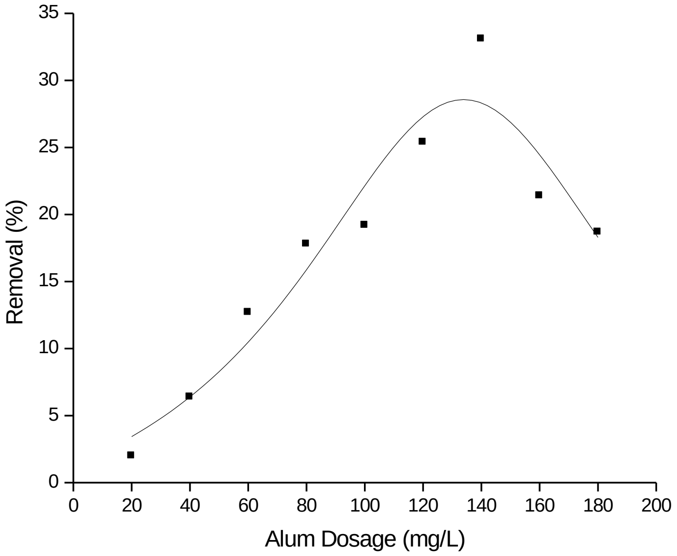

Figure 6: Determination of Optimum Coagulant Dosage (Dye Concentration = 10 mg/L)

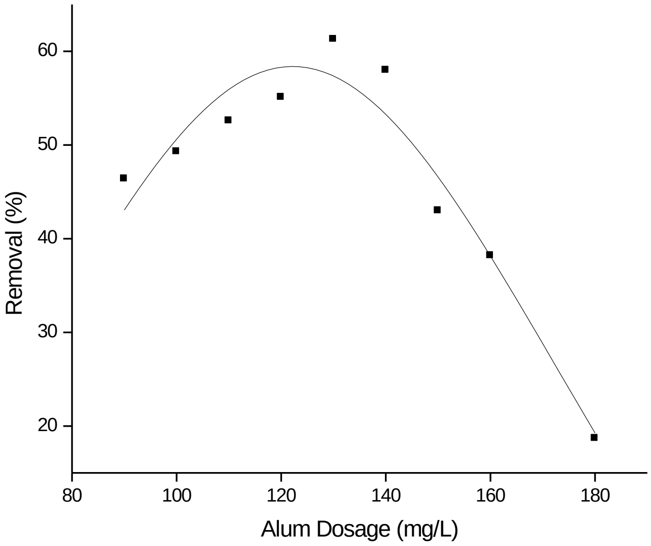

Figure 7: Determination of Optimum Coagulant Dosage (Dye Concentration = 20 mg/L)

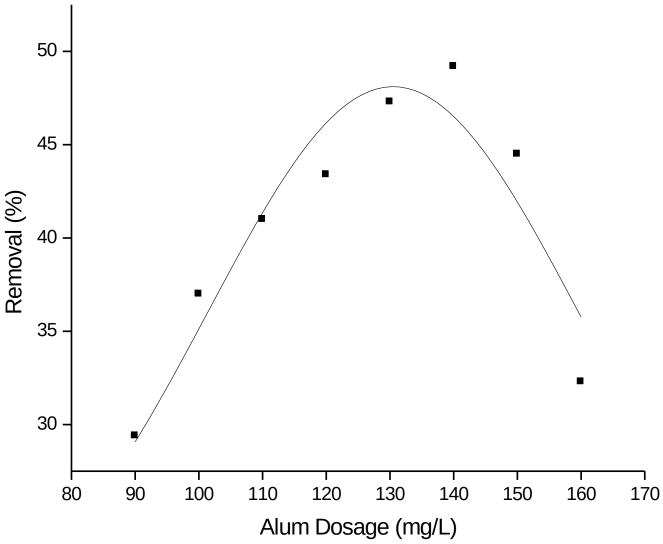

Figure 8: Determination of Optimum Coagulant Dosage (Dye Concentration = 30 mg/L)

For the dye concentration range of 10-30 mg/L, the maximum removal has been achieved at 20 mg/L. At this concentration, the optimum coagulant dosage was found to be 130 mg/L and the maximum removal at the conditions mentioned above has been found to be 61.3%.

3.6 Effect of pH Variation

At the dye concentration of 20 mg/L and at optimum coagulant dosage, pH of the dye solution has been varied by adding calculated quantities of acid (concentrated HCl). Variation in percentage removal with pH has been shown in Figure 9. At pH of 5.9, the maximum removal has been achieved up to 72.6 % for this dye.

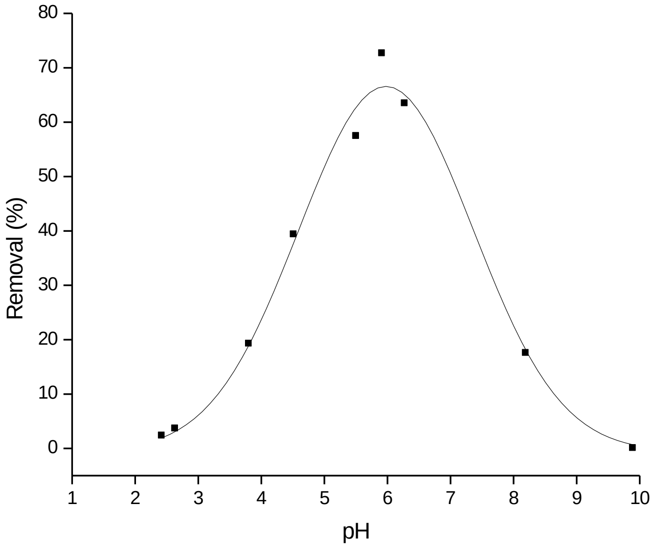

Figure 9: Effect of pH on Removal of the Dye

3.7 Studies on Removal Using Water Treatment Plant Sludge

At optimum conditions for the maximum removal as in case of alum, *i.e.*, at the dye concentration of 20 mg/L, percentage removal for the dye (Acid Red 94) has been determined using the water treatment plant sludge of different sizes. The Sieve sizes varied from greater than 500 μm to less than 75 μm. The ranges other than 75-90, 90-125 and 125-355 μm have been discarded due to insignificant removal (at these sieve size-ranges). Turbidity was also found to rise due to presence of higher quantity of the soil apparently. The removal (%) using water treatment plant sludge has been determined in case of sieve size-ranges of 75-90, 90-125 and 125-355 μm. The results obtained are presented graphically in Figures 10, 11 and 12 respectively.

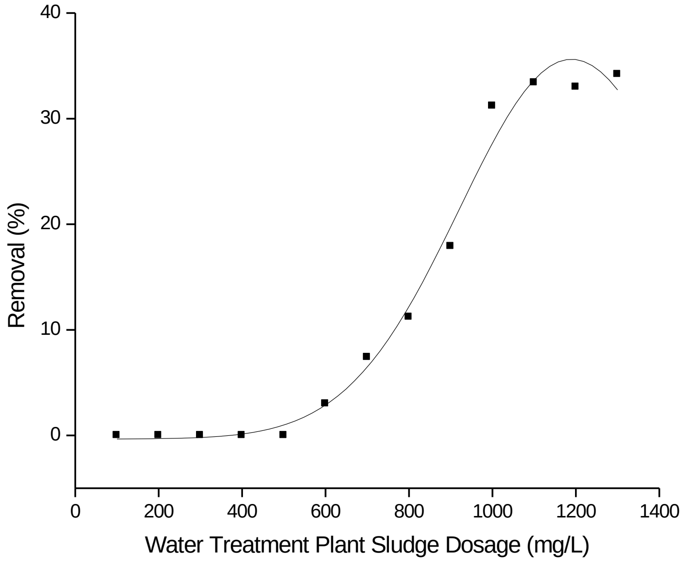

Figure 10: Determination of Optimum Coagulant Dosage (Dye Concentration = 20 mg/L and Sieve Size = 75-90 μm)

Percentage removal was found to increase upto 34.2% at dosage of 1300 mg/L of the water treatment plant sludge. After that dose, the turbidity starts increasing and removal continued to remain between 33 – 37%. Percentage removal employing the water treatment plant sludge of sieve size 90-125 μm has also been studied. The experimental results are shown graphically in Figure 11. Percentage removal was observed to increase upto 41.5% at the sludge dosage of 700 mg/L. After that, turbidity starts going up and the removal was found to lie in the range of 37 – 40%.

Percentage removal using the water treatment plant sludge of sieve size 125-355 μm has also been investigated and the results obtained are shown graphically in Figure 12. Percentage removal increased upto 25% at dosage of 600 mg/L of the water treatment plant sludge. After that, turbidity starts going up and the range of removal has been found to be between 23 – 25%.

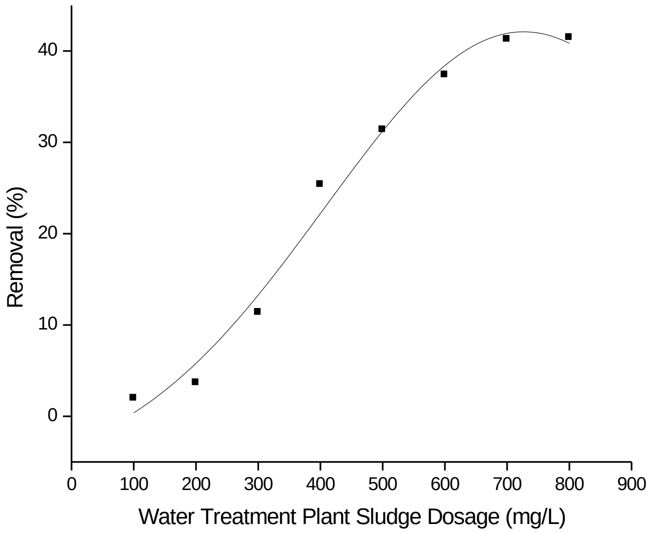

Figure 11: Determination of Optimum Coagulant Dosage (Dye Concentration = 20 mg/L and Sieve Size = 90-125 μm)

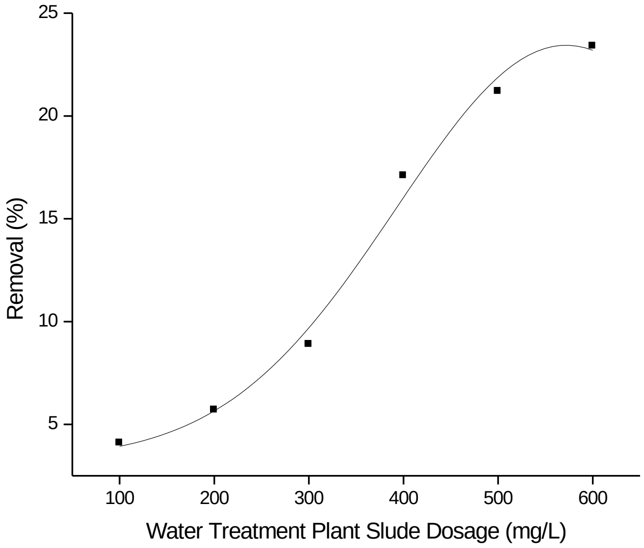

Figure 12: Determination of Optimum Coagulant Dosage (Dye Concentration = 20 mg/L and Sieve Size = 125-355 μm)

4. CONCLUSIONS

The effect on percentage removal of the dye (Acid Red 94) due to changes in concentrations of the coagulants and dye and also, on account of change in pH has been studied. The water treatment plant sludge was heated to ensure dryness and then, ground and sieved. Three size fractions, namely, 75-90, 90-125 and 125-355 μm have been used for this experimental study. The maximum removal for the dye Acid Red 94 with water treatment plant sludge has been found to be 41.5% at the dosage of 700 mg/L (of the sludge) at sieve size of 90 -125 μm. At pH = 6, the optimum coagulant dosage has been found to be the same as for pH obtained without adding acid (concentrated HCl) and the percentage removal is found to increase slightly upto 45.2 %. At constant alum dosage of 100 mg/L and varying the concentration of the dye, maximum removal occurred at a dye concentration of 20 mg/L. Maintaining the dye concentration constant and varying the alum dosage, it was observed that the maximum removal of 61.3% was achieved at a dye concentration of 20 mg/L and alum concentration of 130 mg/L. At pH 5.9, the removal efficiency was the highest, *i.e.*, 72.6%.

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APPLICABILITY OF PHOTOCATALYTIC OXIDATION PROCESS TO EFFLUENT OF THE COMBINED WASTEWATER TREATMENT PLANT

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In this study, advanced oxidation of wastewater of combined treatment plant has been investigated by photocatalytic oxidation process. Efficacy of process was evaluated with the degradation of organic substances and color removal. The removal efficiencies of COD, TOC and color were investigated with alternative catalysts (TiO_2, ZnO, TiO_2+ZnO).

UV/TiO_2/H_2O_2, UV/ZnO/H_2O_2 and UV/TiO_2+ZnO/H_2O_2 series were studied in the presence of 1gL^{-1} catalyst and 30 mM H_2O_2. Optimum pH conditions of process were determined in the first step of the study. Under the acidic conditions the most suitable series was UV/TiO_2/H_2O_2 with 95% color removal and with 90% COD removal. COD removal efficiencies for photocatalytic oxidation with 1g/L TiO_2 were 90%, 77% and 74% at pH 2.5, 7.0 and 11.0; respectively. Reaction rate constants, k were 0.43 h^{-1} at pH 2.5, 0.28 h^{-1} at pH 7.0 and 0.25 h^{-1} at pH 11.0, in the UV/ TiO_2/ H_2O_2 series. In the second step, the photocatalytic degradation of organic matter has been studied at various hydrogen peroxide concentrations (15, 30 and 45 mM) at pH 2.5 for the series of UV/ TiO_2/ H_2O_2**.**

Keywords: *Photocatalytic oxidation, color removal, reaction rate constant, combined wastewater.*

Introduction

Industrial wastewaters include organic substances and complex contaminants. Contaminants in these wastewaters form not only high levels of Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC), but also create color problems due to strong bounds in their structures. Problems that can not be solved with conventional methods emerged the need for advanced treatment techniques. Photocatalytic oxidation process is one of the advanced treatment methods which degrade contaminants using natural or artificial light source, various oxidants and/or catalysts. Numerous studies have been performed about the photocatalytic treatment of wastewater especially sourced from dye mills with using different catalysts. [1-2-3-4-5] Effects of the amount of catalysts, illumination time and pH on the process were evaluated in those studies.

Twenty different pretreated industrial wastewaters (i.e. tires, fermentation, drugs) are canalized to the combined biological treatment plant. Also, 5% of total flow is raw domestic wastewaters. The wastewaters obtained from the outlet of the plant were used in this study. Effluent of the plant had a serious color problem and discharged to Izmit Bay. Improvement of the water quality of the Bay has been depending on the treatment of the color problem. In our previous studies, removal of organic substances and color was investigated in the influent of the same plant by the application of photocatalytic oxidation process. [6] Determination of the photodegradation efficiency of the single and coupled semiconductor systems at different pHs in the effluent of the plant was aimed and the effect of oxidant amounts was examined in this study.

Material and Methods

The wastewater was obtained from the outlet of combined treatment plant. Prior to all experiments, wastewater was filtrated using a rough filter paper. In the experiments, TiO_2 (Degussa P25, mainly anatase, specific surface area 50±15 m^2/g) and ZnO (purchased from Merc) were used as catalyst. H_2O_2 (30% w/w, purchased from Merc) was used as oxidant. Initial pH values of solution were adjusted by H_2SO_4 and NaOH.

Analysis

A CADAS 200 spectrophotometer was used to measure the absorbance by scanning in the wavelength range of 200 to 500 nm. The COD parameter was determined according to the "Close Reflux titrimetric methods" as given in Standard Methods. [7] TOC was measured using a procedure described in ASTM Standards D 4129-98 .[8] Prior the COD analysis, the residual H_2O_2 was determined via molybdate-catalysed iodometric titration. [9]

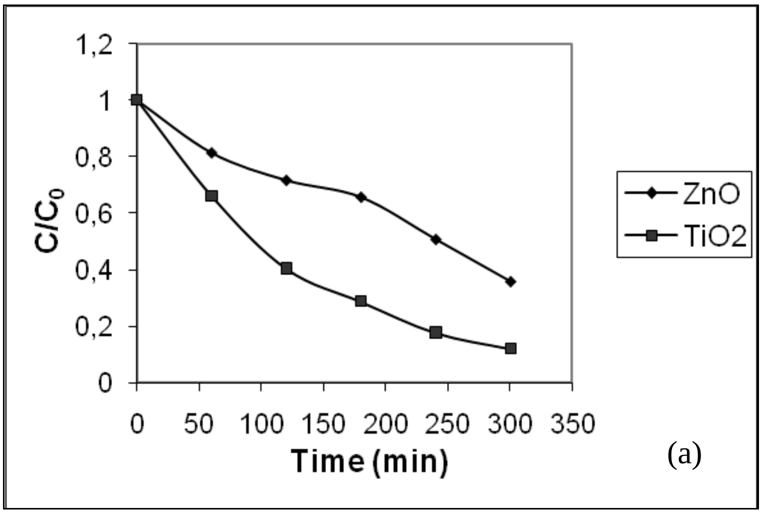
Experimental equipment and procedure

A 5000 mL capacity Plexiglas reactor equipped with 4 low pressure mercury 15W lamps emitting UV-C light at 253.7 nm and being placed into a quartz sleeve housing was used throughout the experiments. The reaction solutions (3000 mL) were vigorously mixed from the bottom of reactor by using a magnetic stirrer to keep the photocatalysts suspended. By using TiO_2 and ZnO, single and coupled semiconductor systems were formed. The total amount of catalysts used was 1 gL^{-1} in all experiments. The weight ratio of catalysts was 1:1 in the coupled system (TiO_2 +ZnO). Photocatalytic reactions were run for 300 min., and 20 mL samples were taken from the reactor in every 30 min. These samples were filtrated through Millipore AP 40 filter papers with 0.45 µm pore size to separate the catalysts.

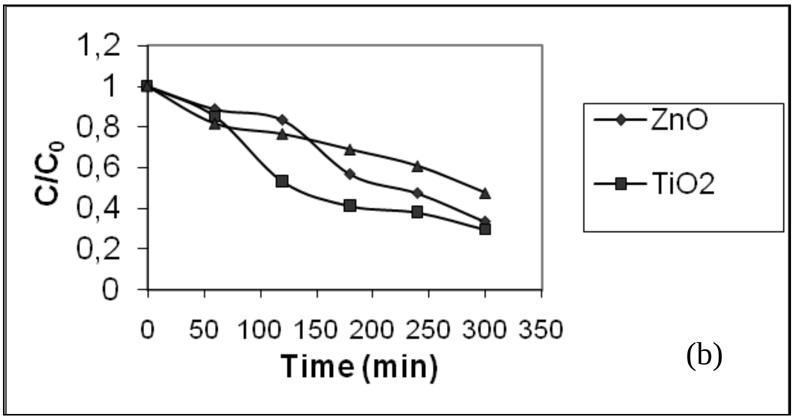
Photocatalytic experiments were performed in two steps. In the first step UV/TiO_2/H_2O_2, UV/ZnO/H_2O_2 and UV/TiO_2+ZnO/H_2O_2 series were studied. The color removal and degradation of organic matter were investigated at different pH conditions in this three series. In the second step, the effect of H_2O_2 amount was examined at pH 2.5 for the UV/TiO_2/H_2O_2 series. In the first and second steps of study, the used wastewaters were sampled on different days. The efficiency of color removal was evaluated by scanning absorbance-wavelength for raw and photocatalyzed wastewaters.

Results and Discussion

The photocatalytic degradation of wastewater was evaluated for UV/TiO_2/H_2O_2, UV/ZnO/H_2O_2 and UV/TiO_2+ZnO/H_2O_2 series in presence of 1gL^{-1} catalysts and 30 mM H_2O_2 at pH 2.5, 7.0 and 11.0 during 300 min. illumination time (Figure 1). So, the effects of initial pH solution were examined in acidic, neutral and alkaline conditions.



(a)



(b)

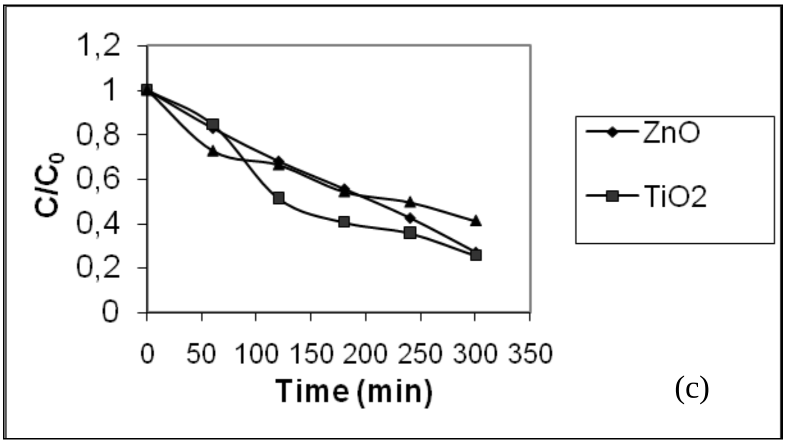


Figure 1. The degradation of organic matter under different pHs (a) pH=2.5 (b) pH=7 (c) pH=11 (in presence of $1gL^{-1}$ catalysts, 30 mM H_2O_2)

Table 1 shows the COD removal efficiency of wastewater as a function of pH.
Table 1. The removal efficiencies of COD (%)

Series	pH 2.5	pH 7.0	pH 11
UV/TiO_2/H_2O_2	90	77	74
UV/ZnO/H_2O_2	86	87	86
UV/TiO_2+ZnO/H_2O_2	-	77	73

The first study demonstrated that the series of UV/TiO_2/H_2O_2 was the most suitable series for the removal of COD at acidic conditions. The removal efficiency of COD decreased with increasing pH in this series. ZnO was more effective than TiO_2 at pH 7 and pH 11. The series of UV/ZnO/H_2O_2 was not influenced by the initial pH values of solutions. The synergistic effect was not observed in the couple UV/TiO_2+ZnO/H_2O_2 system.

In the second step, various amounts of H_2O_2 were studied in the series of UV/TiO_2/H_2O_2 at pH 2.5. The effectiveness of oxidant amount was determined by using concentrations of 15, 30 and 45 mM H_2O_2. In this step the degradation of organic matter was evaluated with COD and TOC parameters (Figure 2 and Figure 3).

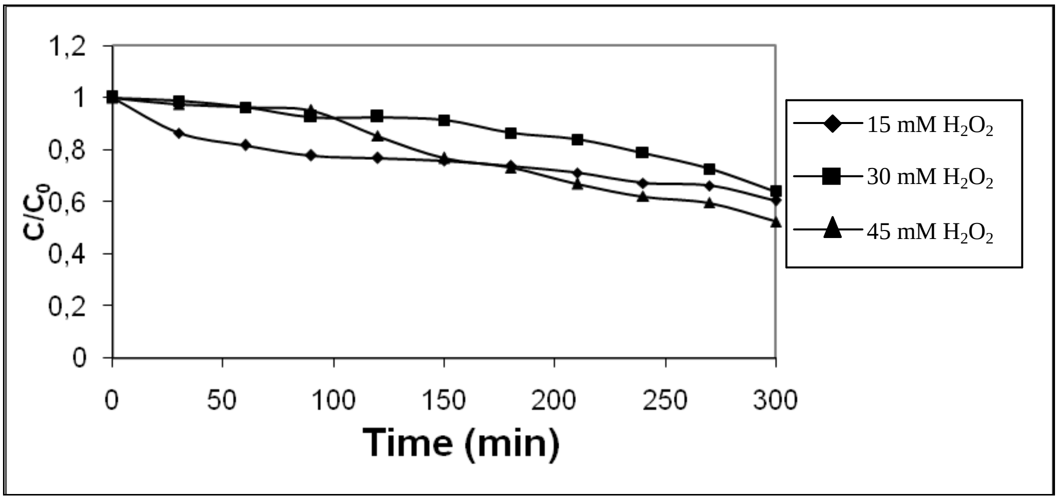


Figure 2.The variation of TOC values versus time at pH 2.5.

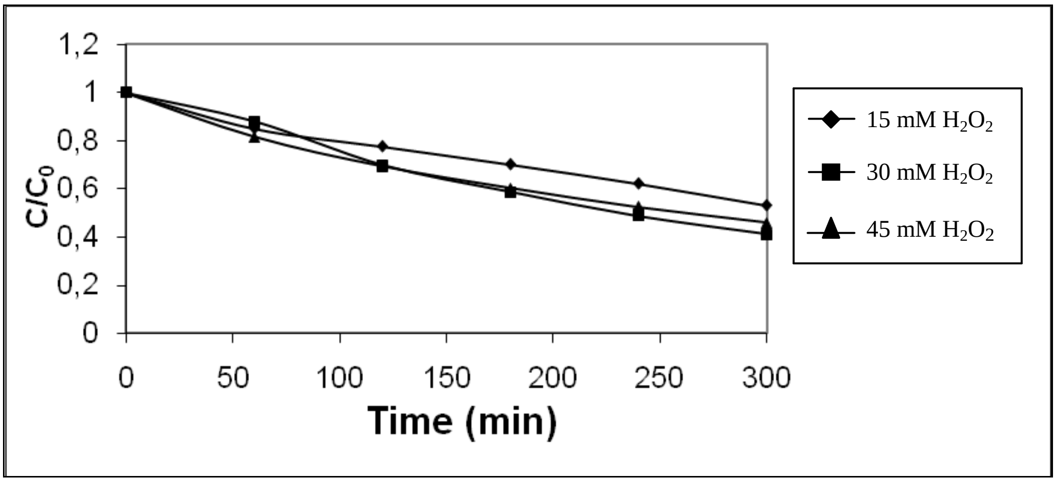


Figure 3. The variation of COD values versus time at pH 2,5.

TOC and COD removals are shown in Table 2.
Table 2. The removal of organic matter (%) for the series of UV/TiO_2/H_2O_2 at pH 2.5

	15 mM H_2O_2	30 mM H_2O_2	45 mM H_2O_2
Removal of TOC (%)	45	55	63
Removal of COD (%)	61	69	67

According to the Table 2, increasing amounts of oxidants increased the TOC removal efficiency, but not COD because of the increase of inorganic carbons with illumination time. The expected removal efficiency was achieved when it considered that wastewater has low initial COD and inert fraction. Hydrogen peroxide is the main absorber for wastewaters with low initial COD. In other words, hydroxyl radicals are mainly formed by direct photolysis of hydrogen peroxide when its initial concentration is higher than 0.01 M.

Kinetics of photocatalytic degradation

Reaction rate constants were calculated in order to evaluate the degradation efficiency.
It has been explained in the literature that the photocatalytic degradation of various organic compounds at low concentrations obeys pseudo first-order reaction kinetics.

$$-\frac{dC}{dt} = k[C]$$

k is reaction rate constant ($time^{-1}$) and [C] is the concentration of organic compounds.

Rate constant, k was estimated from the slop of the $\ln(C/C_0)$ versus time plot in the studied conditions. The photocatalytic activities of the studied series can be compared via the k values (Table 3 and Table 4).

Table 3. Reaction rate constants (k, h^{-1}) for the first step of study

	TiO_2	ZnO	ZnO + TiO_2
pH 2.5	0.43 (0.999)	0.19 (0.952)	--
pH 7	0,28 (0,974)	0,25 (0,968)	0,16 (0,970)
pH 11	0,25 (0,962)	0,22 (0,950)	0,13 (0,965)

Note: Values in the parentheses denote the results of R^2.

According to the Table 3, at pH 2.5, the reaction rate constant of UV/TiO_2/H_2O_2 series was the highest value in all studied series. TiO_2 was more effective than the other catalysts for all different pH conditions.

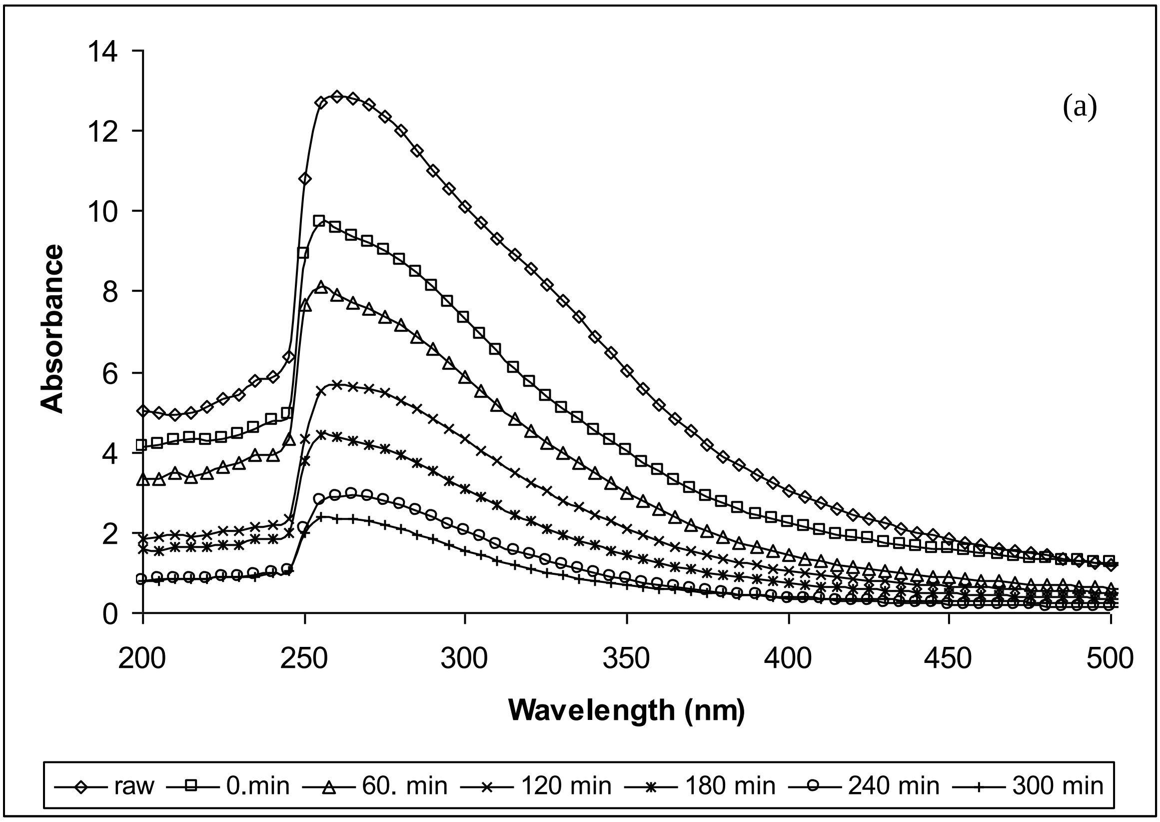
Table 4. Reaction rate constants (k, h^{-1}) for the second step of study (in UV/TiO_2/H_2O_2 series, at pH 2.5)

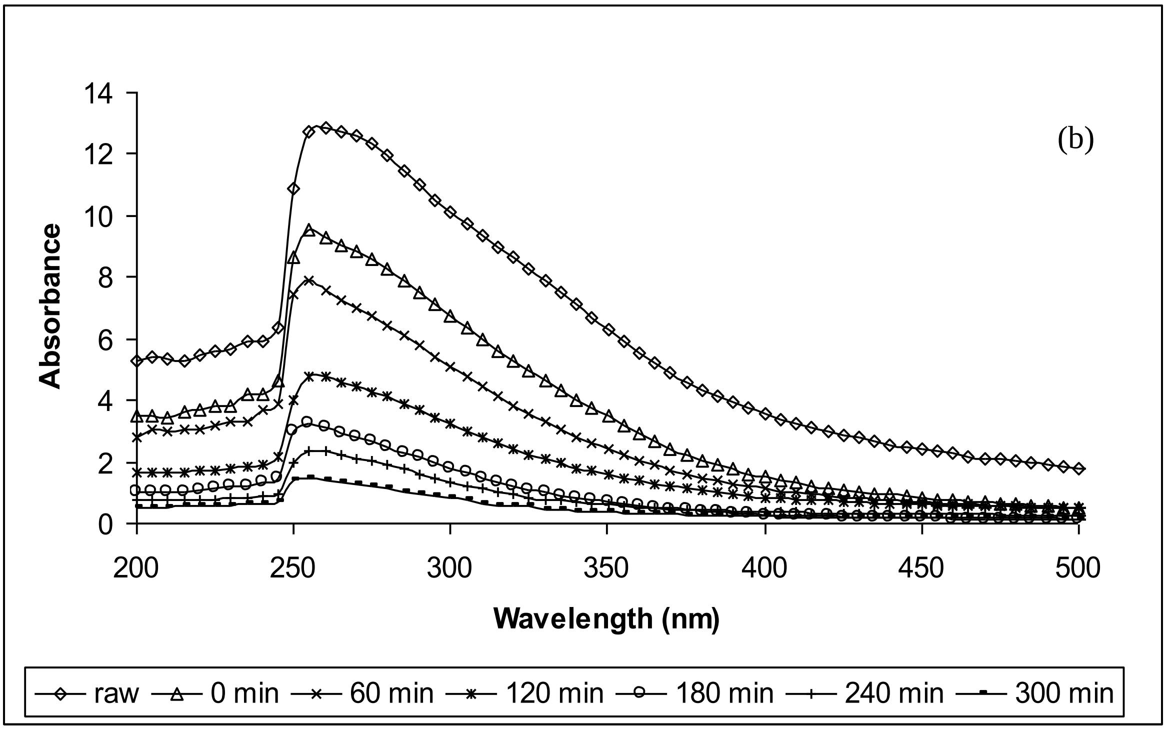
	15 mM H_2O_2	30 mM H_2O_2	45 mM H_2O_2
based on COD	0.11 (0.991)	0.18 (0.997)	0.15 (0.993)
based on TOC	0.08 (0.926)	0.08 (0.910)	0.13 (0.966)

Note: Values in the parentheses denote the results of R^2.

Color removal

In UV/TiO_2/H_2O_2 series, the wavelength–absorbance scanning for raw and photocatalyzed wastewater was given in Figure 4 at pH 2.5. The maximum absorbance was observed at 260 nm in an absorbance spectral scan between 200-800 nm. In the visible region, new absorption bands didn’t appear. Therefore, in all series the wavelength search was limited between 200-400 nm. The removal efficiencies of color was evaluated according to the absorbance values at 260 nm for raw and photocatalyzed wastewaters through 300 min (Table 5).


(a)
Absorbance
0
2
4
6
8
10
12
14
Wavelength (nm)
200
250
300
350
400
450
500
raw
0.min
60. min
120 min
180 min
240 min
300 min


(b)
Absorbance
0
2
4
6
8
10
12
14
Wavelength (nm)
200
250
300
350
400
450
500
raw
0 min
60 min
120 min
180 min
240 min
300 min

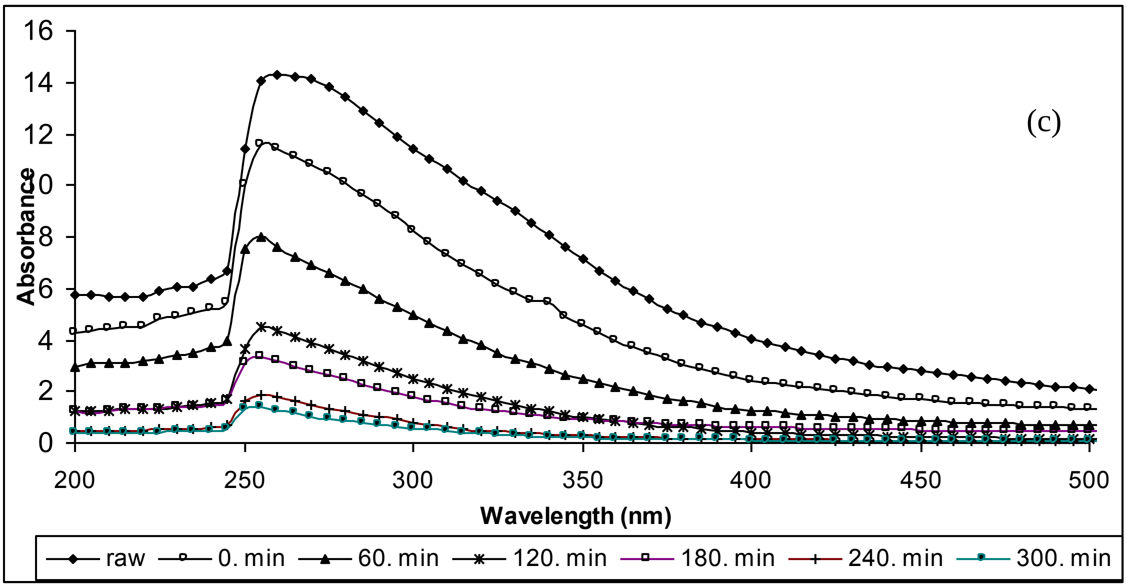


Figure 4. The effect of oxidant on color removal in UV/TiO_2/ H_2O_2 series at pH 2.5
(a) 15 mM H_2O_2 (b) 30 mM H_2O_2 (c) 45 mM H_2O_2

The efficiencies of color removal are shown in Table 5 and Table 6 for the first and second step of the study; respectively.

Table 5. The removal efficiencies of color at different pHs

Series	pH 2.5	pH 7.0	pH 11
UV/TiO_2/H_2O_2	95	43	40
UV/ZnO_2/H_2O_2	88	78	61
UV/TiO_2+ZnO_2/H_2O_2	71	53	29

According to the Table 5, the most effective series was with 95% UV/TiO_2/H_2O_2 series at pH 2.5. At alkaline conditions, color removal decreased in all studied series. Under the acidic conditions, the efficiencies of photocatalytic treatment of wastewater were relatively high (90% for COD removal, 95% for color removal).

Table 6. The removal efficiencies of color for various H_2O_2 concentrations
(in the UV/TiO_2/H_2O_2 series, at pH 2.5).

	15 mM H_2O_2	30 mM H_2O_2	45 mM H_2O_2
Color removal (%)	0	89	91

As it is shown on Table 6, the color removal increased with increasing H_2O_2 concentration, but there was no significant increase in color removal with the usage of 45 mM H_2O_2 ; thus the proper dosage of H_2O_2 was 30 mM/L.

Conclusions

The effluent of the combined treatment plant has inert COD fraction and cause color problem. In this study, the photocatalytic treatment was applied after biological treatment for the removal of organic matter and color.

It has been reported in the literature that, UV lights have been effective in breaking the double bounds in various structures by the presence of catalysts and oxidants. [10-11] Also, in our study with the outlet of combined wastewater treatment plant which has serious color problem, 95% color removal and 90% COD removal efficiency has been achieved by photocatalytic treatment in $UV/TiO_2/H_2O_2$ at pH 2.5 for 300 min. TiO_2 was the most effective catalyst for photocatalytic degradation of organic matter at pH 2.5.

For the studied conditions, most of the photocatalytic degradation was achieved in such a long time of 5 hours. The results indicate that the selection of the most appropriate reaction conditions and photocatalysts in achieving highest removal efficiency is important for the specific treatment cases.

Photodegradation rates of organic matter obey first-order reaction kinetic as reported in the literature previously. In this study, the best reaction rate constant was found at 0.43 h^{-1} for COD removal in $UV/TiO_2/H_2O_2$ series at pH 2.5.

As a result, the photocatalytic oxidation process is an effective alternative in color removal and also COD removal for effluent of combined treatment plant.

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TRACE ELEMENT CONCENTRATIONS OF LICHENS NEAR SEYİTÖMER COAL-FIRED POWER PLANT

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Lichen samples from different parts of the world have been known to accumulate elements to a greater degree than any other higher plants, if they are exposed to these elements from the atmosphere or from water and sediments. It has been hypothesized that lichens can be used to monitor air pollution around point and area emission sources.
In this study, epiphytic lichen Xanthoria parietina was applied as biomonitor of air pollution to determine the environmental impact of Seyitömer coal-fired power plant. The following elements were analyzed in Xanthoria parietina by ICP-MS As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Se, Th, U, V, Zn, and their concentrations were mapped. Mean metal contents of lichen samples were in descending order Fe >Ni > Zn > Cr > V > Cu > Pb > As > Co > Th > Se > U > Cd > Hg. The most polluted areas are found to be those in the vicinity of the coal-fired power plant, particularly in the direction of predominant wind.

Keywords: *Biomonitor, lichen, pollution, trace elements, coal-fired power plant.*

1. Introduction

Fossil fuel use for electricity production is responsible for many environmental problems. Particularly, combustion of coal (including lignite) containing trace elements and naturally occurring radionuclides, may have an impact on environmental pollution level in the vicinity of thermal power plant. Finkelman (1995b) discusses 25 environmentally sensitive elements (Sb, As, Ba, Be, B, Cd, Cl, Cr, Co, Cu, F, Pb, Hg, Mn, Mo, Ni, P, Se, Ag, Tl, Th, Sn, V, U, Zn) that are found in coal, including all of the elements cited in the 1990 Amendments to the Clean Air Act as potential hazardous air pollutants (Finkelman and Gross, 1999). Fly ashes escaping from stacks contain these elements that are concentrated a few times in comparison with their content in coal (Bem et al., 2002). A coal-fired power plant might potentially contaminate its environment depending on the concentration of the trace elements in the different types of coal used, the combustion, the ash content of the coal, the efficiency of the filtering system, the local mean meteorological conditions, etc., (UNSCEAR, 1982; Delfanti et al., 1999).

Lignite, one of the most important energy sources, has intensively been used for the generation of electricity in Turkey since 1950s. Almost one-fourth (23 %) of Turkey’s total electric production (149 882 GWh) was obtained from coal in 2004 (Say, 2006). More than three-fifth of the coal was lignite; the remaining was from hard coal. The lignite available in Turkey is of poor quality, with high ash content and low calorific value. Moreover, Turkish lignite’s appear to have high concentration of trace elements (Karayiğit et al., 2000).

Since the energy and environment are two essential and related aspects of the conservation of healthy living conditions, it is necessary to pay attention to atmospheric pollution by trace elements from coal-fired power plants. Biological monitoring has proved very useful in the assessment of air contamination by persistent pollutants such as trace elements and radionuclides (Loppi et al., 1997). Lichens are particularly useful in these studies since they are not dependent on root uptake and receive nutrients directly from the atmosphere; moreover, since they lack away cuticle and stoma, elements are easily incorporated in their tissues.

Numerous investigations of the interaction of air pollutants and lichens performed within the last three decades. The majority of the investigations for the accumulation of air pollutants by lichens focused on pollutants produced by smelters, power plants, and busy roads in urban and rural sites. These studies of elemental accumulation in lichens around pollution sources yielded tables of elemental content of lichens near industrial / urban or other contaminated sites, apart from unpolluted background regions (Garty, 2001). Recent literatures (Olmez et al., 1985; Garty, 1987; Nimis et al., 1990; Freitas, 1994, 1995; Yenisoy-Karakaş, 2000; Garty et al., 2003; Uğur et al., 2003) referring to lichen biomonitoring have dealt mostly with airborne elements emitted by power plants using fossil fuels, as the case in the present study.

This study has been performed in the surroundings of a lignite-fired power plant located in Seyitömer, Kütahya, in order to evaluate the possible increase of trace element levels by the operation of the plant. Epiphytic lichen (growing on trees) Xanthoria parietina was applied as biomonitor of air pollution to determine the environmental impact of Seyitömer coal-fired power plant.

2. Materials and Methods

2.1 Seyitömer Coal-Fired Power Plant (SeCPP)

At the northwest of Turkey, there are four power plants from west to east Çan (ÇaCPP), Orhaneli (OrCPP), Tunçbilek (TuCPP) and Seyitömer (SeCPP), respectively (Fig.1). The lignite-fired power plant of Seyitömer is located near the city of Kütahya (Fig. 1). The Seyitömer coal basin is one of the most rich lignite basins in northwest Anatolia, Turkey. Mining activities started in 1935 and total reserves were estimated during exploration at 203 million tones lignite. The power plant burns about 6.5 million tones of lignite yearly and produces about 4x150 MW-year of electrical power energy at full capacity. The fuel for the Seyitömer lignite-fired power plant (SeCPP) is supplied from lignite beds which also lie in this region. The lignite available in this region has very low calorific value, high moisture and ash contents. The basic characteristics of the SeCPP are presented in Table 1 and Figure 2 shows its photograph.

Table 1. Basic Characteristics of SeCPP-TURKEY*

Basic Characteristics	**Seyitömer Coal-Fired Power Plant**	
Number of Units	#1-2-3	#4
Working capacity (MWe)	150	150
First running	1973-1974-1977	1989
Caloric value of coal (kcal kg^{-1})	1819	1692
Total coal consumption (ton h^{-1})	188	190
Ash (%)	32.2	35.0
Moisture (%)	32.7	31.7
Airborne matter (%)	29.9	29.7
Efficiency of electro filters (%)	98	98
Chimney height (m) (four chimney)	100	100

*The data in this table were taken from the SeCPP chemistry laboratory.

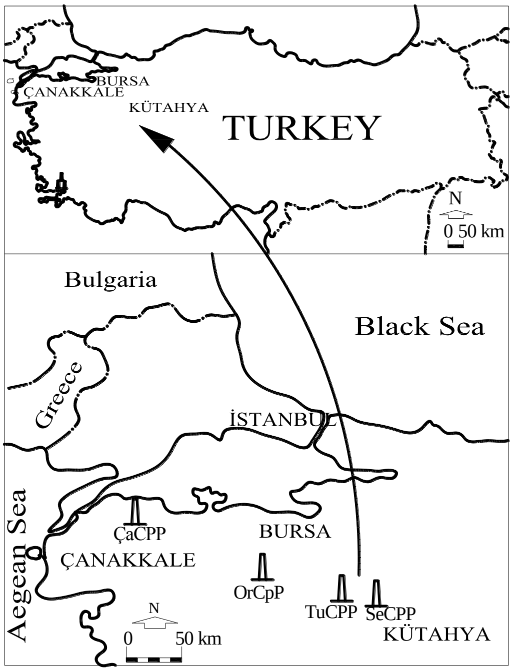


Fig.1. The map of the northwest Turkey indicating the location of coal-fired power plants.

Fig. 2. Seyitömer Lignite-Fired Power Plant

2.2 Sampling, sample preparation and analysis

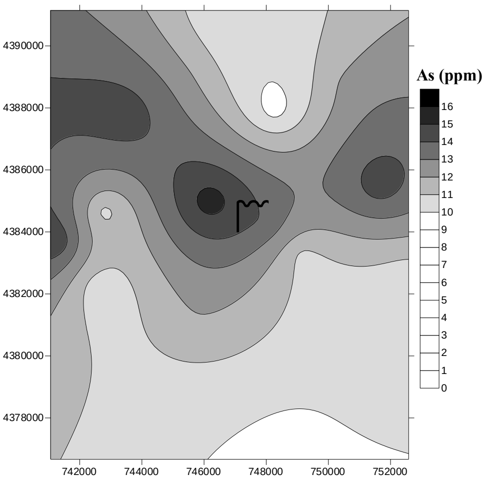
During one yearly survey (2003-2004), totally of 18 lichen samples of Xanthoria parietina were collected from a 150 km^2 area within a circle of 12 km diameter as grids of 3 km x 3 km, centering the Seyitömer power plant. This species was chosen for sampling since they are wide spread throughout the survey area. Foliose lichens are easy to collect and present a large contact surface for atmospheric pollutant. All the samples were collected from at least five different trees at a height above the ground of more than 1 m to reduce contamination with terrigenous material. At each sampling site, about 5-10 g of lichen sampled from not less than five trees were mixed in one bag.

In the laboratory, the lichen samples were first air dried, accurately sorted to remove as much extraneous material as possible, and then stored in a box until analysis. The dry weight was determined on sub-samples brought to constant weight at 85 °C in an oven. The lichen samples were then powdered and homogenized with Retsch vibration disc mill RS 100. Sample preparation and packing were done at clean room of our laboratory. Samples and standard were put in clean polyethylene bags. They were carried to ACME ANALYTICAL LABORATORIES LTD. (ISO 9002 Accredited Co.) in packed form in order to avoid contamination during transportation. Full details of the producers and analytical performances have been reported elsewhere (www.acmelab.com). Total concentrations of trace elements, expressed on a dry weight basis, were determined by Inductively Coupled Plasma-Mass Spectrometer (ICM-MS). Summary statistics were used to obtain the means and standard deviations. The distribution map of trace elements was performed with a suitable software package program.

3. Results and Discussion

3.1 Distribution maps of trace elements

The distribution of trace elements concentrations in Xanthoria parietina from the study area are shown in Figures 3-16.



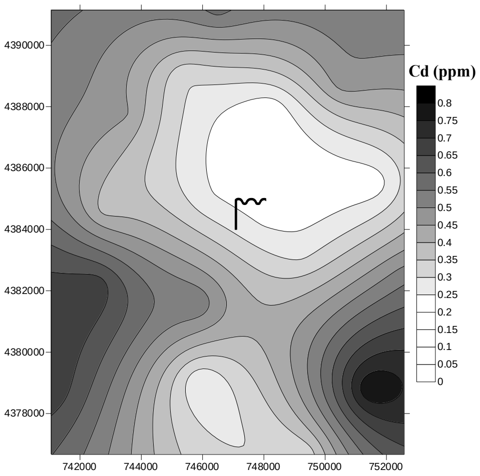
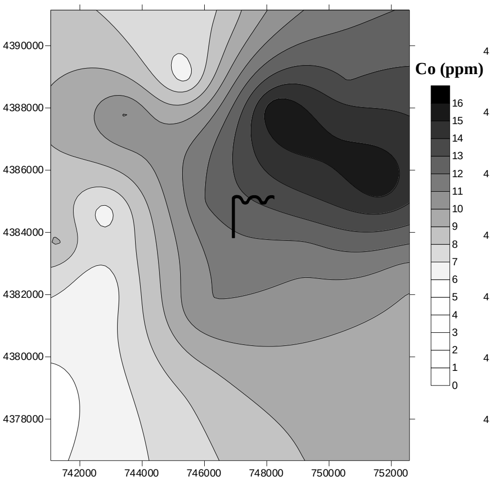


Fig. 3. Lichen concentration for arsenic.

Fig. 4. Lichen concentration for cadmium.



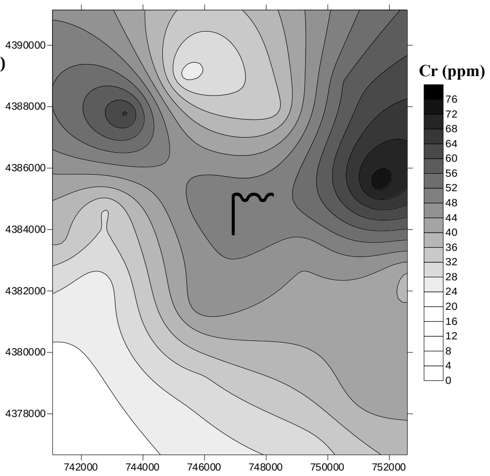
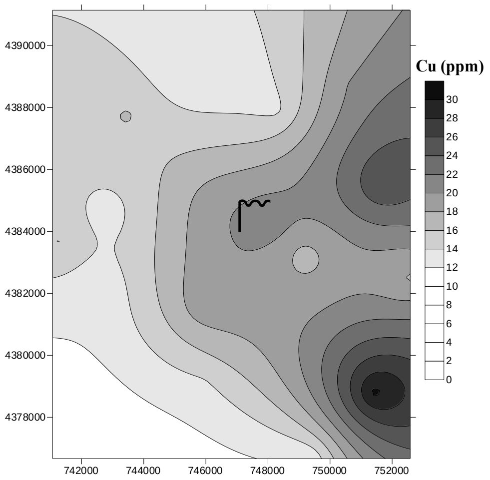


Fig. 5. Lichen concentration for cobalt.

Fig. 6. Lichen concentration for chromium.



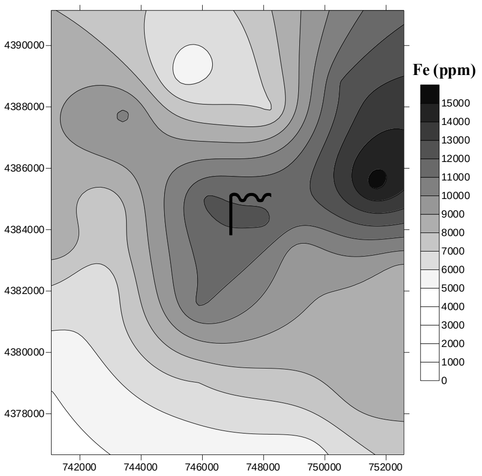
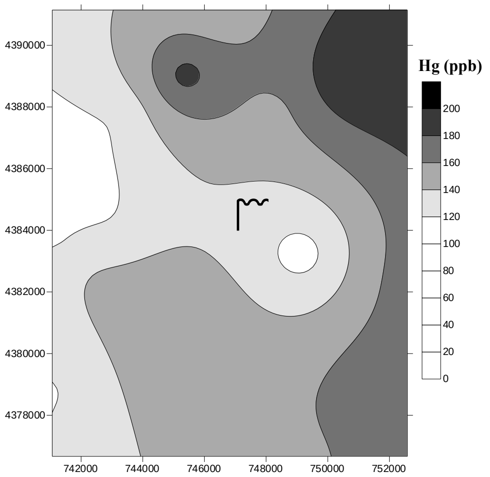


Fig. 7. Lichen concentration for copper.

Fig. 8. Lichen concentration for iron.



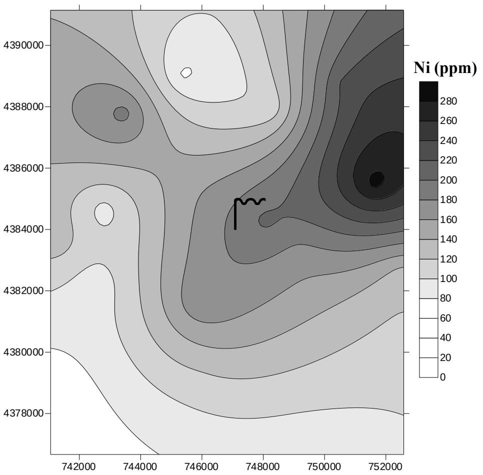
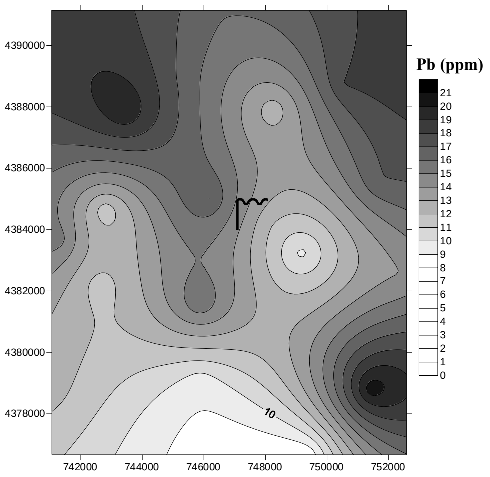


Fig. 9. Lichen concentration for mercury.

Fig. 10. Lichen concentration for nickel.



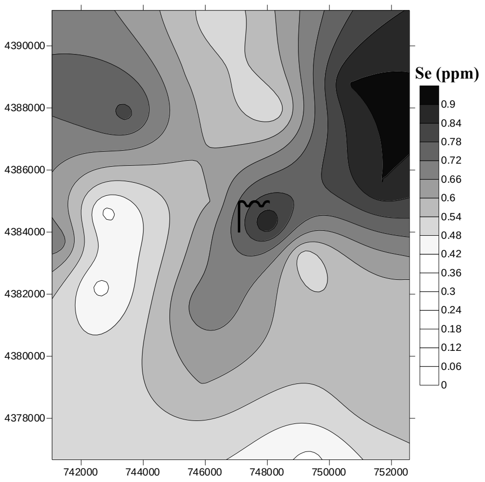
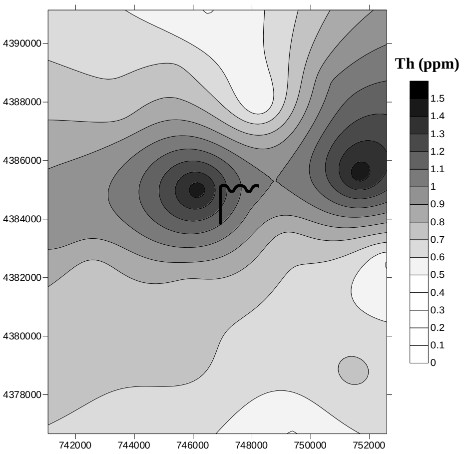


Fig. 11. Lichen concentration for lead.

Fig. 12. Lichen concentration for selenium.



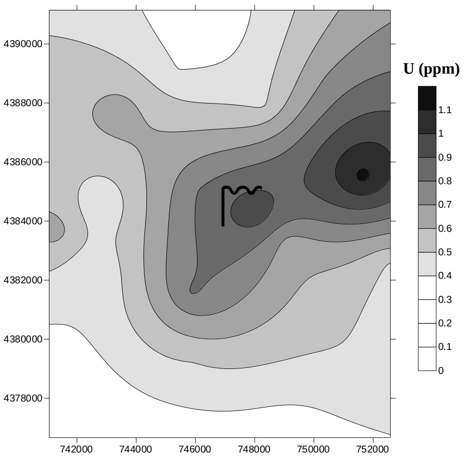
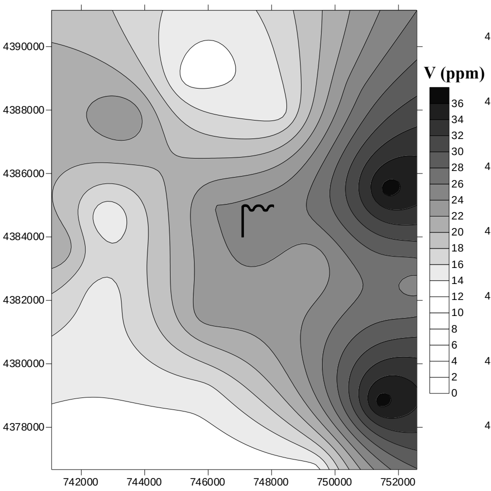


Fig. 13. Lichen concentration for thorium.

Fig. 14. Lichen concentration for uranium.



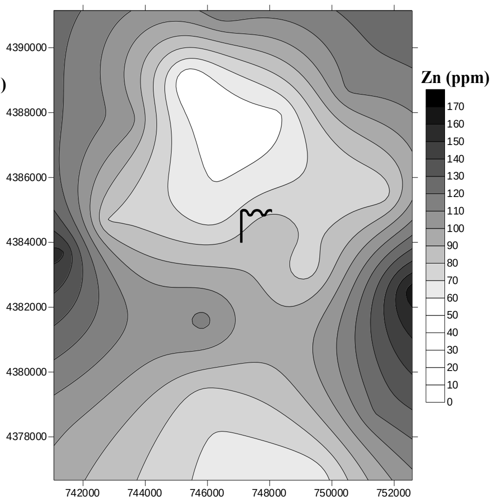


Fig. 15. Lichen concentration for vanadium.

Fig. 16. Lichen concentration for zinc.

As is seen from Figures 3-16, generally high concentrations for As, Co, Fe, Se, Th, U were recorded in samples collected from near SeCPP. In addition, dominating wind directions are from southwest to northeast and from south to north (Figure 17.). Therefore, many of trace element pollutions, were observed mainly along dominating wind directions, could be resulted from the coal-fired power plant. Topographic map belonging to investigation area is shown in Figure 17. As illustrated in this map, there are a lot of flat areas between hills. High trace element concentrations were obtained along these flat areas.

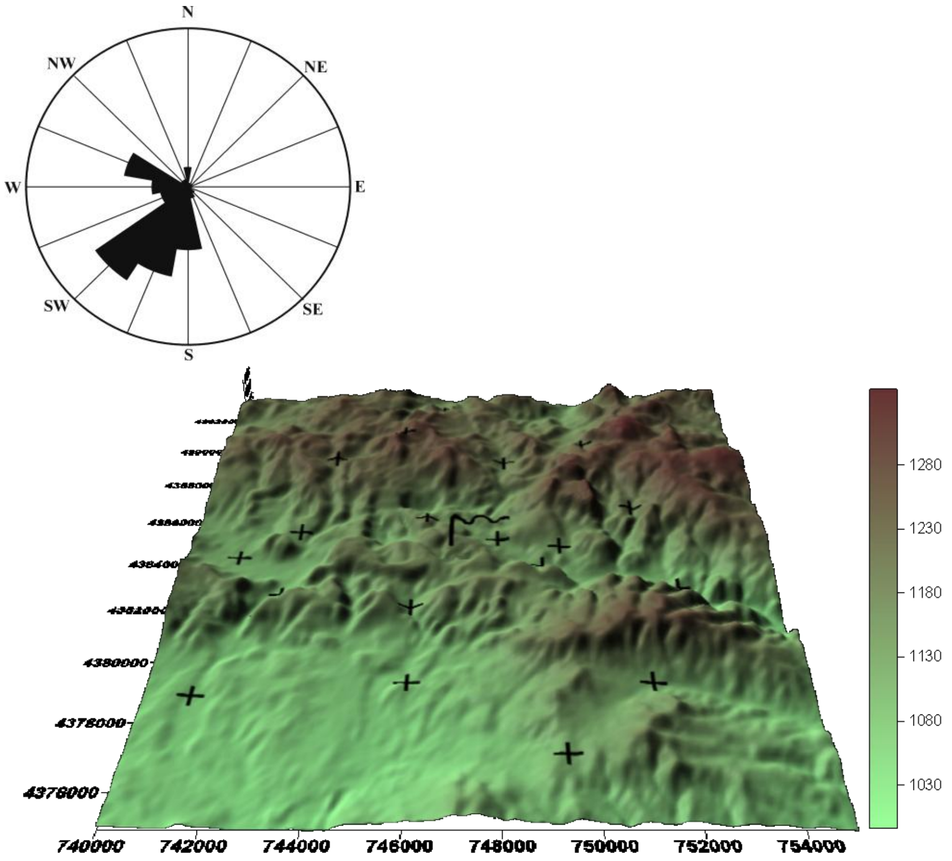


Fig. 17. Topographic map and wind rose of investigation area (+; sampling location site).

3.2 Comparison with literature values

The concentrations of trace elements in 18 lichen samples collected from Seyitömer CPP were analyzed by ICP-MS. Statistical summary of elemental concentration obtained from all lichen data set (Xanthoria parietina) is given in Table 2 that includes number of samples, arithmetic and geometric means with associated standard deviations, range, median and coefficient of variation (CV).

Table 2. Average values of heavy metal (in µg g^{-1} d.w.) in lichen samples around SeCPP

Element (Number of samples)	**Trace Element Concentrations (µg g^{-1})**				**CV (%)**
	Arithmetic Mean ± SD	**Median**	**Geometric Mean**	**Min. - Max.**	
As (18)	11.88 ± 2.03	11.05	11.72	9.20 - 15.60	17
Cd (18)	0.43 ± 0.18	0.42	0.39	0.21 - 0.80	42
Co (18)	10.08 ± 3.04	9.70	9.66	5.58 - 15.89	30
Cr (18)	41.20 ± 14.39	38.15	38.98	20.60 - 74.60	35
Cu (18)	16.91 ± 5.25	16.15	16.24	10.58 - 30.54	31
Fe (18)	8792 ± 2926	8535	8354	4990 - 15450	33
Hg (18)	0.147 ± 0.025	0.150	0.145	0.109 - 0.198	17
Ni (18)	139.39 ± 59.61	120.05	128.57	65.80 - 287.80	43
Pb (18)	14.32 ± 3.62	14.77	13.87	8.10 - 20.67	25
Se (18)	0.61 ± 0.16	0.60	0.59	0.40 - 0.90	26
Th (18)	0.82 ± 0.29	0.73	0.77	0.49 – 1.47	35
U (18)	0.58 ± 0.23	0.48	0.54	0.32 – 1.13	40
V (18)	21.05 ± 7.52	22.00	19.89	13.00 - 37.00	36
Zn (18)	96.49 ± 32.96	97.90	91.25	49.30 - 166.10	34

Around SeCPP, arithmetic mean of concentration values of trace elements in the lichen samples were calculated to be distributed in the following order: Fe >Ni > Zn > Cr > V > Cu > Pb > As > Co > Th > Se > U > Cd > Hg. The local variation in elemental concentrations was expressed in terms of coefficient of variation (CV), defined as standard deviation (S.D.) x 100/mean, to compare the magnitudes of variation. These CV values were changed between 17-43 %. The concentrations of Cd, Ni and U elements have the highest CV values (42, 43, 40), respectively. These results indicate that the concentrations distributed in a wide range of values.

Comparison of the produced data in this study on lichen with literature data is one of the ways of the observing used in environmental research.

Table 3. The comparison of power plant area data with literature values (µg g^{-1})

Element	**Average ± sd *[1]**	**Average ± sd *[2]**	Average ± sd [3]	**Average ± sd [4]**	**Average ± sd [5]**	**Average ± sd [6]**	**This study Average ± sd**
As	3.9 ± 1.0	5.0 ± 2.0	-	-	6.5 ± 1.3	-	11.88 ± 2.03
Cd	1.2 ± 0.2	-	-	-	0.14 ± 0.12	1.93 ± 0.42	0.43 ± 0.18
Co	-	-	-	0.57 ± 0.08	-	10.18 ± 1.40	10.08 ± 3.04
Cr	3.8 ± 1.2	4.6 ± 1.5	9.4 ± 6.5	5.8 ± 1.1	4.3 ± 2.2	13.30 ± 0.99	41.20 ± 14.39
Cu	-	-	13.4 ± 7.1	7.3 ± 4.0	4.9 ± 1.7	8.14 ± 0.79	16.91 ± 5.25
Fe	1400 ± 600	1620 ± 780	-	1218 ± 74	2110 ± 1000	4005 ± 83	8792 ± 2926
Hg	-	-	-	-	0.26 ± 0.29	-	0.147 ± 0.025
Ni	-	-	36 ± 21	5.3 ± 0.9	3.8 ± 2.0	16.64 ± 2.72	139.39 ± 59.61
Pb	-	-	120 ± 73	8.5 ± 1.7	5.6 ± 5.6	58 ± 5	14.32 ± 3.62
Se	1.1 ± 0.8	1.1 ± 0.5	-	-	0.37 ± 0.29	-	0.61 ± 0.16
Th	0.34 ±0.17	0.38 ±0.19	-	-	-	-	0.82 ± 0.29
U	-	-	-	-	-	-	0.58 ± 0.23
V	8.5 ± 2.6	6.8 ± 2.1	-	6.1 ± 0.8	4.7 ± 2.9	-	21.05 ± 7.52
Zn	64 ± 8	68 ± 24	57 ± 30	38.1 ± 7.8	27 ± 24	112 ± 8	96.49 ± 32.96

[*] Ölmez et al., 1985 (A coal-fired power plant, Washington D.C., USA)
[*1]: Parmelia caperata (5 samples)
[*2]: Parmelia rudecta (6 samples)
[3] Garty, 1987 (A coal-fired power plant, Israel), Ramalina duriaei (125 samples)
[4] Garty, 2003 (A coal-fired power plant, Israel), Ramalina lacera (10 samples)
[5] Yenisoy-Karakaş, 2000 (Soma and Yatağan coal-fired power plants, Turkey), Xanthoria parietina (18 samples)
[6] Uğur et al., 2003 (Yatağan coal-fired power plant, Turkey) Rhizoplaca melanophthalma (Epilitic lichen) (10 samples)
Numbers in parenthesis show the number of samples

Results obtained in the current study are generally found to be higher for As, Cr, Cu, Fe, Ni, Th, V elements compared to data reported in literature although there are a few lower values for Cd, Co, Hg, Pb, Se, Zn elements.

4. Conclusions

In the present study, epiphytic lichen was applied as biomonitor of air pollution to determine the environmental impact of a coal-fired power plant. The pollution maps were prepared using the concentration of elements in order to indicate the location of the more polluted and influenced areas. The mostly polluted areas are found in the vicinity of the coal-fired power plant, especially in the direction of dominant wind.

Acknowledgements

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REMOVAL OF TOXIC COPPER AND MANGANESE IONS FROM LEFKE- GEMIKONAĞI DAM WATER

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In this study, Lefke-Gemikonağı dam water which have Copper and Manganese ions in high concentrations (Copper : 193.7 µg/L , Manganese : 855.9 etc.) was treated with Calcium oxide and these ions were precipitated. After treatment, dam water can be used as agricultural irrigation water in this area without any risk of toxicity.

INTRODUCTION

The name of the island “Cyprus” comes from “copper” mines which are found around the Lefke distirict in Northhern Cyprus (TRNC = KKTC).

Copper mines were extracted and concentrated by **CMC** (Cyprus Mining Corporation Company) between 1961-1971. Beside the copper ores, gold and pyrite ores were also obtained as side-products.

CMC is directly responsible for environmental pollution problems that still threat the nature and of course human health seriously. In 1971, The Union of Lefke farmers and later Lefke municipality applied to international courts for irresponsibility of CMC about environmental pollution but there was no positive response at all.

In 1974, with the advent of war in the area, the dream came to an abrupt halt and the real trouble began. Claiming that CMC were forcibly ejected from the island, the company left all as it stood and has never returned to Northern Cyprus. The fact that they refused point black to accept any form of responsibility whatsoever caused environmental problems since they left the island and yet still claim compensation rights for economic and equipment losses.

The people who live in Lefke district have been suffering from environmental pollution for a long time. Agricultural irrigation water, sea water, soil and air pollution problems cause serious and harmful damages on the environment and the habitants’ lives around this area. The concentrations of Copper and Manganese ions in Gemikonağı dam water is much higher than toxic levels that are indicated in international standards. In addition to that, Hydrogen Sulfide (H_2S) and other sulfurous gases produced biochemically are continuously emit from the huge sulfurous solid waste heaps in this area.

Gemikonağı dam that is near the Lefke having 4 million m^3 of water capacity was built in 1994 for agricaltural purposes because of rainless and dry climate of Cyprus. Planned irrigation area around the dam is nearly 130 hectares. According to chemical analysis reports made by Govermental Laboratory (in Nicossia) and different Universities; concentration of copper and manganese ions in dam water was found 3-5 times more than standard toxic limits. Some results of analysis are given in Table 1.

In our study, some Gemikonağı dam toxic water samples containing in high concentrations of copper and manganese ions were investigated and tried to remove these ions for agricultural irrigation water by precipitation with calcium oxide, CaO.

Table l
Some Results of Chemical Analysis of Gemikonağı Dam Water (obtained from Govermental Laboratory – Nicossia- reports)

Date of Analysis	**Places of Samples**	**Al µg/L**	**Cu µg/L**	**Mn µg/L**	**Fe µg/L**
12.04.1994	Lefke Mine Stream	482	**640**	**567**	43.2
26.08.1997	Bottom Part of the Dam	448.3	**384**	**2113**	2367
28.08.1997	Lefke Mine Stream	449.6	**381.5**	**1623**	336
8.11.2000	Lefke Irrigation Valve	112.8	36	**564**	104.7
6.04.2000	Middle Part of the Dam	142.6	**332.3**	**375.8**	274.1
15.05.2000	Shore side of the Dam	210	**221**	**445.5**	68
28.07.2000	Bağlıköy (Lefke) Irrigation Valve	192.9	**242**	**856.8**	635.3

Toxic Limits of Some Metal Ions (for long term agricaltural irrigation waters) :

Metal Ions	Toxic Limits (**µg/L**)
Iron (Fe)	5000
Aluminum (Al)	500
Copper (Cu)	200
Manganese (Mn)	200

Comparing the results of reports in Table 1 with standard limits, we can see high toxicities of Cu and Mn ions in water samples.

EXPERIMENTAL PROCEDURES

Materials and Equipment

$CuSO_4.5H_2O$ (analytical grade)
$Mn\ SO_4.H_2O$ (analytical grade)
$CrCl_3$ (analytical grade)
CaO (technical grade)

Unicam 939 V AA Model Spectrometer

Precipitation and Analysis

In the experiments, toxic Cu and Mn ions are precipitated from the synthetic solutions and original dam water samples using CaO as a precipitant chemical. Precipitation was made at pH : 9.5 in the beakers and precipitates of metal hydroxides were filtered . Copper and Manganese ions in the filtrates collected after precipitation and original dam water samples were analyzed by Atomic Absorption Spectrometer (Unicam 939 V AA Model).

Precipitation reactions :

$$\mathbf{Cu^{2+} + 2\ OH^- \longrightarrow Cu\,(OH)_2 \quad \text{(Blue-green precipitate)}}$$

$$\mathbf{Mn^{2+} + 2\ OH^- \longrightarrow Mn\,(OH)_2 \xrightarrow{\text{(oxydation)}} MnO(OH)_2 \quad \text{(Brown precipitate)}}$$

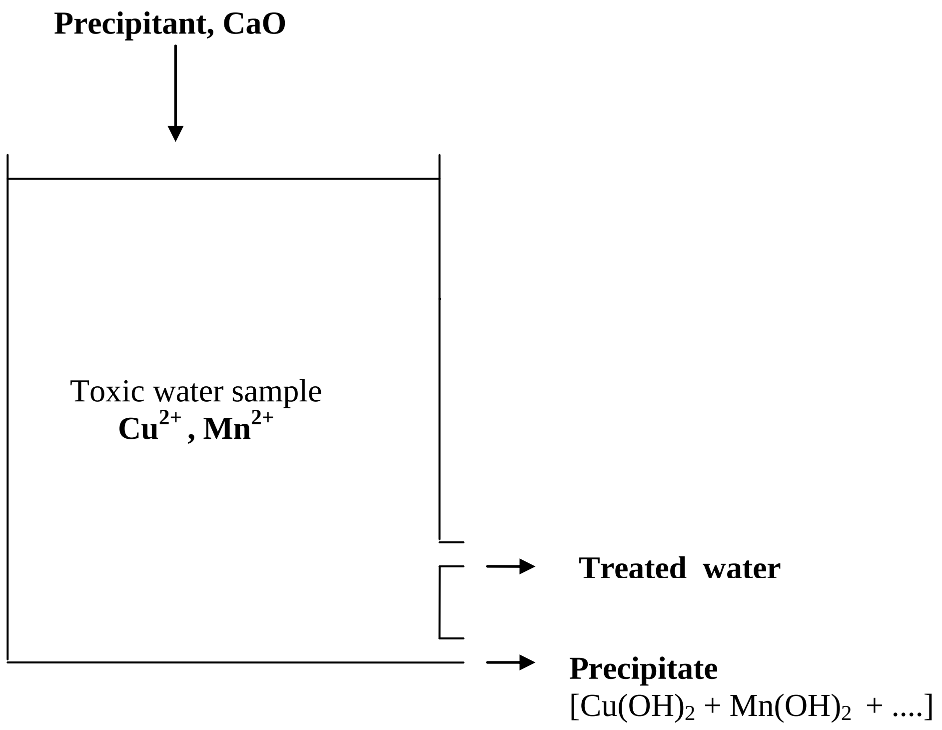

Figure 1. Precipitation of Copper and Manganese ions

Results of Analysis

The results of analysis of synthetic and original dam water samples obtained before and after precipitation with CaO are shown in Table 2 and Table 3.

Table 2
Precipitation of Copper and Manganese Ions in Synthetic Water Samples by CaO

Ionic Concentrations before CaO Treatment (µg/L)		Ionic Concentrations after CaO Treatment (µg/L)	
Cu^{2+}	Mn^{2+}	Cu^{2+}	Mn^{2+}
3400	**1345**	**0.00**	**0.00**

Table 3
Precipitation of Copper and Manganese Ions in Gemikonağı Dam Water by CaO

Places of Samples	**Ionic Concentrations before CaO Treatment (µg/L)**		**Ionic Concentrations after CaO Treatment (µg/L)**	
	Cu^{2+}	**Mn^{2+}**	**Cu^{2+}**	**Mn^{2+}**
No.6 Water Entrance To the Dam	31.5	**363.9**	**0.00**	**0.00**
Near the No.6 Water Entrance to the Dam	**193.7**	**855.9**	**0.00**	**0.00**
Opposite side to the TurkishBaths	41.7	**414.0**	**0.00**	**0.00**

CONCLUSIONS

1. We have shown that toxic Copper and Manganese ions can be removed easily and economically by precipitation with CaO.
2. Dam water should be used without any risk of toxicity for agricultural irrigation purposes after precipitation method by CaO. That means, an applicable project should be made after some more analysises and investigations. Because there is no another chance for irrigation water at the moment around his area.
3. Goverment, municipility, environmental societies and of course researchers should try to cooparate and solve this urgent polluted dam water problem.
4. Also solid wastes and air pollution problems should not forgotten.

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DEVELOPMENT AND ENVIRONMENTAL POLLUTION IN TURKEY AND IN KOCAELİ

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Turkey has met the environmental pollution since 1960’s. Firstly, air pollution was observed in some big cities, soon after some alarming news have reached about the pollution of sea shores. İzmit bay were the pioneer examples of sea pollution in Turkey. In Kocaeli the history of pollution and the history of industrial development have almost been together.

We belive the brief overwiev on the pollution and industrial development will be necessary and some important points will help the solution

Introduction

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We belive the brief overwiev on the pollution and industrial development will be necessary and some important points will help the solution.

Population and Urbanisation in Turkey

The early 1950’s were the beginning of remarkable social and economic transformations in Turkey. The social and economic equilibrium based on the old and strong rooted traditions until 1950’s. As a result of new understanding in economic and social political approaches, rapid and radical changings have been observed. The rural people have tended to move from their traditional settlements and villages to the big city centres. When they have settled in the cities, new and many problems have born. The traditional structures of the old cities have never been ready to meet the needs of the newcomers, owing to the cities never have sufficient infrastructure.

The community has reached to the doorsteps of the new era. Economic and social developments were observed as a result of new public investments. The cities have been centres of social and economic attaraction. Increasing rural population and decreasing income have pushed some of the people to immigrate to the city centres. The rate of urbanisation has sharply increased. The rates of rural and urban population have gradually changed. In early 50’s, rural population was about 74.9% and urban population was 25.1%. In early 80’s the ratio of rural and urban population was 55.7% and 44.3%. The immigration of the rural population has caused this change. The population has increased about 2.5% per year since the beginning of 1950’s. With this percentage of population increase, Turkey has been one of the countries at top of the list among OECD countries.

While the population was about 13.7 million in 1927, it has reached up to about 70.0 million in in early 2005's. It is expected that the population will be about 80 million in 2010.

The main reasons of this population movements can be outlined in four points, which explained below.

The people are attracted by favourable social and economic opportunities of the city centres.

The people are pushed by the unfavourable social and economic conditions of the rural settlements.

Furthermore mechanised agriculture has also been one of the reasons of immigration from rural areas to the urban areas. The mechanisation saved the labour in the field.

And another important reason which should be expressed. Developing transport means and new roads have encouraged the rural population to move to the big cities.

Internal immigration commencing in 50's has changed its direction from internal points to the Western European Countries in early 60's.

The cities receiving immigrants have never been ready to welcomme the new comers. Irregular housing has been a rapid solution in early 70's. The newcomers have brought in their own solutions in consructing houses. The peripherial circle of the main cities has been invaded with the quickly and illegally built cement cottages. They have built houses on the plots obtained from agricultural and forest areas around the cities.
In some cities, irregular urbanisation has also invaded the watersheds of city water reservoirs as it has recently been observed in İstanbul. As a result of unplanned urbanisation, the fresh water reservoirs have been heavily polluted.

The people which have rushed to the cities and built their houses. They created their own urban systems and subsystems, such as transport infrastructure, markets and cultural habits etc. Today, these people have realised that they created a big devil as a result of unplanned developments. Today's people are suffering from results of environmental pollution which was created as a result of rapid urbanisation.

Industrial Development in Turkey

Turkey's industrialisation can be studied in two periods. Before 1923 and after 1923, which is the important corner stone because of the establishment of the Turkish Republic.

Before 1923, weak and preliminary steps of industrial develepment were observed. For the some basic needs of the navy, the army and the Palace of the Otoman Empire, such as shoes, furniture, clothes, and some weapons, were being produced.

Main steps in national industrialisation have been observed since the beginning of Turkish Republic in 1923.

The governments of the Turkish Republic have always been established public incentives to help the economic develepment.

In 1930's, centrally prepared Industrial Development Plans opened a new era for industrial development. Textiles, cement, iron and steel, metals, mining and metallurgy, sugar, railroad materials, pulp and paper and construction were the main sectors until the 1950's.

First, pulp and paper factory was built and started to produce in 1936. Later on tyres, petrochemicals, refinary etc followed. Following years of 1960, the private sector has had an important role in trade and industry. In 2000's the private sector has reached up an effective role in Turkey's economy.

Environmental Pollution

Industrial development was the big dream of the Turkish people. But nobody cared about environmental pollution in the beginning of industrial development. Until early 1970's. Everyone has been very happy with the industrial development. Later on air and water pollution have been understood by the people. While the people were working and earning money for the better living conditions nobody has thought, the environment is very important for their health. As a result of industrial and urban development, almost all sorts of environmental problems have been appeared. The people, working and living in the areas of intensively urbanised and industrialised, have been suffered from the pollution.

In 1960's and 1970's, Ankara, the capital of Turkey, was under the heavy concentration of air pollution from heating systems. In 1960's the people, have met the air pollution in Ankara. In the following years, serious precautions have been taken to control pollution. But almost 15 years Ankara was suffered from air pollution before 1980's.

Air, is polluted by the emissions of exhaust gases of petrol consuming transport means and emissions of chimneys of houses and industrial establishments. Urgently built houses of newcomers have, spreaded over around the cities. These houses are heated with low quality lignites which emmit high sulphurdioxide.Emissions of industry are also another and significant source of aif pollution in many cities.

Solid wastes of irregularly and rapidly urbanised areas cannot be rationally controlled. Collection transportation, classification, recycling and incineration of the solid wastes, in the cities irregularly expanded without sufficient infrastructure, cannot be properly managed.

Water pollution has covered all kinds of water sources such as sea, lakes and streams river reservoirs and underground waters were also poliuted. The water sources are under the threat of domestic industrial and agricultural sewage through run off or draiage.

Noise and visual pollution are also observed as inevitable results of rapid and irregular urbanisation.

Kocaeli and its Ecological Conditions

Kocaeli is an example of the urbanisation and pollution problems. Kocaeli is a province in the Northwestern part of Turkey and in Marmara region. The area lays between the Black Sea in the northern end of the İzmit bay which is part of Marmara Sea, in the South. The total area covers 3626 km2. Total population is about 930.702 (1990) . The intensity of population reaches the highest level on the southern sector, around the sea shores of the bay. The administrative centre of the province is İzmit which is situated at the eastern end of Izmit bay.

The area has favourable ecological conditions and rich natural sources such as forest, fertile agricultural soils and fresh waters. The climate reflects the characteristics of transition zone of The Black Sea and the Mediterranean. Mean temperature is about 13.0, 14.0°C and annual precipicatatian is over 750 mm , the difference between min. and max. tempertures is not very high. According to the these climatic parameters the climate is accepted modarete. About 90% of the soils is suitable for agriculture. About 58% of total area is covered with forests. Agricutural potential is pretty good.

Industrial Development and Urbanisation in Kocaeli

Because of convenient ecological parameters and transport possibilities between İstanbul and Anatolian cities, Izmit has always been a centre of attraction for ages. Many civilisations passed by road or by sea through the zone. In the historical records, some notes on military port and yard can be seen. In 15-16 centuries. The Ottoman Palace established a military port and the navy was hosted many years in the area. Convenient ecological conditions and vicinity to Istanbul have been remarkable criteria for area to establish governerships and support stations.

Towards the end of the Ottoman period, new industries were established to produce textiles and clothes to meet the needs of palace and military.

In the early years of the new "The Republic of Turkey", some public investments were directed to the area. First pulp and paper factory was opened in İzmit, in 1936. This was also first industrial establishment for the area. In the following years trained labour, accumulation of industrial experience, the needs of expanding Istanbul industry have helped the development of the region. Intensive public incentives to invite the investment capital have been succesful and Izmit attracted the new industrial investments. Both national and international funds covering different sectors such as petro-chemical, fertilisers, auto tyres, metal, petrol etc. came and establised factories.

Investments has created job opportiunities and active socio-economic life consequently a great population rush have been seen since early 50's, up to the recent years. The total population increased from 300.000 to 970.000 (1990) and is expected 1.6 millon in 2010.

Active economic development was followed by social developments. The traditionall core of the old city was not ready to invite great rush. Housing has been an important problem. The area has expanded on the direction of west and east. The average rate of expansion is about 1.0 km/year on the direction of west-east and is about 250 m/year on the direction of south-north owing to narrow coastal strip within about last 35 years. After a great earthquake in 1999, urban areas have tended to the north.

Kocaeli has been one of the leading developed provinces of Turkey with the 20.43% production share of total.

As a result of socio-economic developments, some of the people reached wealth to some extend. But they have also met heavy environmental problems such as air, water, noise, soil pollution .

Izmit was traditional type of small Anatolian city until 30 year ago. During the last three decades the city has been one of the most industrialised region but also been one of the outstanding example of environmental polluition.

Now there are serious attempts to control environmental pollution, but the cost is high. In this case, we all have to remember the classical saying "Prevention is better than cure". Unfortunately in Kocaeli this saying has never been in reality. In other saying Kocaeli has missed the opportunity of prevention.
For the future, from the environmental pollution control point of view, the city planners. Local outhorities and public administrations and politicians should have a greater responsibility in their decisions in forming new cities and pollution prevention.

Social Reactions To Environmental Pollution

The people were happy and satisfied in their works, they have naver thought environmental pollution. The results of the pollution have started to affect the people’s living standearts and the health. In the beginning of the second half of since 70’s. The serious reactions of the local people have been observed. Especially air pollution resulted from lignite and fuel oil burning for house heating.

Precautions Against Pollution

Reactions of individuals, NGO’s and Local newspapers have pushed the scientists, public authorities, Local governments has pait more attention to the environmental pollution. In the beginning of 1990’s a great public effort has been observed. The new university has opened the Dept. Of Environmental Engineering The Local Government has estsblished the Environmental Protection Department. And The Central Covernment opened an office “The Diroctorate of Envşronment” under the Kocaeli Province. NGO’s have turned their atfention on the environment. Many activities have been organised to enlight the local people. Private sectur and industry have paid more atfention on the subject. Every year increasing number of companies have tended to get ISO14000 Environmental Management System Certificates.

Conclusions

Kocaeli, as an important center of industrialisation has met the industrial pollution for about 40 years.

The history of industrial development has also been history of pollution. These two events have developed together. Industrial development has been the reason of local reactions. The reactions have pushed the Ceatral Government, Local governments, academicians, Journalists, NGO's etc. I in the beginning of 1990's a new page has been opened to protect the environmental problems. The new organisational bodies have foeused their attention on the new protects covering prevention and remediation.

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ZOOPLANKTON COMPOSITION AND WATER QUALITY OF LAKE GOLBASI (HATAY-TURKEY)

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Zooplankton composition, abundance, distribution and some water quality parameters were investigated to determine the apparent response of the zooplankton community to water quality conditions in Lake Golbasi between April 2003 and March 2004. Water quality parameters of pH, dissolved oxygen, temperature, salinity, chemical oxygen demand (COD), total alkalinity and hardness, ammonia, nitrite, nitrate, phosphate, sulphite, sulphate, chloride, potassium, sodium and silica analyses were done. Zooplankton abundance and species distribution is considered in relation to water quality parameters. The highest zooplankton abundance was found in August, whereas the lowest determined in January. The zooplankton composition of the lake consisted of Rotifera, Cladocera and Copepoda. Number of species of Rotifera was higher than the other taxa. A total of 62 species of Rotifera, 20 species of Cladocera, and 10 species Copepoda were found. Rotifera species of *Dipleuchlanis propatula* is the first records for Turkish inland waters. The annual mean concentration of chlorophyll *a* was measured as 37.87 µg/L. The levels of nutrients (mean values of total phosphorus and nitrate-nitrogen: 0.21 mg/L and 12.36 mg/L , respectively) were high enough to assume the lake at eutrophic level.

Key words Zooplankton, Rotifera, Water Quality, Lake Golbasi, Turkey

1. Introduction

Rotifera, Cladocera and Copepoda species in zooplanktonic groups, which are the first link in the food chain in freshwater ecosystems, are present in all kinds of freshwater systems. They are the major food source of fish and other aquatic animals, and they play an important role in freshwater reservoirs. For this reason, the amount of these organisms in the unit water mass is vital for fry in reservoirs and they are also a characteristic indicator of water quality, eutrophication and pollution levels.

Their short generation time and fast population renewal makes rotifers the most important group among zooplankton. They are sensitive against to changes in water quality and able to respond rapidly to environmental changes comparing with other zooplankton. Rotifers with their major effect on the behavior, distribution, growth, condition and larval survival rate for all species of freshwater fish are also one of the main biotic factors in the aquatic environment. They play an important role as grazers, suspension feeders and predators within the zooplankton community and also serve as an essential food source for invertebrate and vertebrate predators (Yiğit, 2002).

While no previous water quality assessments exist, Lake Golbasi is generally considered to be a pristine environment with no point sources with high levels of nutrient inputs or other pollutants. However, absence of a proper sewage treatment system and widespread use of agricultural fertilizers, high levels of recreational activity and over-fishing are the negative factors impacting the Lake Golbasi environment. These activities along with fishing in the lake are expected to and may have already started to impact the ecology of the Lake Golbasi and its ecosystems.

Naz and Turkmen (2004) provided phytoplankton biomass and species composition of the lake, however, there are no previous studies providing information on the water quality and zooplanktonic populations throughout Lake Golbasi. The zooplankton composition together with water quality parameters were investigated in the present study.

2. Materials and Methods

Lake Golbasi is located in the eastern Mediterranean region of Turkey, 50 km north of the city of Antakya (36º 29′ E, 36º 30′ N). The lake is a natural lake with a surface area of 12 km^2 and altitude of 18 m. The volume of the lake is 8 x 10^6 m^3 with a maximum depth of 4.3 m. Since, it supplies water to surrounded cotton fields; the water level is lower in spring and summer. The lake has no incoming or outgoing creeks and is only fed by spring water. Water samples were collected from two stations. Station one was located near by the village and stations two was across the station one and close by the pump (Figure 1).

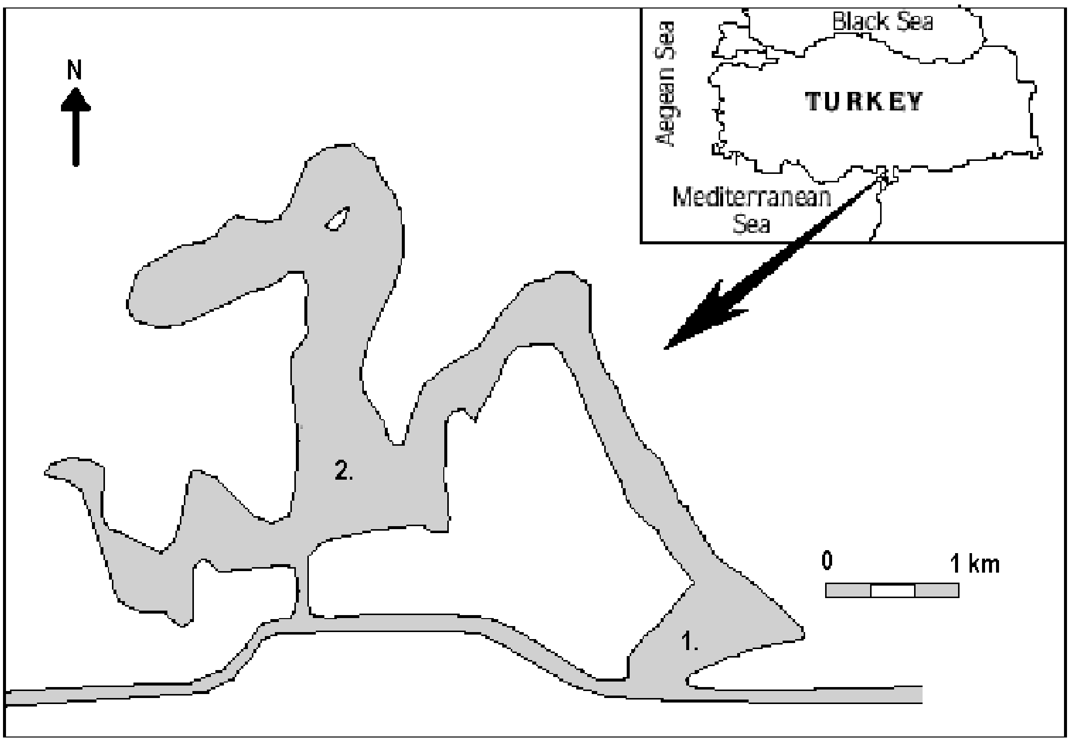

Figure 1. Location map of Lake Golbasi

2.1. Water Analyses:

The study was carried out a year between April 2003 and March 2004 by collecting water samples monthly. Sampling bottles were acid washed a day before sampling day. 1-2 % HCl solution was used for acid wash and sampling bottles, which then were rinsed through distilled water, were dried in the drying oven (Boyd and Tucker, 1992). Water samples were taken from the 10 cm depth from the surface by holding the bottles upward and immediately transferred to the laboratories for analyses. Oxygen, temperature, pH and salinity were measured directly at the field by the means of digital instruments. Oxygen and temperature were measured by YSI model 52 oxygenmeter, pH by Orion model 420A pH meter and salinity by YSI model 30 salinometer.

Other water quality parameters such as chemical oxygen demand (COD), total alkalinity and hardness, ammonia, nitrite, nitrate, phosphate, sulphite, sulphate, chloride, potassium, sodium and silica analyses were done on the same day in the Mustafa Kemal University, Faculty of Aquaculture and Fisheries Laboratories. Titration methods were used for total alkalinity and total hardness and results from both analyses were expressed as mg/L $CaCO_3$. Chloride (Cl_2) analyses were done by titration method with $Hg(NO_3)_2$. Chemical oxygen demand (COD) analyses were carried out by titration method with ferrous ammonium sulphate, which basically calculate the amount of oxygen spent to oxidize all organic matter in water. Nitrate (NO_3), nitrite (NO_2^-) and total ammonia nitrogen (TAN) ($NH_3 + NH_4^+$) and phosphate (PO_4^{3-}) measurements, which require photometric measurements, were done according to standard procedures by using Shimadzu brand UV-1601PC model spectrophotometer. Water analyses were done according to procedures described by Boyd and Tucker (1992). Water quality measurement data were obtained by averaging the values from two stations.

Zooplankton samples were taken from the determined stations with horizontal and vertical draws by using 60 µm mesh size plankton net. Depth of the first and second stations were 2 m and 2.5 m, respectively. Samples, after 15 minutes drawing and filtering about 7 m^3 water, were replaced into glass jar and fixed with 4% formaldehyde. While qualitative (systematic) analyzers were made on samples, obtained from both horizontal and vertical drawings, quantitative analyzers were made only on samples obtained from vertical drawings. Vertical drawings were made from bottom to surface with 15 cm diameter vertical plankton net, and horizontal drawings were made with 30 cm diameter horizontal plankton net. The following taxonomic literature was used for identifying the zooplankton groups; Edmondson (1959), Koste (1978), Kolisko (1974), Dussart (1969), Stemberger (1979), Scourfield and Harding (1966), Negrea (1983), Kiefer and Fryer (1978), Borutski (1963). Zooplankton density (according to species) was estimated by optical inverted microscopy according to Wetzel, 1975. The density and biomass of Rotifera and Crustacea (by species) were estimated following the method of Edmondson (1959). Number of organism in a liter was determined by counting the all vertical samples. Zooplankton biomass was defined as the sum of the biomass of Rotifera and Crustacea.

3. Results

Water temperature ranged from a low of 13ºC in December to a high of 28.1 ºC in August and averaged 21.8 ºC over the year. pH values were ranged between 7.19 and 7.89 with the average of 7.52 through the study. pH values increased month by month starting from May to December.

The highest and lowest dissolved oxygen levels were 9.72 mg/L and 3.23 mg/L recorded in March and August, respectively. The average dissolved oxygen concentration was 5.94 mg/L over the study period (Figure 2).

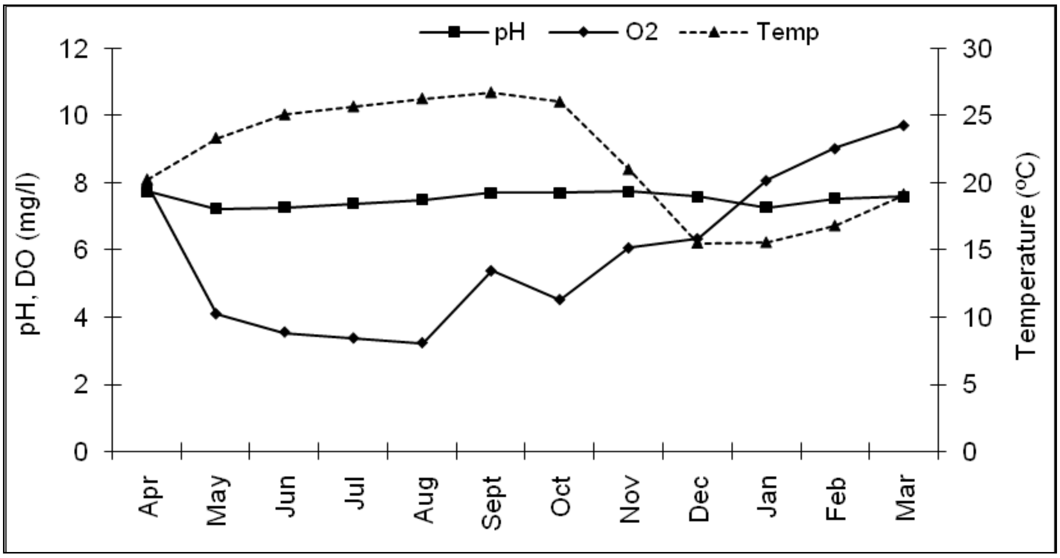

Figure 2. Monthly variation in water temperature, dissolved oxygen, and pH.

Chemical oxygen demand (COD) was stagnant for five months at the beginning of the study and increased month by month for the rest of the study period up to 42.5 mg/L. Nitrate, and nitrite levels showed similar patterns during the study period and max levels were recorded in January. The other nitrogen derivative, ammonia fluctuations over the year, was similar to nitrate and nitrate. Ammonia concentration in July was minimum with 0.24 mg/L and increased each month up to 0.85 mg/L in December. The mean ammonia measurements were 0.61 mg/L at the end of the study (Figure 3).

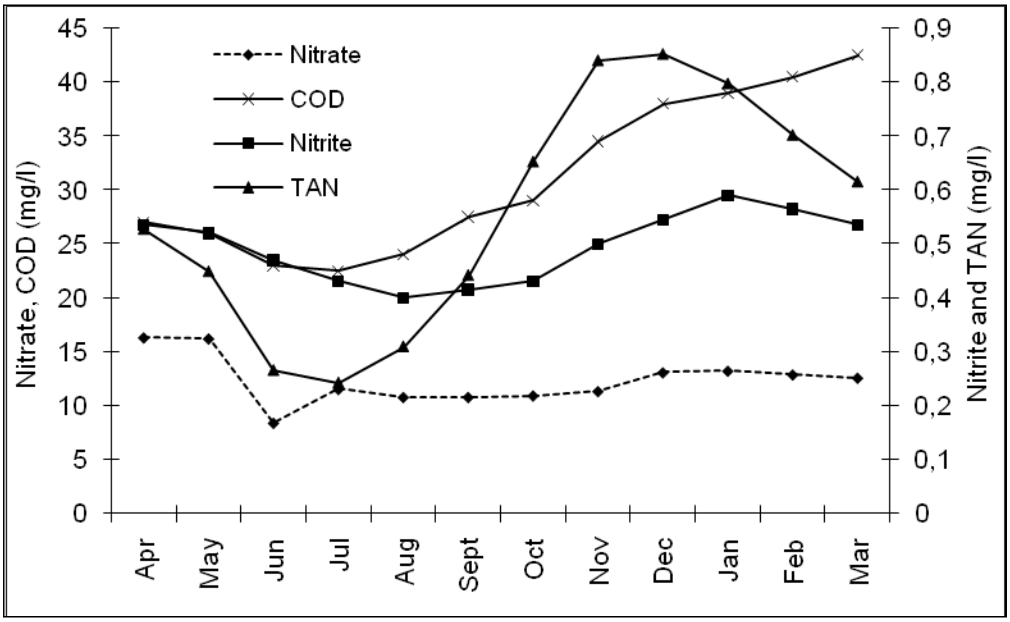

Figure 3. Monthly variation in nitrate, nitrite and TAN concentrations.

Salinity, as expected, did not change much from month to month and averaged 0.24 ppt through the year. Fluctuations in total alkalinity and total hardness were similar but the amount of the total hardness was significantly greater than that of the total alkalinity. The average total alkalinity and total hardness values were 277 mg/L and 457 mg/L, respectively. The average silica level was 10.29 mg/L. Starting with 9.05 mg/L in April, silica levels were gradually decreased down to 8.3 mg/L in August then increased to 13 mg/L each month until January. The maximum sodium level of 126 mg/L was recorded in December and averaged 95.37 mg/L through the study. Chloride levels were 0.22 mg/L at the beginning of the study and increased each month until October. The average chloride level was 0.33 mg/L over the year. Potassium levels started from 0.75 mg/l in April and increased gradually each month until January up to 3.05 mg/L then dropped back to 1.75 mg/L in March. The average potassium levels were 2.14 mg/L over the study period (Table 1).

Date	Alkalinity	Hardness	Chloride	Silica	Salinity	Sodium	Potassium
Apr	276,0	455	0,221	9,05	0,2	88	1,30
May	273,0	451	0,251	8,8	0,2	84	1,40
Jun	270,0	448	0,312	8,6	0,2	79,5	1,95
Jul	268,5	450	0,371	8,45	0,3	78	2,10
Aug	270,5	450	0,407	8,3	0,3	80,5	2,35
Sept	272,0	452	0,441	9,75	0,3	85,5	2,00
Oct	274,5	454	0,463	10,05	0,2	91	2,30
Nov	276,5	456	0,388	11,75	0,2	107,5	2,70
Dec	278,0	457	0,311	13,4	0,3	126,5	3,00
Jan	281,5	459	0,293	13	0,3	121,5	3,05
Feb	279,0	458	0,248	11,65	0,2	104,5	2,40
Mar	277,5	357	0,233	10,75	0,2	98	1,75

Table 1. Some water quality parameters in the lake.

Phosphate, the most vital nutrient effecting productivity of natural water resources, measurements averaged 0.22 mg/L. Phosphate levels were increased during the summer until August and gradual decrease has seen after this month.

Sulphate concentrations were showed the maximum values in October with 258 mg/L and the average sulphate concentrations were 163 mg/L for the study period. Sulfite concentration was 5.6 mg/L in April and increased each month up to 12 mg/L in December then showed decrease down to 6.41 mg/L. The average sulfite concentration calculated as 8.3 mg/L. Chlorophyl-a was averaged 37.87 µg /L ranging from 22.48 in January to 51.1 in April (Figure 4).

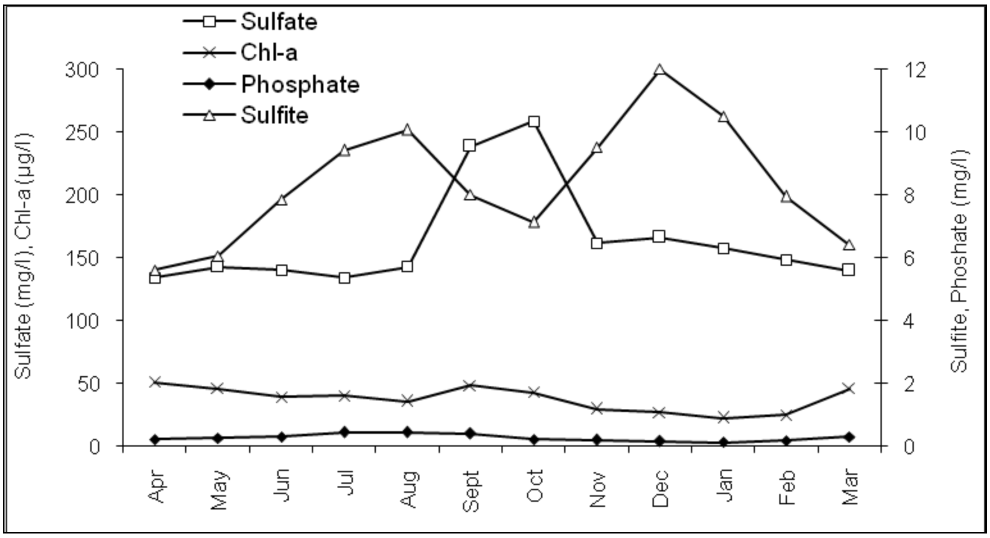

Figure 4. Monthly variation of some water quality parameters

Zooplankton community

The zooplankton abundance and species identified in Lake Golbasi are shown in Table 2 and 3. The zooplankton assemblage included 92 species. Rotifera had the highest proportion with 62 species followed by Cladocera with 20 species, Copepoda with 10 species. *Polyarthra dolichoptera*, *Synchaeta* sp, *S. Stylata* were present through the whole study period.

Months	**Ap**	**May**	**Jun**	**Jul**	**Au**	**Sep**	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Tot.**
Rotifer	**(ind/l)**												
Brachionus angularis	92	50	6	3	3			1				62	**217**
B. calyciflorus		12	5	2	3			2			1	7	**32**
B. quadridentatus	2		2	1	2			1					**8**
B. patulus								1					**1**
Lecane clasterocerca	1	3										1	**5**
L. stenroosi			3										**3**
L. hastata								3					**3**
L. bulla	1	2	6	3	3			1					**16**
L. quadridentata		3	2	3				1					**9**
L. lunaris				2				2			1		**5**
L. papuana			2	2	4								**8**
L. luna		2	4	3				4			4		**17**
L. ohioensis		1											**1**
L. ludwigi	2	1						1				4	**8**
Polyarthra dolichoptera	23	158	7	5	3	9	13	6	23	17	3	35	**302**
Hexarthra fennica	16	14	7	5	4			1			1	15	**63**
Testudinella patina	1	7	4	2	2			1			2		**19**
Testudinella mucronata				1	1	5	4	2	2				**15**
Cephalodella gibba	1	8		4				4			2	2	**21**
C. forficula	1		1	1	1								**4**
Keratella valga	255	481	41	2	30	12	19	6			2	220	**1068**
K. cochlearis cochlearis	1	5	3	1	4							4	**18**
K. cochlearis tecta			3	2	2								**7**
K. tropica				1	2	10	14	3					**30**
K. quadrata	5	11		2				3	7	5	2	11	**46**

Table 1 Cont.

Synchaeta sp	311	356	25	27	20	60	70	27	29	20	8	292	**1245**
S. stylata	141	62	11	12	7	9	15	2	8	6	1	143	**417**
Trichotria tetractis		8	11	3				2			1		**25**
T. pocillum		1	4	7	3			1			1		**17**
Asplanchna priodonta	2	4										3	**9**
A. sieboldi	2	6		4	7	2		2			2	4	**29**
Lophocharis salpina	2	3	4	5	4							1	**19**
Rotaria neptunia								2			1		**3**
Eosphora najas													
Euchlanis dilatata	9	12	6	2		11	14	2			3		**59**
Dipleuchlanis propatula		1											**1**
Dicranophorus grandis				2		3	5	2					**12**
Beauchampiella eudactylota eudactylota	2			1									**3**
Lepadella patella	2					4	3	6	1		1		**17**
L. ovalis				1		5	2	3					**11**
L. rhomboides						1	1	2					**4**
Anuraeopsis coelata				2				2	5	4	3		**16**
Trichocerca longiseta	1						2	3			2		**8**
T. iernis			4	2	4		3	2					**15**
T. porcellus	2						3	4			2		**11**
T. stylata							3	4					**7**
T. elongate	3			1			4	7			2	7	**24**
Squatinella mutica similis								2	2	5	2		**11**
S. mutica tridentate								1	5	3	6		**15**
Platyias quadricornis	1							1					**2**
Scaridium longicaudum								1			1		**2**
Colurella adriatica								1			1		**2**
C. uncinata								2			1		**3**
Wolga spinifera	1					13	18	2			1		**35**

Table 1 Cont.

Notommata copeus	2												**2**
Notholca squamula	1										3		**4**
Notholca acuminate	1												**1**
Mytilina mucronata	1										2		**3**
M. ventralis											3		**3**
Pompholyx sulcata											1		**1**
Monommata longiseta	1							1			1		**3**
Filinia longiseta	3	9	5	2	5						1	5	**30**
Total	**889**	**1220**	**166**	**116**	**114**	**144**	**193**	**127**	**82**	**60**	**68**	**816**	**3995**

Table 2. Monthly Abundance (ind/l) of Rotifera in Lake Golbasi.

Months	**Ap**	**May**	**Jun**	**Jul**	**Au**	**Sep**	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Tot.**
Cladocera	**(ind/l)**												
Diaphanasoma brachyurum	2	2		2				2				4	**12**
Bosmina longirostris	19	5	5	2	4			2			2	8	**47**
Moina micrura		3		3	6						2		**14**
İlyocryptus sordidus	1			1		3	4	2			2		**13**
Ceriodaphnia pulchella	3	4						1			1	3	**12**
Daphnia manga	1												**1**
Simocephalus serrulatus	2										1		**3**
Macrothrix laticornis	2	2									2	3	**9**
Scapholeberis kingi				1									**1**
Camptocercus uncinatus	1	1		1							1		**4**
Alonella exigua	3			1				1			1		**6**
Alonella excisa											1		**1**
Alona rectangula	2	2		1		3	5	2			2	3	**20**
Alona costata								1					**1**
Chydorus sphaericus	2	2		1				1			3	4	**13**

Table 2 Cont

Graptoleberis testudinaria								1					**1**
Pseudochydorus globosus	1												**1**
Dunhavedia crassa								1					**1**
Pleuroxus laevis	2	2		1		1	2	2			1	1	**12**
P. uncinatus	2	1										1	**4**
Total	**43**	**24**	**5**	**14**	**10**	**7**	**11**	**16**			**19**	**27**	**176**

Table 3. Monthly Abundance (ind/l) of Cladocera and Copepoda in Lake Golbasi

Eucyclops speratus	2			2				2	5	4			**15**
Cryptocyclops bicolor	1						4	2	2	2			**11**
Macrocyclops albidus	1								4	3			**8**
Megacyclops viridis	2	2							1	1		3	**9**
Paracyclops fimbriatus chiltoni									1	1	1		**3**
Diacyclops bicuspidatus	1								2	3			**6**
Eudiaptomus drieschi									3	3			**6**
Nitocra hibernica	2		1	2	3			1	1	3	2		**14**
Onychocamptus mohammed			3	3	5	3	5	2	1	3			**25**
Larnea cyprinacea		1											**1**
Naupli	37	96	3	2	4	19	24	3	15	12	1	42	**258**
Total	**46**	**99**	**7**	**9**	**12**	**25**	**33**	**10**	**35**	**35**	**4**	**45**	**360**

Keratella valga was found for 10 months, *H. fennica*, *K. quadrata*, *A. sieboldi*, *Euchlanis dilatata* (rotifera), *Bosmina longirostris*, *Alona rectangula*, *Pleuroxus laevis* (cladocera), *Nitocra hibernica*, *Onychocamptus mohammed* (copepoda) were found 8 months. The least recorded species were as follows; *B. patulus*, *Lecane stenroosi*, *L. ohioensis*, *Dipleuchlanis propatula*, *Notommata copeus*, *Notholca acuminata*, *M. ventralis*, *Pompholyx sulcata* (rotifera); *Daphnia magna*, *Scapholeberis kingi*, *Alonella excisa*, *Alona costata*, *Graptoleberis testudinaria*, *Pseudochydorus globosus*, *Dunhavedia crassa* (cladocera); *Lernea cyprinacea* (copepoda).

In terms of number, according to monthly distribution of the groups, the greatest rotifera were accounted with 43 species in November, followed by 33 species recorded in July and February, 32 species found in April and only 7 species were determined in January (Table 2). Cladocera showed the maximum number of species in April with 14 species, followed by February with 12 species and November with 11 species. No cladocera was found in June, December and January samples. Copepoda showed the maximum diversity with 10 species in December and January, followed by April with 7 species and November with 5 species. Only two copepoda species appeared in March (Table 3).

The average numbers of groups were 167 ind/l, 8 ind/l, and 15 ind/l for rotifera, cladocera and copepoda, respectively. Rotifera and copepoda were increase in terms of number from April to May, reached to highest level (610 ind/l and 49 ind/l, respectively) and then decreased until July while an increase has seen from August to November. After then rotifera were decrease but copepoda were increase until January. The minimum number (30 ind/l) of rotifera appeared in January, and only 2 individual of copepoda were found in February.
Cladocera reached the maximum number (22 ind/l) in April, and decreased after this month until November. None cladocera was found in December and January, and only three individuals were found in June. Annual mean of the groups were 167 ind/l for rotifera, 8 ind/l for cladocera and 15 ind/l for copepoda (Figure 5).

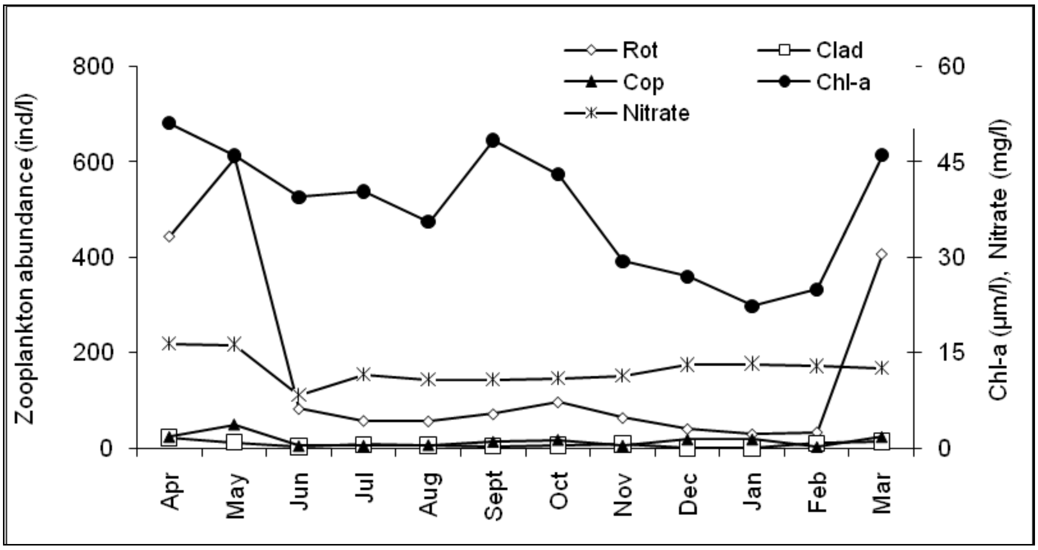

Figure 5. Monthly variation of zooplankton abundance, nitrate and chlorophyll-a.

Rotifera species of *Dipleuchlanis propatula* determined in this study is the first records for Turkish inland waters (Figure 6).

4. Discussion

Lake Golbasi is a relatively small lake and so it is expected that a high degree of homogeneity may exist for various physical parameters. Since, there was no significant spatial variability for most physicochemical parameters, the water quality measurement data were taken by averaging the values of two stations.

Dissolved oxygen concentrations were above 5 mg/L which was sufficient enough to support aquatic life, specially the zooplankton community. The increase in dissolved oxygen levels might be the result runoffs occurred by winter rains (Tepe and Mutlu 2004).
Natural waters with high or moderate alkalinity usually have lower pH change during the day, because of the buffering capacity afforded by the higher alkalinity (Boyd 1990). The total alkalinity of the lake is quite high to buffer pH to increase too high.

The carbonate system provides acid buffering through two alkaline compounds: bicarbonate ($HC0_3^-$) and carbonate (CO_3^{--}). These compounds are usually found with two hardness ions: calcium (Ca^{++}) and magnesium (Mg^{++}). The mean value of chlorophyll-a was relatively high and indicated that the lake is at eutrophic class according to the tropic static classification (Table 4). The annual mean values of total phosphorus with 0.22 mg/L also make the lake in eutrophic class (Wetzel, 1983).

PHOSPHORUS AND CHLOROPHYLL CONCENTRATIONS AND SECCHI DISK DEPTHS CHARACTERISTIC OF THE TROPIC CLASSIFICATION OF LAKES			
MEASURED PARAMETER	Oligotrophic	Mesotrophic	Eutrophic
Total Phosphorus (mg/m3) Average	8	26.7	84.4
Range	3.0 - 17.7	10.9 - 95.6	16 - 386
Chlorophyll *a* (mg/m3) Average	1.7	4.7	14.3
Range	0.3 - 4.5	3 - 11	3 - 78

Table 4. The tropic classification of lakes (Wetzel, 1975)

Dissolved oxygen showed inverse proportion with zooplankton biomass. Dissolved oxygen levels were low in the months when zooplankton biomass showed increase. The reason of this might be the use of dissolved oxygen by zooplankton in the respiration. Cholorophly-a increased by increase in dissolved oxygen and decreased by decrease in dissolved oxygen showing direct proportion with dissolved oxygen. Cholorophly-a was inversely proportional with Sulfite and Potassium (Figure 6).

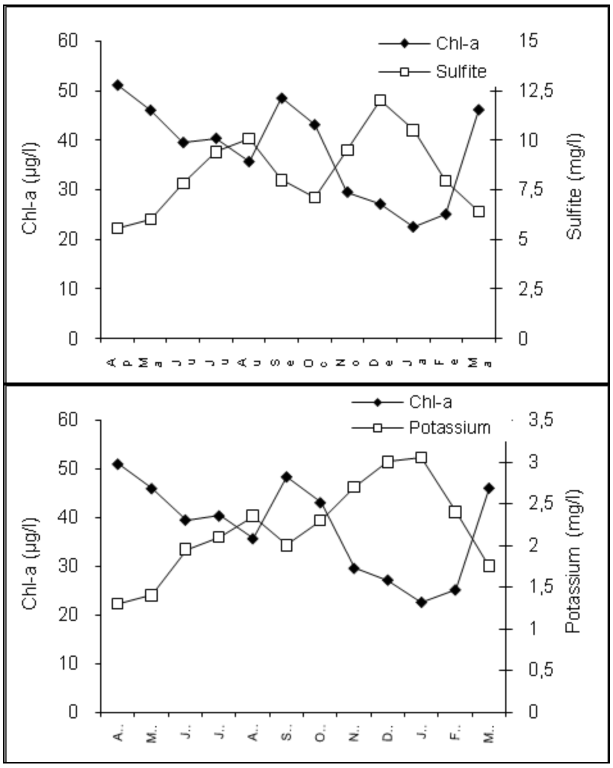

Figure 6. Monthly variation of Chlorophyll-a and sulfite, potassium

Oxygen production of phytoplankton by photosynthesis might be the reason of this direct proportion. Cholorophly-a showed parallel patterns with nitrate but not with nitrite and TAN. On the contrary, TAN showed inverse patterns with phosphate over all year round (Figure 7).

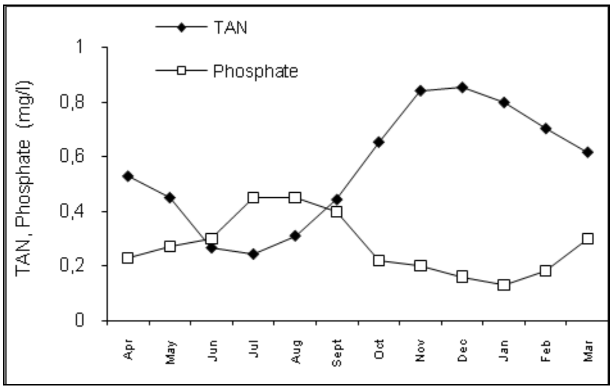

Figure 7. Monthly variation of TAN and Phosphate

Zooplankton showed inverse patterns with nitrite, sulfite, potassium, and nitrate through the all year round, inversely proportional with phosphate until November and showed direct proportion afterwards; directly proportional with sulfate and Cholorophly-a; directly proportional with TAN until November and showed inverse proportion afterwards (Figure 8).

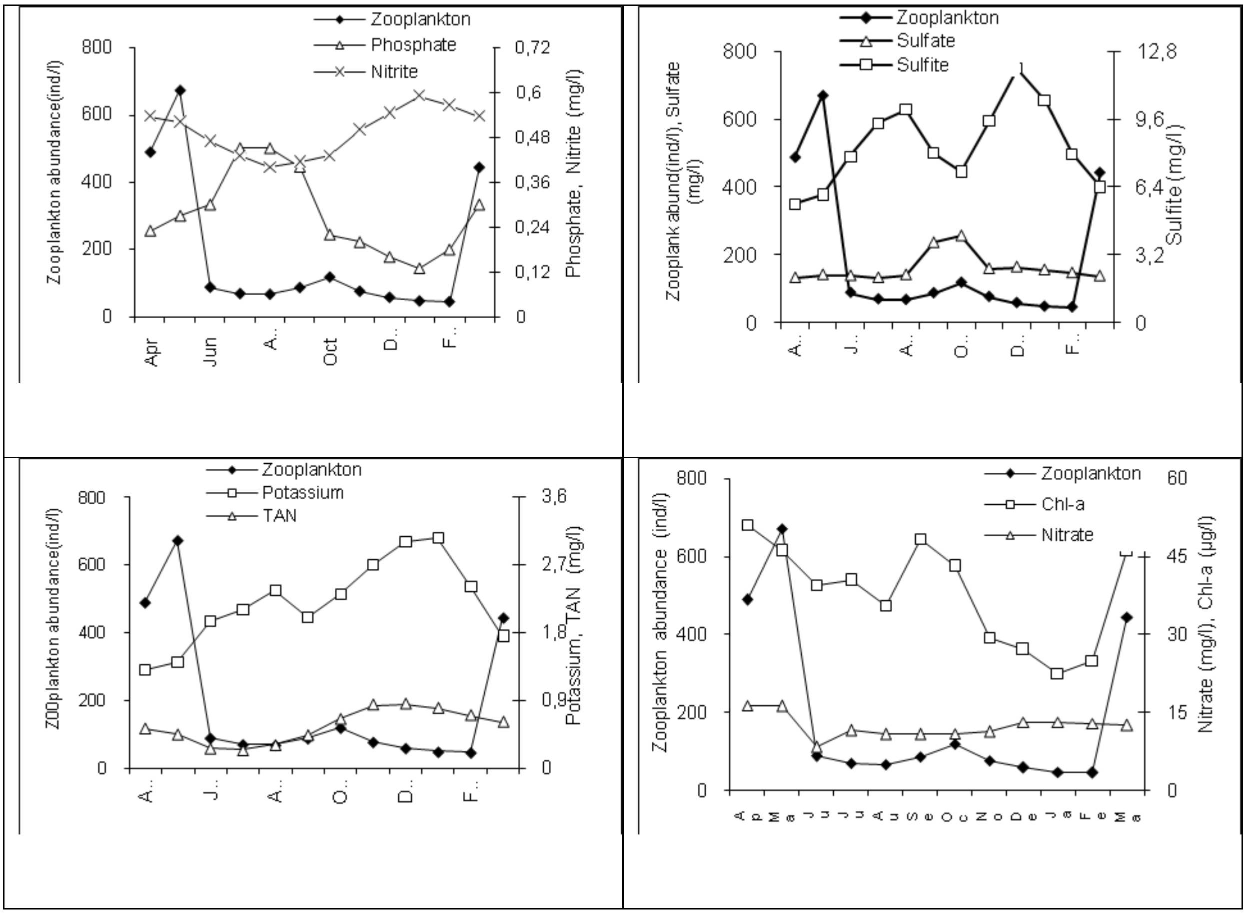

Figure 8. Monthly variation of zooplankton and some water quality

Some researchers determined positive correlation between Cholorophly-a and phosphate and also between nitrogen, phosphate and zooplankton. They specially declared increased rotifer and crustacean number with increase nutrient amount (Vakkilainen et, al., 2004; Esler et. al 2001)

Nitrogen does not occur naturally in soil minerals, but is a major component of all organic matter including both plant and animal. Decomposing organic matter releases ammonia, which is converted to nitrate if oxygen is present (Boyd and Tucker, 1998). This conversion occurs more rapidly at higher water temperatures (Emerson *et al.*, 1975). All inorganic forms of nitrogen (NO_3-, NO_2- and NH_4+) can be used by aquatic plants and algae. If these inorganic forms of nitrogen exceed 0.3 mg/l (as N) in spring, it means there is sufficient nitrogen to support summer algae blooms. The concentrations of nitrogen forms in Lake Golbasi were sufficient to support summer algae blooms and zooplankton biomass.

According to Welch (1935), it is well known that annual fluctuations occur in phytoplankton and zooplankton biomass as well as two increases, in spring and autumn, and decreases in summer and winter. Chlorophyl-a was high in spring and autumn while low in summer and winter parallel to zooplankton biomass.

Since, there is a close relation between phytoplankton and zooplankton because of feed chain, increase in zooplankton biomass was observed following the phytoplankton bloom. The highest amount of rotifera reported in the area where phytoplankton bloom occurred, and they consequently found the abundant supply of food (Kolisko, 1974; Horn ve Goldman, 1994; Noges, 1997). Similar results were found in the present study. In April, cchlorophyll-a was decreased parallel to increase in zooplankton and in the following months, zooplankton amount were decrease up to decrease in chlorophyll-a and increase with increase in chlorophyll-a. Especially in March, identical increase in zooplankton amount and chlorophyll-a was obviously observed.

The determined species in Lake Golbasi such as *Brachionus calyciflorus*, *B. angularis*, *Keratella quadrata*, *K. cochlearis*, *Polyarthra dolichoptera*, *Euchlanis dilatata*, *Lecane luna*, *Pompholyx sulcata*, *Filinia longiseta*, Trichocerca species (rotifera); *Bosmina longirostris*, *Chydorus sphaericus*, *Daphnia cucullata* (cladocera) are also reported to be eutrophic species (Rylov, 1963; Borutski, 1963; Brooks, 1971; Voigt and Koste, 1978).

From the identified the rotifers, *Asplanchna*, *Brachionus*, *Keratella*, *Cephalodella*, *Lecane*, *Lepadella*, *Monostyla*, *Mytilina*, *Notholca*, and *Trichocerca* are the most common cosmopolitan inhabitants of the lake littoral region's vegetation. *Alona* and *Chydorus* of the cladocera are also the most common forms, found on or near the bottom in weedy littoral areas (Smith, 2001). The zooplankton composition of the lake showed the characteristics of a weedy littoral habitat.

Dipleuchlanis propatula, determined in this study, is the first record rotifera species for Turkish inland waters. *Dipleuchlanis propatula* has oval body shape, truncate in front, rounded behind. The foot is short, slender and three jointed; there are no setae on the dorsal side of the penultimate foot-joint. The toes are very long, parallel sided, very slender, cylindrical and slightly swollen near their bases. The rami are triangular in ventral view, and the unci each have ten, or more, long, slender, teeth, clubbed at the tips (Figure 9).

Figure 9. *Dipleuchlanis propatula*

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THE SUSTAINABILITY OF WASTE DISPOSAL: POLLUTION OF UNDERGROUND WATER BY LEACHATES FROM OLD BURDENS (DUMPSITE)

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The project assessed the elemental composition of underground water around three dumpsite in Ibadan , the second largest city in Africa. to determine the extent of underground water pollution from dumpsites around the three areas where ground water for analysis was taken. Consistently, areas around the dumpsites have higher quantities of the elements assessed namely sodium(Na) , calcium(Ca) , magnesium(Mg) and silicon(Si) and the quantities of these elements also exceeded the maximum permissible levels in water by the World Health Organisation (WHO). Areas father away from the dumpsite had lower levels of these elements. The amount decreased in the order: Ca, Na and Si. The nature of the substratum was found to play an important and significant effect on what finally seeps into underground water as proof of the formation of ligands were seen.. Clay soil absorbs more of the pollutants than all other soil types. An urgent review of the use of dumpsites has now become pertinent, as they affect life and all life forms in there immediate vicinity usually adversely.

INTRODUCTION

Pollution is a term applied to any environmental state or manifestation which is harmful or unpleasant to life resulting from man’s failure to achieve or maintain control over chemical, physical, biological consequences or side effects of his scientific industrial and social habits. This broad definition of environmental pollution is not concerned with environmental changes that may have adverse consequences for man. Man through his technological process converts. Natural resources to energy and goods for use, which bring about changes in his environment some of which may be detrimental. The human environment consists of three major components, the air we breathe, the water we drink and the land from which we derive our investment, with a very complex interrelationship between all components. Through this very complex interrelationship, pollutants from one phase enter into another with the component of land pollution seeping through and to pollute underground water. This component is collectively called leachates, which forms the major thrust of this research.

In Lagos State, for instance, large amount of waste is generated, with the Lagos State Waste management Authority (LAWMA) being the authority in charge of waste. Records of total waste disposed between 1988 and 1994 indicate a total tonnage of 16,418,661, with breakdown as shown in Table 1.

Table 1: Total waste collected and disposed by Lagos State Waste Management Authority.

	Year	**Tonnage of household waste collected and disposed**
	1988	2,109,910
	1989	3,194,148
	1990	3,527,107
	1991	2,368,770
	1992	1,999,682
	1993	2,024,197
	1994	1,396,846

Of all waste generated, studies by Lavalin[2] indicated that domestic or household derived waste accounted for 78% of the total waste generated while the remaining 22% could be classified as institutional, market, commercial and industrial wastes.

The domestic portion of the waste can be further broken down into the following: vegetable/perishable matter making up 68%, the remaining being metals, plastics, glass, textiles, rubber, cardboard and wood.

The organic biodegradable components in solid wastes begin to undergo bacterial decomposition in these waste dump site under aerobic conditions deriving its source of micro/organisms from surrounding soil material. There are also physical and chemical process during decomposition. These are (a) decay of hydrolysable organic materials under aerobic conditions which are catalyzed by enzymes produced by saprophytic micro-organisms which may be present in the soil or in the waste itself. Harmless end products including carton dioxide, water and energy are produced under aerobic conditions. The resultant products are alcohol, a mixture of gases (methane, carbon dioxide and hydrogen sulphide). It is this process that is explored in the production of bio-gas.

b. Chemical oxidation and reduction of dumpsite materials particularly wastes of pharmaceuticals and chemical origin, some of which are toxic.
c. The diffusion of leachates: a solution and suspension of toxic and non toxic organic and inorganic materials produced in “a” and “b” above plus sharp ended finely particulate. The leachate may migrate from the dumpsite either as surface flow or percolate through the underlying layers of soil to recharge and contaminate ground water. They may as consequence be transported considerable distance from the source by water flow. The composition of leachates monitored over time is as shown in Table 2:

Table 2: The variation in leachates composition between acetogenic and methanogenic stages of waste decomposition[3]

	Constituents	**Acetogenic phase mg/L**	**Methanogenic phase mg/L**
1	Calcium	1000	100-400
2	Magnesium	250	50-200
3	Potassium	30	50-400
4	Total Iron	60	20-200
5	Chloride	500	100-400
6	Sulphate	300	20-50
7	Sodium	500	100-200
8	Organic Nitrogen	200	20-40
9	Total phosphorous	30	5-10

The other composite constituents of leachates are sulphides, oil and grease, arsenics, barium, tin, phenolics, copper, lead, mercury, nickel, selenium, silver, zinc, nitrite and microbes. As leachates percolates though the underlying strata, many of contained in it will be removed by filtering and adsorptive action of the material composing the strata. The extent of this action depends on the characteristics of the soil[4.]

Chergui et al[5] (1997) assessed the quality of ground water in urban industrial units

a. Sugar factory
b. Distillery and
c. A fertilizer factory in an area of Pradesh in India. Some 216 water samples from land pumps bore holes and poor quality industrial effluents of various characteristics were found to have some become pollutants in the water content.

Legret[6] (1950) also assessed landfill leachates in the Athens region of Greece. Samples from wells in the area up to three kilometers from the landfill, show results indicating very high levels of concentration of leachates.

Bakare[7] (2000) also examined the effects of leachates collected around Ibadan metroplis dumpsite on actively dividing gonadal cells of rats. Observations of a higher incidence of abnormally shaped spermatozoon was noted. Carcinogenesis was also suspected as a possibility.

Evans[8] investigated the chemical composition and specification of leachate samples from four Southern Ontario Municipal solid waste landfill and discovered that cadmium concentration in all the leachate sample exceeded maximum acceptable levels for portable water indicating the problem of heavy metal contaminating the water in the environment.

The emission of cadmium to water from point source has resulted in increased concentrations in the area around the land fills[9].
Davies[10] analysed the Lead (Pb) content of leachates in a former waste disposal near Kansas City in the United State of America. Lead leachates effected soil nutrient percentage of these nutrients, reduced the growth of plants and vegetable in the area.

MATERIALS AND METHODS

The three locations for the research work was Gege, in Ibadan North East Local government area, University of Ibadan dumpsite and Ibode all in Oyo State. A geographic description of the site would be to say they are found within Ibadan metropolis.Solid and domestic wastes are creating very serious problem and are difficult to manage because of the system of disposal. Emissions from dumpsites where these wastes are dumped makes the assessment of local environmental risks a priority. With increasing population, the dumping problem is daily increasing as incidences of the dumping of solid waste by road side becomes a more common place. Traffic blockades have resulted often due to the rendering of most part of the road impassable. Dramas have also been known to be fully blocked causing flooding of adjourning residences during rainy season.
Objectively the study was to determine the levels of elements present in ground water around the dumpsite environment over a period of six months. Our polluted environment has been the object of increase concern particularly water pollution with groundwater receiving plenty of emphasis being the central source of domestic water supply in the areas where the study was carried out. Ground water is the most threatened past of modern hydrologic environment with the threat coming from the improper disposal of domestic and municipal waste. Communities are currently subtly rejecting the traditional open burning dump and recognizing the need for safe and sanitary conscious management of solid waste.

COLLECTION OF WATER

Collection of water samples from the three sites was done from wells. As characteristic of the areas around the three sites, hand dug wells were the only source of water for domestic use, Augers were used to drill at an equidistant location of 50 meters. From the sites, Depth varied with the water table in the particular area. Water which sewed as control was taken around the area, about 200 meters from the landfill site.

PREPARATION OF WATER SAMPLES

100 ml of underground water was taken using a bucket from the well. On site, the samples were filtered through a plastic membrane filter 0.45mm pore size to remove any sediments from the water. 5 mils of concentrated hydrochloric acid was added to each sample with part of the acidified water sample transferred with a 50 ml graduated flask and refrigerated at 4^0C prior to analysis. The essence of the acidification was to prevent the formation of precipitation or the adsorption of trace ICP-MS analysis elements into the wall of sample containers.
Biological action would also be minimized for each 50 ml of sample kept in the refrigerator, 1 ml of Yttrium internal standard was added and agitated properly. 5 ml of this sample was measured into the ICP-MS sample tube and then placed in the sample injection port for analysis of pollutants.

RESULTS

Table 3: Shows the levels of Pollutants at the different sites

	MAY				
	Na	Ca	Mg	Si	Al
L1	5.0	9.8	1.9	7.49	0.0
	9.0	9.5	2.2	7.6	0.0
	12.6	9.9	2.3	7.15	0.0
	7.4	10.0	2.2	7.15	0.0
MEAN	8.5	9.8	2.1	7.4	0.0
1.2	6.0	7.1	0.0	0.65	0.0
	3.0	6.6	0.0	0.45	0.0
	2.5	7.8	0.0	0.55	0.0
	4.5	6.5	0.0	0.65	0.0
MEAN	4.0	7.0	0.0	0.58	0.0
1.3	7.0	36.8	0.0	0.2	0.0
	6.0	37.6	0.0	0.19	0.0
	8.0	36.4	0.0	0.21	0.0
	5.0	39.6	0.0	0.2	0.0
MEAN	6.5	37.6	0.0	0.2	0.0
	JUNE				
L1	8.0	9.6	1.8	6.8	0.0
	7.8	9.8	2.2	7.0	0.0
	8.2	9.65	2.4	7.2	0.0
	9.2	9.35	2.3	7.0	0.0
MEAN	8.3	9.6	2.18	7.0	0.0
L2	3.82	7.2	0.0	0.5	0.0
	4.26	6.9	0.0	0.47	0.0
	3.66	6.8	0.0	0.60	0.0
	4.41	7.0	0.0	0.57	0.0
MEAN	4.04	6.98	0.0	0.54	0.0
L3	5.8	32.6	0.0	0.18	0.0
	6.0	34.8	0.0	0.19	0.0
	6.3	36.2	0.0	0.22	0.0

Table 3. Cont.

MEAN	6.2	34.35	0.0	0.19	0.0
	JULY				
L1	79	9.0	1.6	6.5	0.0
	7.4	9.42	1.9	6.7	0.0
	7.8	9.3	1.8	6.8	0.0
	8.9	8.9	2.0	7.0	0.0
MEAN	8.0	9.16	1.83	6.75	0.0
L2	4.1	6.9	0.0	0.42	0.0
	3.6	6.5	0.0	0.60	0.0
	3.7	6.3	0.0	0.57	0.0
	3.9	7.1	0.0	0.58	0.0
MEAN	3.83	6.7	0.0	0.54	0.0
L3	5.6	33.2	0.0	0.17	0.0
	5.9	34.0	0.0	0.20	0.0
	6.2	36.3	0.0	0.21	0.0
	5.9	31.6	0.0	0.15	0.0
MEAN	5.9	31.26	0.0	0.18	0.0
	AUG				
L1	8.22	8.8	0.9	6.4	0.0
	7.85	8.7	1.9	6.6	0.0
	7.53	9.0	1.7	6.9	0.0
	7.6	8.3	1.8	6.5	00
MEAN	7.8	8.7	1.56	6.6	
L2	3.94	6.4	0.0	0.37	0.0
	3.68	6.5	0.0	0.5	0.0
	3.80	6.3	0.0	0.6	0.0
	3.62	6.8	0.0	0.55	0.0
MEAN	3.76	6.5	0.0	0.57	0.0
L3	5.4	31.2	0.0	0.14	0.0
	5.6	33.4	0.0	0.20	0.0
	5.5	32.0	0.0	0.13	0.0
	5.9	34.6	0.0	0.18	0.0
MEAN	5.6	32.8	0.0	0.16	0.0
	SEPT				

Table 3 Cont.

L1	7.2	8.6	1.9	6.1	0.0
	7.6	8.4	1.12	5.9	0.0
	7.4	8.5	1.4	6.3	0.0
	7.3	8.2	1.2	6.4	0.0
MEAN	7.4	8.4	1.4	6.3	0.0
L2	3.6	6.2	0.0	0.41	0.0
	3.8	6.1	0.0	0.43	0.0
	3.4	5.9	0.0	0.51	0.0
	3.5	5.8	0.0	0.49	0.0
MEAN	3.56	6.0	0.0	0.46	0.0
L3	5.2	30.8	0.0	0.12	0.0
	5.6	32.2	0.0	0.14	0.0
	4.9	31.0	0.0	0.10	0.0
MEAN	5.25	31.75	0.0	0.13	0.0
	OCT				
L1	7.1	8.2	1.6	6.0	0.0
	7.0	8.1	1.4	5.8	0.0
	6.8	8.0	1.12	6.0	0.0
	6.9	8.3	1.2	5.6	0.0
MEAN	6.95	8.15	1.33	5.85	0.0
L2	3.4	6.0	0.0	0.43	0.0
	3.21	5.8	0.0	0.38	0.0
	3.0	5.7	0.0	0.44	0.0
	3.2	5.6	0.0	0.42	0.0
MEAN	3.20	5.78	0.0	0.42	0.0
L3	5.0	29.0	0.0	0.10	0.0
	4.8	30.0	0.0	0.12	0.0
	4.9	31.0	0.0	0.09	0.0
	4.8	32.0	0.0	0.12	0.0
MEAN	4.88	30.5	0.0	0.12	0.0
Mean L1	7.8	8.79	1.73	6.65	0.0
Mean L2	3.73	6.50	0.0	0.5	0.0
Mean L3	5.7	33.04	0.0	0.16	0.0

DISCUSSION

Location 1 is the Gege area dumpsite, while location II is the UI dumpsite and location III the Ibode dumpsite. The concentration of twenty elements were considered with only five being absence since the remaining observed to be absent hence necessitating their fifteen was consistently absent being left out. Report on Sodium, Calcium, Magnesium, Silicon and Aluminium was reported. Generally the results showed a trend of being lower as the year progressed. This is due to the dilution effect of water as rainfall increased from may to October, with higher levels of water percolation within this season due to the enlargement of soil pore size.

Also consistently the order of magnitude was Ca >Na >Si, at all the three sample sites. Reasons adducible for this may be higher mobility of the Ca ion with respect to others elements[11].

For all the sites and across the months, the concentration of Ca ions was also more. The large amount of bores deposited at this site may not be unconnected with this trend, as majority of this dumpsites are frequented by owners of restaurants. Swill is deposited on these dumpsites.

Absence of heavy metals like lead and mercury can be explained by the fact that industrial activities around these areas are almost absent. Areas around this sites. The home or domestic waste preclude the presence any heavy metals.

Further apart from the effects of high precipitation during the raining season, the nature of the substratum can also play a very significant role in the levels of the elements in water. It is possible that ligands formation between the elements and soil hence considerably reducing the amount of such elements that would percolate as leachates into the underground water.

Also the depth of the water table is also an important factor. The deeper the well, the less the amount of pollutants found in it. This is because of the fact that some of the elements are held back as metallic/non-metalic ligands as the water percolates the substratum, especially with clay soil, which was found to be the dominant substratum type in the areas where the experiment took place. The water chemistry of most underground wells depend on a member of environmental factors operating simultaneously, some of which
are highlighted above. Generally higher concentrations would be observed in soil than in water.
Finally, the concentration of elements in water at the three locations depends on the characteristics of the waste disposed at the location, seasonality of water level due to amount of rainfall, the geological nature of the soil and the physiochemical conditions of the soil. The sustainable disposal of waste in an environment safe way must a matter of priority begin to look into safer methods of complexing elements so that they do not get into the environment. Recently the inclusion of incineration ash into cement is one of such advances. Also methods of the abatement of what finally gets to the waste dumps as done in the developed world where waste is sorted based on its composition should be encourage. Potentially dangerous inputs would be separated before they get to the dumpsites.

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NOISE AS AN INFLUENTIAL ENVIRONMENTAL PROBLEM. CASE STUDY: LEVELS OF DISTURBANCE BY ROAD TRAFFIC NOISE IN THE CITY OF NIGDE

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One of the important environmental problems is the road traffic noise in cities. Increase in the number of motor cars as living condition improves, make the problem more influential. Therefore, road traffic noise levels are measured to investigate how influential the noise levels are. Then precautions, if necessary, are to be imposed.

In this study, levels of disturbance by road traffic noise in Nigde were determined. The authors are involved in a project called "**Determination of Traffic Noise Conditions and Preparation of Noise Map for Nigde Town Center**", funded by the Nigde University. Therefore, road traffic noise measurements were performed at selected 61 stations on the main roads of Nigde, and to reveal the disturbance levels, 199 prepared questionnaires were applied to the people who live around the measured stations. Disturbance levels were evaluated at five grade appreciations. For each station, noise levels of L10 and outcome of questioners were compared to determine whether there is a correlation between them.
The results showed a significant negative correlation between appreciation levels and L10.

Key words: *Road Traffic Noise, Disturbance, Appreciation*

Introduction

One of the most important environmental problems is road traffic noise [1]. Various results of road traffic noise measurements and surveys showed negative impact on residential buildings, offices, schools, hospital and temples. Therefore, control of road traffic noise was necessitated. Standard levels and criteria need to be imposed. Various applications of these were studied by [2, 3, 4, 5, 6, 7]. Along with noise measurement, a survey to reveal the level of disturbance should be carried out. Gambart et al. [8] and Ali and Tamura [9] investigated this type research.

In Nigde, road traffic noise measurements were first performed by a project titled "Determination of Traffic Noise Conditions and Preparation of Noise Map for Nigde Town Center" in which the authors were involved. However, disturbance level in the area were not investigated.

The aim of this paper was to determine levels of disturbance by road traffic noise in the city of Nigde.

Material Method

Lmin, Lmax, and LAeq measurements were taken 8:30-9:30 hours as morning session, 13:00-14:30 hours as noon session, and 17:00-18:30 hours as evening session by RION NL-21 Sound Level Meter on 61 measurement stations determined on the main roads and roundabouts within the area of 5,5km^2.

199 prepared questionnaires were applied to the people who live around the measured stations. Disturbance levels were evaluated at 5 grade disturbance levels. These were 1) High, 2) Normal, 3) Low, 4) Very low, and 5) No disturbance. In addition to that, Noise sources were divided in to three categories, noise coming from neighbors, bump noise coming from neighbors, and environmental noise. Environmental noise sources were also divided into four sources, i.e. vehicle, mobile sellers, animals, and others.

For each station, noise levels of L10 and outcome of questionnaires were compared to determine whether there is a correlation between them. Evaluation of the survey outcome was performed by using SPSS 12.0 software and Pearson correlation method.

Results

Levels of road traffic noise in Nigde are presented in Table 1. Standard values for each measure are given in brackets in the head of the table. Bold typed levels show that they exceed or are equal to the standard value for that specific measure.

Table 1 Comparison of Noise Measurements with Standard Noise Levels[10]

Station Name	**LNP (62) [dBA]**	**L90 (63) [dBA]**	**TNI (74) [dBA]**	**L10 (70) [dBA]**	**L50 (65) [dBA]**	**Leq (55) [dBA]**
Egitim	**86,9**	60,0	**91,0**	**75,3**	**67,5**	**72,0**
Kardele	**83,5**	62,0	**82,8**	**74,7**	**68,0**	**72,4**
Total	**83,8**	**63,0**	**82,0**	**75,2**	**68,9**	**72,3**
Valilik	**83,1**	**63,0**	**81,2**	**75,0**	**68,4**	**71,8**
Migros	**85,1**	58,0	**90,5**	**73,6**	**65,1**	**71,1**
Pasaka	**82,8**	57,3	**87,9**	**72,4**	63,6	**70,4**
Rektörl	**84,3**	55,5	**92,0**	**72,1**	62,8	**69,8**
Sabancı	**82,6**	50,0	**94,2**	68,5	57,8	**66,0**
Spor	**80,2**	51,9	**87,8**	68,4	58,9	**66,5**
Termin	**85,1**	61,7	**86,6**	**75,4**	**72,1**	**72,5**
Amas	**82,5**	57,6	**85,7**	**72,1**	64,2√	**69,1**

It is clear from the table that most of the stations exceeded the standard levels. Therefore, to reveal the disturbance levels, 199 prepared questionnaires were applied to the people who live around the measured stations. Figure 1 presents the ages, education, and sensibility status of people in the survey.

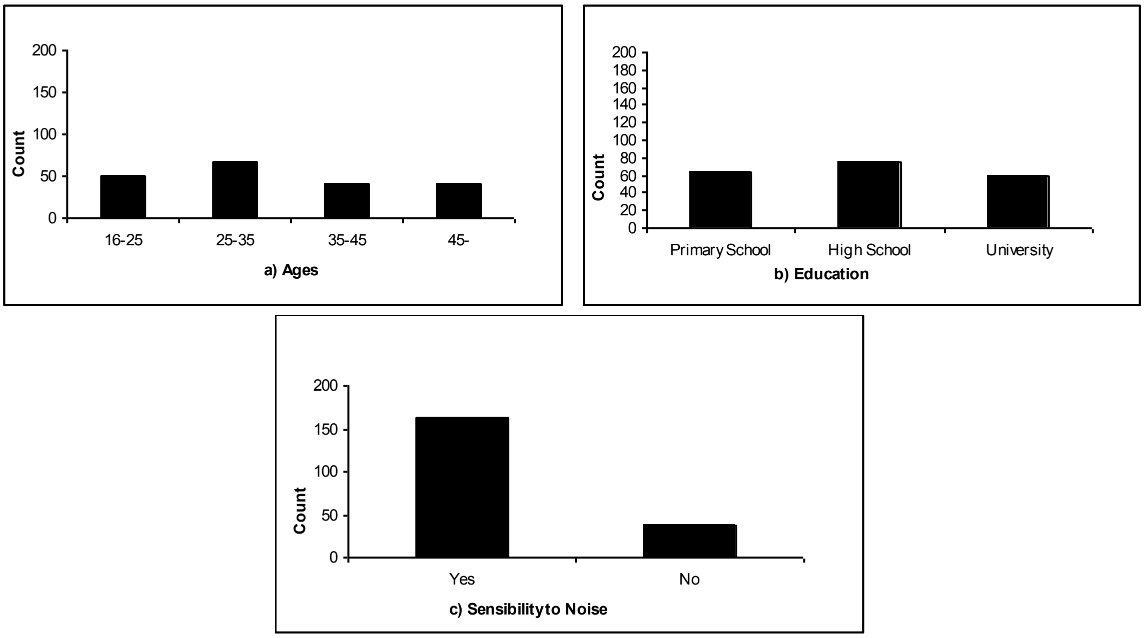

Figure 1 Ages, education, and sensibility to noise of the people in the survey

Results of five grade noise and bump noise coming from neighbors and environmental noise sources are represented in figure 2.

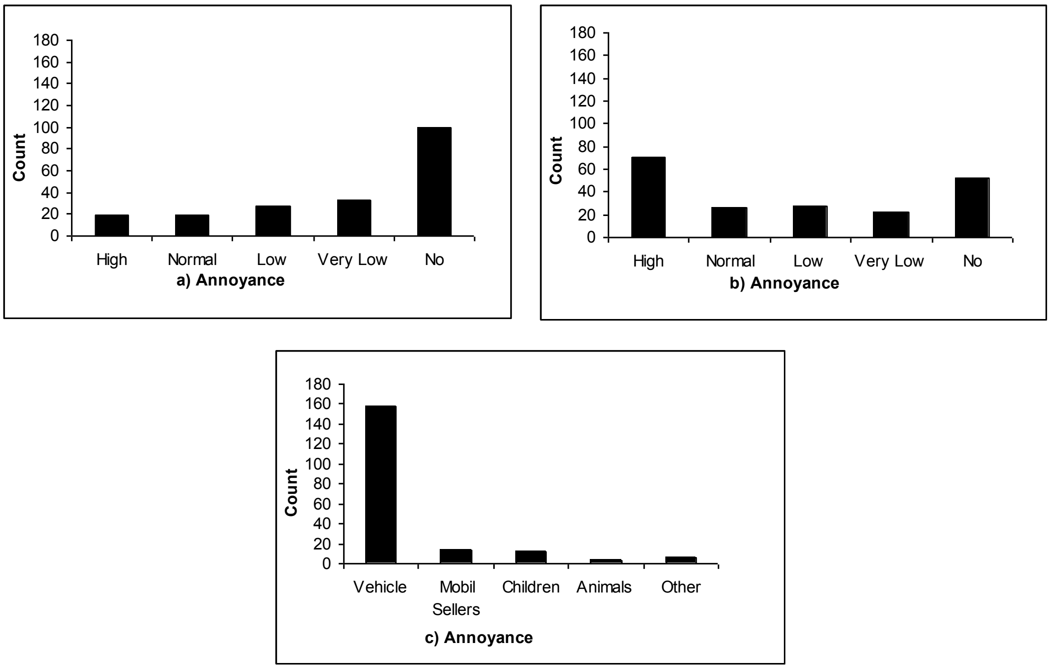

Figure 2 Noise coming from neighbors, bump noise, and effects of environmental noise

It can be seen from figure 2c that the most disturbing noise source is the noise coming from vehicles. This outcome is consistent with road traffic noise measurement (Table 1).

Pearson correlation between disturbance points from survey and noise level L10 is given in Table 2. It showed a negative (-0.173) correlation between them. This result is not consistent with measured noise levels. It is expected that there should be positive significant correlation between noise levels and disturbing level L10.

Tablo 2 Comparison of Appreciation Point to L10 Level

		L10	Appreciation Points
L10	Pearson Correlation	1	-,173(*)
	Sig. (2-tailed)	.	,016
	N	1016	193
Appreciation Points	Pearson Correlation	-,173(*)	1
	Sig. (2-tailed)	,016	.
	N	193	193

* Correlation is significant at the 0.05 level (2-tailed)

One explanation of negative correlation may be socioeconomic conditions. Participant people who live at the same location gave different response to the high noise. One participant found it very annoying, another no disturbance. In the area, some participants have high income some are low. Some participants live in a luxury home, some don't. Luxury homes have good insulations. Some participants preferred back rooms as living room and bedrooms, which located in the opposite side of the road. Interestingly, this result showed consistency with the study of Onnu,[11]

Conclusion

Levels of disturbance by road traffic noise in Nigde were determined at selected 61 stations on the main roads of Nigde and to reveal the disturbance levels, 199 prepared questionnaires were applied to the people who live around the measured stations.

Road traffic noise in Nigde was found high compared to standard levels.

Outcome of the survey showed a negative correlation between 5- grade appreciation levels and noise level L10.

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RECOVERY OF ZINC FROM QUARTZ BY RHAMNOLIPID BIOSURFACTANT

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In this study, a microbial surfactant, rhamnolipid, was investigated for its potential to enhance recovery of Zn(II) from quartz as a soil component. To determine the effect of pH on the desorption efficiency of Zn(II), pH was varied between 5.0 and 7.6 and maximum Zn(II) recovery efficiency was obtained at pH 6.8. As the concentration of rhamnolipid was increased from 12.5 to 100 mM, optimum desorption efficiency of zinc from quartz was obtained at 25 mM rhamnolipid concentration and determined as 90.9% of the sorbed Zn(II) at 1 mM initial Zn(II) ion concentration in solution (0.66 mmol Zn (II)/kg quartz). As the concentration of Zn(II) loaded to quartz was increased from 0.3 to 1.5 mmol Zn (II)/kg quartz, maximum Zn(II) desorption efficiency was 97.14 % of the sorbed Zn(II) at 0.89 mmol Zn (II)/kg quartz, at 25 mM rhamnolipid concentration and at pH 6.8.

1. Introduction

Contamination of soil by heavy metals is a widespread problem due to the former activities of metal processing, surface treatment and mining industry and the uncontrolled dumping of waste in landfills. Several methods exist to treat soil. [1] Traditional remediation technologies for heavy metal contaminated soils are isolation, immobilisation, toxicitiy reduction, physical seperation and extraction. [2] Bioremediation has potential for the remediation of heavy metal contaminated sites. Although the use of bacteria or bacterial exopolymers for complexation of metals from waste streams has been extensively studied and reviewed, the application of smaller biomolecules for metal complexation is of special interest for application to in to soil washing and pump-and-treat remediation technologies. [3] Metal-cell and metal-exopolymer complexes would be filtered out by the soil during washing or flushing. [4] The size of a bacterial cell (0.2 mm in diameter) is higher than that of soil pores (less than 2 μm). Biosurfactants may offer an advantage over microorganisms and bacterial exopolymers because of their relatively small size. [5] Rhamnolipid aggregates are predominatly small vesicles, < 50 nm in diameter and micelles (5 nm diameter) at pH> 6. [3] Biosurfactants are microbially produced surface-active compounds. Surfactants are amphiphilic molecules, consisting of hydrophobic domains. In aqueous solution, surfactants reduce surface tension by accumulating at interfaces and facilitating the formation of emulsions between liquids of different polarities can enhance the mobility of heavy metals. [6-9] Biosurfactants can be classified into several broad groups: glycolipids, lipopeptides, lipopolysaccharides, phospholipids, and fatty acids/neutral lipids.

The biosurfactant used in this study, a rhamnolipid, was from the glycolipid group and was produced by *Pseudomonas aeruginosa.* [10] Biosurfactants possess some advantages, such as low critical micelle concentration and high biodegradability, over synthetic surfactants and, therefore, are particulary well suited for environmental applications such as bioremediation and the dispersion of oil spills. [11] The type of soil, presence of various components such as clays, feldispats, iron oxides in soil play an important role in the removal of heavy metal ions from soil by rhamnolipid biosurfactant. [10] In this study the recovery (desorption) of Zn(II) ions from quartz, a component of soil, by rhamnolipid biosurfactant was studied. The objective of this study was to investigate the effects of rhamnolipid concentration, pH, and loaded Zn(II) quantity per unit weight of quartz on the recovery of Zn(II) ions from quartz by rhamnolipid biosurfactant.

2. Materials and Methods

The biosurfactant, JBR 425 was obtained from Jeneil Biosurfactant Co. (USA). Two major types of rhamnolipids, RLL(R1) and RRLL(R2), are mixed in the solution. R1 ($C_{26}H_{48}O_9$) is L-rhamnosyl-β-hydroxydecanoyl- β-hydroxydecanoate. R2 ($C_{32}H_{58}O_{13}$) is L-rhamnosyl-β-L-rhamnosyl-β-hydroxydecanoyl-β-hydroxydecanoate.

2.1. Zn(II) sorption by quartz

To investigate Zn(II) complexation by rhamnolipids from quartz, firstly quartz sorbed Zn(II) ions. 1.5 g of quartz was placed into 40-mL centrifuge tubes. The range of concentrations of prepared metal solutions varied from 0.47 to 4.2 mM. The tubes containing Zn(II) ions and quartz as an adsorbent were agitated on a shaker at 25^oC and 150 rpm for 72 h. After reaching ultimate equilibrium, the tubes were centrifuged, and the supernatant was diluted into 1% HNO_3 for atomic absorption analysis. Sorbed metal ion concentration was calculated from the difference between initial metal ion concentration and metal ion concentration remained in the supernatant after sorption.

2.2. Recovery of Zn(II) ions by rhamnolipid biosurfactant from quartz

The metal-loaded quartz was suspended in 5 mL solution containing 12.5, 25, 50, 80 and 100 mM rhamnolipid. The centrifuge tubes containing quartz mixed with rhamnolipid solution were agitated on a shaker at 25^oC and 150 rpm for 72 h and then centrifuged at 19000x g for 20 min. The supernatant was analyzed for Zn(II) ion concentration by atomic absorption analysis. The pH of supernatant samples used for atomic absorption analysis was then adjusted using 0.1 mL of concentrated HNO_3 to < 2 to precipitate the rhamnolipid. To remove the rhamnolipid pellets, each sample was centrifuged and then the supernatant was diluted in 1% HNO_3 for atomic absorption analysis. To guarantee that all Zn(II) ions were desorbed from the rhamnolipid pellets, the pellets were treated a second time with 1% HNO_3 and the supernatant was analyzed ones again.

3. Results and Discussion

3.1. Zn(II) sorption by quartz

As the concentration of Zn(II) ion in solution was increased from 0.47 to 4.2 mM, sorption efficiencies of Zn(II) ions to quartz decreased from 24.19 to 10.72%. Zn(II) sorption efficiencies of quartz are shown in Table 1.

Table 1. Zn(II) sorption efficiencies of the quartz

C_i (mmol/L)	Sorption efficiency (%)
0.47	24.19
0.87	22.98
1.55	17.15
1.89	18.55
2.27	17.78
2.67	16.57
3.44	13.11
4.2	10.72

3.2. Effect of pH on recovery of Zn(II) ions by rhamnolipid biosurfactant from quartz

To determine the effect of pH on the desorption efficiencies of Zn(II) ions, pH was varied between 5.0 and 7.6. This range was chosen for several reasons. Rhamnolipid aggregate morphology undergoes significant changes in the pH region of 6.0-7.5. Rhamnolipid has a pK_a of 5.6 and thus precipitates on acidification. To minimize the size of the metal-ligand complex, the solution pH must be optimized, thus avoiding filtration by small soil pores. The size of rhamnolipid aggregates is pH dependent and the structues are predominately small vesicles and micelles at pH>6.0. Under conditions of reduced interfacial tension, biosurfactants will accumulate at the solid-solution interface. This may allow direct contact between the biosurfactant and the sorbed metal. The surface tension of rhamnolipid solutions is also quite sensitive to pH. The surface activity of the rhamnolipid was reported to be highest between pH 7.0 and 7.5. [12] As the pH is increased above 7.5, there is a slight decrease in surface activity that resulted in an increase in surface tension.

As shown in Fig. 1, the best recovery efficiency, 88% of the sorbed Zn(II), was achieved by adjusting the initial pH value to 6.8 at 1.0 mM initial Zn(II) ion concentration in solution (0.63mmol Zn(II) / kg quartz) and at 25 mM rhamnolipid concentration.

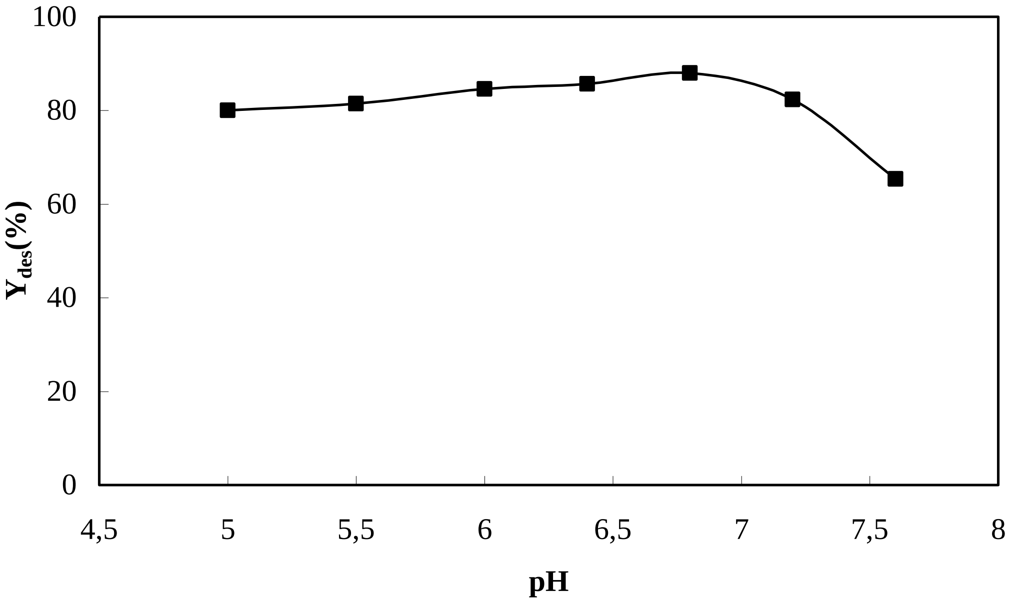

Fig. 1. Effect of pH on recovery of Zn(II) ions by rhamnolipid biosurfactant from quartz

3.3. Effect of rhamnolipid concentration on the recovery of Zn(II) ions by rhamnolipid biosurfactant from quartz

When the initial Zn(II) ion concentration in solution was held constant at 1.0 mM, the rhamnolipid concentration was varied from 12.5 to 100 mM at pH 6.8 and, at 25^{o}C. As shown in Fig. 2, the desorption of Zn(II) ions by rhamnolipid biosurfactant from soil increased with increasing rhamnolipid concentration up to 25 mM, and the highest removal efficiency of Zn(II) ions from soil was found to be about 90.9% (0.66 mmol/kg) at 25 mM rhamnolipid concentration. Introduction of excess rhamnolipids into soils containing quartz is not required because of process economy, prevention of plugging in soil pores by the dispersion of fine materials, or by the formation of viscous emulsions. Use of excess biosurfactant in spite of the high degree of biodegradability of rhamnolipids may also be lead to another environmental pollution.

3.4. Effect of Zn(II) amount loaded to quartz on recovery of Zn(II) ions by rhamnolipid biosurfactant

As the amount of Zn(II) loaded to quartz was increased from 0.3 to 1.5 mmol Zn (II)/kg quartz, maximum Zn(II) desorption efficiency was 97.14 % of the sorbed Zn(II) at 0.89 mmol Zn (II)/kg quartz, at 25 mM rhamnolipid concentration and at pH 6.8.

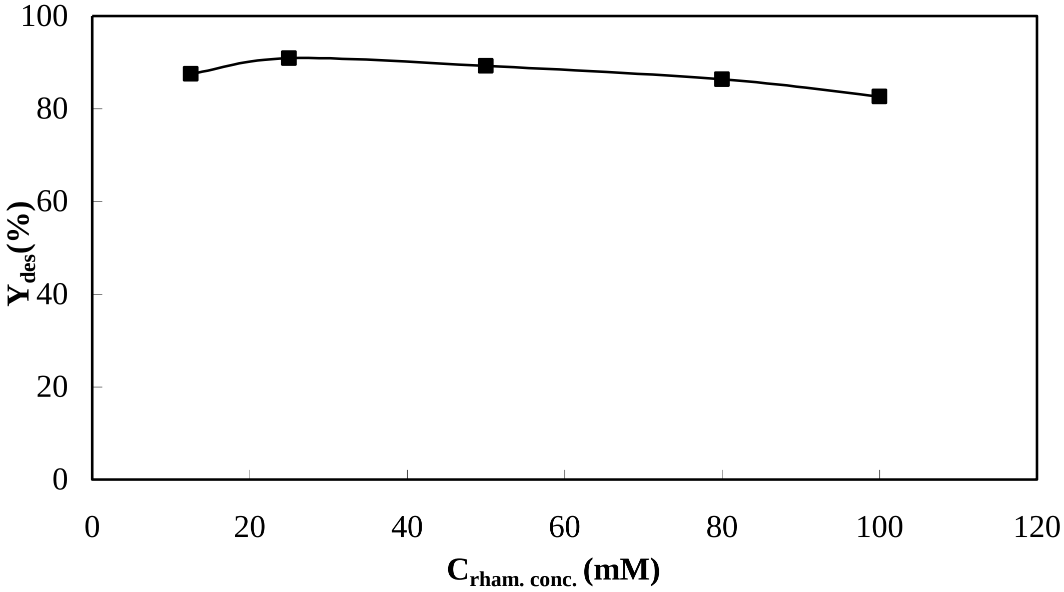

Fig. 2. Effect of rhamnolipid concentration on the recovery of Zn(II) ions by rhamnolipid biosurfactant from quartz

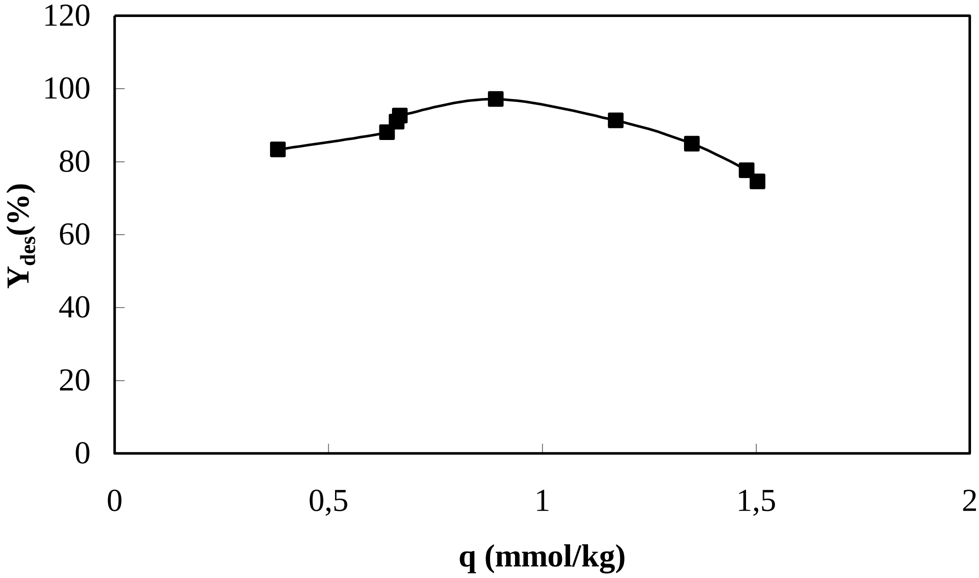

Fig. 3. Effect of Zn(II) amount loaded to the quartz on recovery of Zn(II) ions by rhamnolipid biosurfactant from quartz

The research in the area for removal of contaminants using biosurfactants from soils is still quite limited, particularly where metal removal is concerned. Soil pH, soil type, soil constituting components, cation exchange capacity, permeabilities, and contaminants all affect removal efficiencies. High clay, organic matter contents, low permeability clays, heterogeneity of soils were reported to be detrimental for the application of the bioremediation of soils using biosurfactants. [13] High quartz content of soil seems to provide a good advantage. Data from this study proved that Zn(II) ions from quartz can be desorbed successfuly in significant amounts by rhamnolipid biosurfactant. Zn(II) recovery efficiencies of 82.6 -97.1 % of sorbed Zn(II) were achieved by the rhamnolipid solutions at the concentrations varying from 12.5 to 100 mM.

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DRAINAGE GEOCHEMISTRY AND ENVIRONMENTAL IMPACT OF THE WHITTLE COALFIELD AREA, NORTHERN UK

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This study investigates drainage geochemistry and environmental impact at Fe-Mn passive treatment system in the Whittle coalfield area. In this respect, major and trace element contents (Ca, Mg, Na, K, Fe, Mn, Al, Zn, Si, As, Cd, Co, Cr, Ni, Pb, F, Cl, SO_4, Br, PO_4 and NO_3) in the surface waters, in different fractions (<75; <106; <150; <180 µm) of the riverbed sediments and plants (algae and moss) were analysed. The imaging capabilities of the scanning electron microscope (SEM) coupled with the elemental analysis provided by the energy dispersive spectroscopy (EDS) were used to acquire both chemical and physical information in the different media (<180; <106 µm size fractions sediments and algae). X-ray diffractometry (XRD) analysis were conducted to determine mineral compositions of the sediment samples.

It was observed that the passive treatment system is the most effective to decreasing of the Fe and Mn concentrations in the groundwater in the Whittle coalfield area. However the Fe and Mn concentrations show significant contamination from seepage waters in different locations of surface waters such as Fe (2 mgL^{-1}), Fe (10 mgL^{-1}) and Mn (3.7 mgL^{-1}) at HB 8, HB 9 and HB 11 sampling sites, respectively.

Cd, Co, Fe, Mn, Cu, Ni, Cr concentrations are lower than those of other elements in HB 13 where algae exist in a large quantity and As, Pb and Si are also depleted in different algae species along the downstream. Besides, Cl and SO_4 are above background levels in the all sample locations. Quartz, clay minerals (kaolinite and chlorite) and feldspar group minerals (plagioclase, alkaline feldspar) dominate the mineral suite in the sediment samples.Results of this study; plants, adsorption processes and mixing between tributaries and seepage waters are thought to easily alter of the mineralogical composition of the river waters and riverbed sediments in the passive treatment system areas.

Key words: Heavy metal, ICP, EDS, SEM, XRD, Whittle coalfield.

Introduction

The Whittle coalfields are located in the Landranger Series, at coordinates of 604800N-418300E on the map 81 in the north of United Kingdam (Figure 1) where there are two rivers, one of them the Hazon Burn and the other River Conquet. The Hazon Burn is a tributary of the River Conquet, itself one of the 27 river SSSIs (Sites of Special Scientific Interest) in Britain.

The Whittle coalfields were operated since the turn of the century and they were abandoned in March 1997. The Main contaminants of iron and manganese resulted in a potential pollution of the Hazon Burn and River Conquet from an uncontrolled outbreak of mine water. That is why passive treatment system was constructed in 2002. But water pollution problems could not be solved in the Whittle coalfield area.

Previous studies have focus on facies and microfacies relationships and coal-forming models (Johnson, 1992; Thomas, 2002). These investigators have demonstrated that the Whittle coals were deposited in marine carbonate platform setting.

According to Adams & Younger (2001) and Younger (2004), a typology of known impacts arising from mine voids and wastes in coal mining district was developed which recognises many subcategories of impacts under five major headings: air pollution, fire hazards, ground deformation, water pollution and water source depletion. These investigators say that, a robust understanding of geochemical processes is a key to understanding how these impacts arise, and to developing sustainable mitigation strategies.

Several investigations have carried out about river pollution up to now (Klein *et al*. 1957; Klein *et al*. 1962; Klein, 1966; Laenen & Dunette 1997 etc.).

Geochemical studies of toxic trace elements in coal mining areas have intensified in recent years. Coal mining operations, agricultural operations and industrial processes, are a major source of potentially hazardous air pollutants, water pollution, soil pollution and plant pollution which include As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se and radionucleides, such as Th and U (Finkelman, 1994; Helble, 1994; Qiu *et al*., 1999; Liu, *et al*, 2004; Yang, *et al*, 2004; Lee, *et al*, 2006). Systematic studies of the potentially hazardous elements in a coal mine have therefore been conducted to determine the possible environmental impacts of coal utilization (e.g. Swaine, 2000; Finkelman & Gross, 1999).

This study is concentrated on element contents of surface waters, sediments, algae and mosses samples, petrological features of the river sediments and drainage geochemistry of the Whittle coalfield and to determine the mode of metal occurrence in the sediments, waters and provide a geochemical pattern for predicting the ability to release metallic pollutants to the aquatic environments.

Geological Setting of the Whittle Coalfield area

The Whittle Colliery is located at the northern end of the site and the land beyond the colliery cartilage rises sharply to the east towards the disused Whittle Quarry and High Whittle. To the west the colliery is bounded by the woodland fringed Hazon Burn, which flows in a southerly direction in a channel which laying several metres below the level of the main colliery area. The Whittle Coal seam takes part of the Upper Limestone Group in the Lower Carboniferous Sequence. The Great Limestone is presented by Hazon Burn log in this area (Entec, 1998; 2001).

The Whittle Coal mine area is included to the lower delta plain deposits which change to mudstone, inter-bedded sandstones and mud stone and limestones to the top (Johnson, 1992). The lower delta plain is characterised by coal mudstones with irregularly distributed limestones and siderite (Thomas, 2002). The local stratigraphic section shows that the Whittle seam is conformable with the overlying the Shilbottle Seam (Figure 2).

Sampling and analytical methods

Water, sediment, moss and algae samples in the study area were collected from surface waters, recharge waters and riverbeds. Water sampling was performed from river water of the Hazon Burn (HB), River Conquet (RC), lagoon water (S4-S5), recharge water (S6-S7) and little stream water (S2-S3): Sediment samples were collected in the riverbed of the Hazon Burn (upstream HB 1, HB 2, HB 3, HB 4, HB 5; downstream HB 6, HB 7, HB 8, HB 9, HB 10), River Conquet (upstream RC 1 and downstream RC 2), little stream (S 2, S 3); lagoon (S 4, S 5) and recharge bed (S 6); moss samples were taken from the little river bed (SM 2, SM 3), Hazon Burn river bed (HB 9) and reed ın the recharge bed (SM 6): Algae samples were taken from the Hazon Burn river bed (HBA 5- HBA 6- HBA 7- HBA 10) and particularly in some samples collected at the junction of the rivers. Sediment sampling was performed along the Hazon Burn, from the Whittle Colliery to the River Conquet, along a transect totally of 5.8 km of length. The purpose is to study change of the elements contents and mineral compositions in the different media (water, sediment, algae and moss) between the Whittle Colliery and the River Conquet. All sample locations were marked on the location map (Figure 1). Physicochemical features such as pH, Eh, conductivity and temperature were measured at the sample locations using 6P Mayron Model Ultrameter which was calibrated daily. The water samples were analysed for the cations (Ca, Mg, Fe, Mn, Al, Si, As, Cd, Co, Cr, Cu, Ni, Pb) which were taken into two pre-acidified 125-ml polyethylene bottles. 1 mol HNO_3 (Merc^{TM} ultra pure) was added into the samples for the metal analyses. One of these samples was filtered at 0.45 µm in the field using sealed disposable filters and syringes; the other sample was unfiltered. Unfiltered samples were also taken in an unacidified 125-ml polythene bottle for the anions (sulphate, chloride, nitrate, bromide, phosphate and fluoride). While the samples were being injected into the ion-chromatograph, all of them were filtered via a 0.2µm filter. Alkalinity was measured by adding 100 mL of sample to 125 mL flask, and adding 2-3 drops of methyl orange indicator solution then titrated with standard acid until colour changes from yellow-orange-purple, and calculated from follow equation.

Alk= mL acid/sample volume =1 mg alk as $CaCO_3$ /mL

All samples were kept in clean polythene bags and transferred quickly to the laboratory for granulometric and chemical analyses.

Sediment samples were air-dried and sieved at different size fraction (<75, <106, <150, <180 µm), which collected from each of sample sites (from HB 1 to HB 10; RC 1, RC 2; S2 S3 and lagoon precipitates S4-S5) than aqua regia digestion procedure consist of digesting sediment samples on a hotplate with 3:1 mixture of HCL and HNO_3 (Niewenhuize *et al*., 1991), conventional aqua regia digestion was performed in 250 mL glass beakers covered with watch glasses. A well-mixed sample of 0.5000 g was digested in a 12 mL of aqua regia on a hoteplate for 3 h at 110 ^{0}C. After evaporation to near dryness, the sample was diluted with 20 mL of 2% (v/v with H_2O) nitric acid and transferred into a 100 mL volumetric flask after filtering through Whatman no. 42 paper and diluted to 100 mL with DDW. All of them were analysed by ICP-OES using the SEPA standards.

Moss and algae samples were washed by distilled deionised water (DDW) in the laboratory and dried naturally air 24 h. The one gram analyte was mixed with 10 mL of a 1:1 solution of sulphuric acid and DDW in a covered 100 mL beaker. This solution was heated on a hot plate in a fume hood for 10 minutes and then cooled. An aliquot (5 mL) of concentrated nitric acid was added and the solution was covered and heated for 30 minutes. If brown fumes were emitted indicating oxidation of the sample by nitric acid, the step was repeated until the fumes ceased. The same amount of nitric acid was added to the each sample for quality assurance of the samples. Once this is reached, the solution is heated for two hours. After cooled, 2 mL of DDW and 3 mL of 30 % hydrogen peroxide were added. Hydrogen peroxide (1 mL aliquots) was added to the sample until effervescence subsided (no more than 10 mL of hydrogen peroxide was added to each sample). The sample was heated for another 2 hours, cooled, and concentrated hydrogen acid (10 mL) was added. The solution was quantitatively transferred to a 100 mL volumetric flask using DDW. The volumetric was then filled with DDW and the solution analyzed with the ICP-OES (Soster, 1990).

All of the media (water, sediment and algae samples) were analysed at the Environmental Institute Laboratories in the Newcastle University. Sediment and algae samples, mineral compositions and species were analysed at ACMA, Newcastle University.

Ion Chromatography (IC) Analysis

Major anions were measured in filtered samples by automated ion chromatography (NO_3, PO_4, F, Cl and SO_4, as well as other anions). For the calibration 5; 10; 20; 20; 20; 30 mg $L^{-}1$; standards were used for F, Cl, Br, NO_2, SO_4 and PO_4. Interval time was between 1.88 and 3.331 (Fig. 4). S 2 and S 3 (the little stream) samples were diluted 2 twice. The Lagoon and recharge water samples (S 4, S 5, S 6 and S 7) were diluted 50 times with respect to Cl and SO_4. HB 1, HB 8, HB 9, HB 10, HB 11, HB 12, HB 13 samples were diluted 10 times.

2.2 ICP-OES (Inductively Coupled Plasma and Optic Emission Spectrophotometry) Analysis

The ICP analyses conducted for this study presented here were calibrated with
Standard 1: 0.1 mg L^{-1} Zn, Cd, Co, Cr, Cu, Ni; 0.2 mgL^{-1} Fe, Pb; 0.5 mgL^{-1} Mn, As, Al; % 1 v/v $HNO_{3,}$ *Standard 2:* Al 5, Ca 20, Fe 10, K 50, Mg 10, Mn 5, Na 10, Zn 5, Si 10 mgL^{-1}. Blank (HNO_3% 1v/v) was used before analyses.

Sediment samples were sieved at four different fractions (<75, <106, <150, <180 μm). Then all different size fractions were analysed by ICP-OES. Alternatively some studies have used different digestive methods, specially, As and Cd have concluded by microwave aqua regia + HF digestion greater accuracy (94%) (Chen and Ma, 1998). Although sediment analysis resulted in less accuracy for the digestion (74%), using the hotplate aqua regia. Microwave digestions could not performed because of absence of a microwave oven in the laboratory.

SEM and EDS (Scanning Electron Microscopy and Energy Dispersive Spectroscopy) Analysis

In order to identify algae species, suitable samples were selected (HBA-8) for scanning electron microscopy (SEM)analysis. Due to their high trace element contents, sediment samples with different size fractions (<106 μm) (downstream HB 10, upstream HB-1) were selected for the SEM analyses and equipped with energy dispersive spectroscopy (EDS). For SEM analysis, samples were attached to carbon stubs, coated with carbon film in a sputter-coater and observed by SEM and EDS with the help of Centaurus Detector –Rontec UHV Dewar Detector.

XRD (X-Ray Diffractometer) Analysis

Sediment samples were analysed for only two different size fractions (-106, -180 μm) with XRD (HB 1, HB 6; S3, S2, Lagoon (S 5) and recharge sediment (SR 6) samples). Mineral compositions were identified by PANalytical X'Pert Pro diffractometer, fitted with an X'Celerator**.** The X'Celerator is a relatively new attachment to the X'Pert and it provides a good quality pattern in a fraction. A secondary monochromator would eliminate fluorescent scattering from the specimen, resulting in a good peak: background ratio for samples containing transition metals and rare earths etc. However, for the presence work the monochromator was unavailable, therefore, the background scatter is significant in some scans. Two theta values were interpreted according to Bayliss *et. al* (1986).

Results and discussion

Distribution of the major, trace elements and anions in the surface waters

Ca, Mg, Na, K, Fe, Mn, Al, Zn, Si, As, Cd, Co, Cr, Ni, Pb were analysed in surface waters in the Passive treatment system area, particularly from Hazon Burn to River Conquet.

Analysis results show that the element concentrations change from upstream to downstream. The sample HB 1 collected from the upstream have high Zn values, but Mg, Ca, Na, K and Si have the highest concentrations in HB 5-HB 6 locations (Table 1). In the HB 9 location, concentration of Fe (10 mgL^{-1}) is higher than other locations, actually Mn (2 mgL^{-1}) has high value only in sample HB 6. Fe has the second high value in sample HB 10 (3.7 mgL^{-1}), which has been probably affected from the seepage waters on the right side of the Hazon Burn. Pb concentrations are high in samples HB 5 (0.3 mgL^{-1}) and HB 6 (0.33 mgL^{-1}), but it decreases towards the sample HB 7. This may be due to adsorbing of Pb by organic matter in sample HB 7. Cu, Ni, Cr have also low values in HB 7. Cd and Co values are compatible with Fe and Mn concentrations which are depleted by the organic matter in sample HB 7 like other trace elements. As, Pb, Si concentrations increase downstream along the Hazon Burn (Figure 3). Zn values also show increase trends in samples HB 1 (0.65 mgL^{-1}) and RC 1 (0.65 mgL^{-1}) (Table 1 & Figure 3). This indicates that alkalinity must have affected Zn composition from the passive treatment system area to River Conquet.

Table 1 shows that Ca, Mg, Na, K, Fe, Al, Si, Cl, SO_4 and NO_3 median values in the Hazon Burn river water are about 23; 23; 22.5; 21; 3.4; 2.3; 1.88; 43; 45.54 and 15 times higher than those of average of world river waters. Cd has the least ionic potential value (1.5), and therefore, it has been adsorbed by carbonate/organic matter and may be clay minerals. Although Ni, Cr, Co and Zn have the same ionic potential value (2.4) as Co, their concentrations in water are higher than that of Co. This indicates that even if alkalinity is high, Zn may be making up dissolved cations in river waters. Distribution of Al and Zn is similar to each other. However Al makes up hydroxides in waters because of its higher ionic potential value (4.92) in comparison to that of Zn. Cr, Ni and Cu, which are found in low concentrations in samples HB 9 – HB 7 (Figure 3). Algaes have made up of large quantity due to lower topographic slide and slower water flows. These elements have been probably adsorbed by algae and other organic matters in the sample locations.

If we Eh and pH values are measured in waters, it is possible to calculate oxygen pressure and dissolved oxygen fugacity. Naturally, Eh values must be high in surface waters but Eh value is observed to be decreasing interval 0.08 to 0.1 Volt, and dissolved oxygen activity values are also very low ([O_2 (di)]: 10^{-44} - 10^{-45} mol/L) in Hazon Burn river water. This case may be explained by maximum suspension matter in the Hazon Burn. The stability of the suspension depends on the thickness of the diffuse layer of ions, a thickness determined by the electric potential, and on the ionic strength of the solution. Probably, Eh values must have been affected from enrichment of organic material and dissolved ions within the Hazon Burn.
In Table 2, molar concentrations, activity coefficients and activities of the most abundant elements are listed. The other dissolved ions in the Hazon Burn river water are associated with decreasing SO_4 concentrations by 16%, Ca 16.25% and As 33.3% as the ionic strength and ionic charge increase with decreasing the activity coefficient. Ionic strength of average of the world river and lake waters is 0.001 (Akcay, 2002). The Hazon Burn river water has an ionic strength of 0.038, which is 38 times more than the average of world river waters. As the ionic strength increases in the river waters, Eh values, oxygen pressure (1) and dissolved oxygen (2) are also expected to decrease. Table 2 shows that ion concentrations in the Hazon Burn river waters have a low effect on Na, K and SO_4 activities.

The Na/K ratio in the surface waters increases by the weathering of plagioclases and alkali feldspars (e.g albite, anorthite, and orthoclase). Ionic strength has a great effect on the activity of NO_3 23 % (Nitrate) which is the principal form of nitrogen in water as the completely oxidized state. In surface waters, the nitrates are quickly transformed to the organic nitrogen by the photosynthesis of aquatic plants, both phytoplankton and rooted plants.

Alkalinity is the capacity of water to neutralize acids (Krouskopf, 1979; Krouskopf & Bird, 1995). Alkalinity is expressed in milligrams per liter of equivalent calcium carbonate. In this study, alkalinity was measured on three different locations (HB 10, $CaCO_3$ 186 mgL^{-1}; HB 6, $CaCO_3$ 136 $mgL^{-1}$and RC 1, $CaCO_3$78 mgL^{-1}). Krouskopf (1979) presented world average HCO_3^- concentrations in several rivers as 58.4mgL^{-1}. In the study area HCO_3^- values are about 3; 2.33 and 1.35 times higher than the world average values such as the carbonate, bicarbonate, hydroxide and occasionally borate, silicate, phosphate and other ionic constituents . Alkalinity does not behave as pH since water is not necessarily to be strongly basic (high pH) to have a high alkalinity. For example, alkalinity has the highest value (186 mgL^{-1}) in sample HB 10 (pH 7.49). As temperature increases, conductivity also increases. The conductivity (dissolved matter concentrations) has a great effect on Eh and pH.

Besides, high conductivity values were observed in the study area (from HB1 to HB 10; 764,4 - 486 μS/cm; RC 1- RC 2; 231,5 - 394,5 μS/cm). Between conductivity and temperature is shown positive correlation relationships (r=+0.67). As temperature increases conductivity increases. Besides, there is negative and poor positive correlation coefficient between conductivity and Eh; pH (r=-0.23; 0.34). This indicates that, the conductivity (dissolved matter concentrations) has been affected on Eh, pH. This indicates that amount of dissolved matter is considerably high in the Hazon Burn in the Whittle coalfield district.

SO_4 and Cl values are showed in Table 1 that both of them are the highest value according to average of world river waters. Fe is usually associated with pyrite in high sulphur coals, and a positive correlation between Fe and sulphur is commonly observed in most coal measures (Liu *et al*., 2001). According to Younger (1998), in coal seams, a pyritic sulphur content of 0.25 wt % is a low value. This is clearly a high S environment, reflecting the strong influence of marine water during diagenesis of the coal (Younger 2004).

Both goethite and ferrihydrite may absorb SO_4, especially at low pH where their surface is not positively charged, but the total quantity of SO_4 is associated with the solid phase (Bingham, 1990). SO_4 is stable ion in oxidation zones (Krauskopf, 1989). Although SO_4^{2-} is the most stable phase, the others are meta-stable forms that may persist for long periods of time (Cook & Kelley 2006).

Aside from normal coals with average Cl contents, there are ‘’saline’’ coals, strongly enriched in Cl, up to 1 % wt and more. Such coals were mainly formed in epigenesis-when coal beds were influenced by basinal chloride brines, containing also some ore elements such as As, Pb, Zn etc. (Yudovich & Ketris, 2006). It is partly trapped on geochemical barriers because most Cl-salts are highly soluble, and widespread clay and humic colloids are negatively charged and do not capture the Cl^- ion.

Distribution of the major and minor elements in the river sediments

The sediment samples collected from the riverbed of the Hazon Burn and River Conquet, consisting of silt-size (<75 µm, <106 µm, <150 µm, <180 µm) particles are markedly composed of estuarine sediments, particularly those collected at the junction of the rivers.

Table 3 shows that heavy metal concentrations appear to be related to the increase in fine size fraction (<75 µm). Fe, Mg, Na, K, Fe and Al are the major chemical components of the sediments, which is in good agreement with their mineral composition. In the different size fractions (<75 µm, <106 µm, <150 µm and <180 µm), the sediments are strongly enriched in Zn (up to 126.03 mg/kg in <75 µm), Pb (48.926 mg/kg in <75 µm), Cu (20.384 mg/kg in <75 µm), Ni (27.154 mg/kg in <75 µm), Cr (18.404 mg/kg in <75 µm), Co (16.262 mg/kg in <75 µm), Cd (1.11 mg/kg in <75 µm) and As (6.573 mg/kg in <106 µm). Co is higher than NIST value SRM-2704, and As and Cd values are higher than average of continental crust compositions. There is a significant grain size effect on the Si content. As quartz is especially concentrated in coarse-grained sediments, Si content is the highest value in the RC 2 (<106 µm). Si enrichment may be derived from silica shells of diatoms . Zn has the highest concentrations in fine size fractions in the clay minerals, but is concentrated in sediments coarse of size fractions next to the seepage water (HB 10, <180 µm). High Cu, Zn and Pb concentrations are generally found in the ancient sedimentary rocks and also in coarse grained sediments (HB 10;<180 µm).

Comparison of the water and sediment samples in the Hazon Burn shows that, excluding Zn, Si and Pb, the other trace elements are harmonious (Figure 4).

Mineralogical features of the stream sediments

In this section distribution of mineral compositions along the Hazon Burn will be discussed. Quartz, clay minerals (kaolinite and chlorite) and feldspar group minerals (plagioclase, alkali feldspar) dominate the mineral suites with average total contents in the Hazon Burn and the River Conquet area. Microscopic observation and XRD results (HB 1; HB 6; S2; S3) have revealed that the mineral compositions of the different size sediments comprise of quartz (45-60 %), kaolinite (10-18 %), muscovite (6-12 %), plagioclase (5-12 %), chlorite (10-5 %) and other minerals (5 %) (Figure 5). Lagoon sediment (S5) have formed anhedral goethite. As quartz decreases in the coarse grain fractions, the abundance of fine fractions increases. In terms of mineral paragenesis, kaolinite is formed during the weathering of felsic rocks, usually replacing K-rich micas and feldspars, kaolinite should be favored by acid solutions and good drainage (equal; 3, 4, 5). The chlorite group minerals have structures in which mica-like sheets are formed during the weathering of mafic rocks at low temperatures. Chlorite is a common authigenic mineral lining the pores of sandstones. In some cases, the presence of authigenic minerals on sand grains can inhibit the growth of pore-filling cements during diagenesis and preserve pore space for occupation by hydrocarbons. An investigation was made regarding the sorption of Ni^{2+} to chlorite due to radionuclide migration sorption of Ni^{2+} by Gustafson (2004) and in the pH range of 7-11, and a result, the sorptionmaxima was found (6).

Sediment variations can give clues to the impact of environment on weathering. Clay minerals involve a high content of cations such as magnesium, iron and potassium.
Aluminum silicates involve the further complication that one product of their weathering is practically always clay mineral.

$4KAl\,Si_3O_8 + 22H_2O \longrightarrow 4K^+ + 4OH^- + Al_4\,Si_4O_{10}\,(OH)_8 + 8H_4SiO_4$ (3)
K-feldspar **Kaolinite**

$3/2\ KAlSi_3O_8 + H^+ \longrightarrow 1/2\ KAl_3Si_3O_{10}(OH)_2 + 3SiO_2 + K^+$
K-feldspar **Muscovite** **Quartz** (4)

$KAl_3Si_3O_{10}(OH)_2 + H^+ + 3/2\ H_2O \longrightarrow 3/2\ Al_2Si_2O_5(OH)_4 + K^+$
Muscovite **Kaolinite** (5)

$Chl\_OH + 2H2O + Ni^{2+} \leftrightarrow Chl\_ONi(OH)2 + 3H^+$ (6)

This indicates that Ni has been adsorbed by clay minerals of fine size fraction.
Results of XRD analyses show the presence of faujasite in the sediment samples (79- 2Theta and 6.18 intensity). Faujasite which is the source of alumina (sodium aluminate) and silica in alkaline aqueous solution facilitates transformation to zeolite.

Results of EDS and SEM analysis have been given in the 106 μ size fractions (upstream HB 1; downstream HB 10), (Figure 6 A; Figure 6B). According to EDS analysis results;
Si>Ti>Mn>S>O>K>Al>Mg>Fe>Na in the HB1 and 106 μ size fraction. Si>Ti>Mn>S>Ca>K>O>Al>Fe>Mg>Na in the HB 10 and 106 μ size fraction.

In addition to XRD results, SEM images show the presence of quartz, siderite, carbonate minerals, muscovite, pyrite (isometric) and salt minerals. Results of EDS analysis yielded the following mineral compositions; quartz>ilmenite>manganese minerals>carbonate or sulphate/sulphur minerals>K-feldspar>varieties clay minerals are found to be increased in fine size fractions (106 μ) of the Hazon Burn river sediments.

Anatase (TiO_2) is probably very common in pyrite- and goethite-bearing solutions but noticeably absent in magnetite-bearing solutions. Titanium could be mobilized by dissolution of biotite and Fe–Ti oxides, such as ilmenite, under reducing conditions in a microenvironment scale, with reprecipitation of titanium oxide. Such dissolution may take place in solutions (Morad & Aldahan, 1986; Poter, 1993). But titanium makes a compelling case for its mobilization and precipitation by hydrocarbons.

The mineral composition of the river sediments is controlled by the mineral products of chemical reactions induced by acid mine drainage (Elbaz *et al.*, 1999) such as sulphate minerals (tropical climate) and pyrite/marcasite.

SEM analysis indicates that widespread kaolinite is bounded to euhedral crystals, quartz as well as calcite.

According to Smalley (2006), clay minerals and trace element relationships may be in different forms. 1) adsorbed on to the surface of a single plate; 2) as free chains inside the gel phase; 3) as free chains in the supernant fluid surrounding the gel; 4) as bridges between the clay minerals layers, adsorbed on to the surface two neighboring layers.

Algae species and their chemical features

Cladophora glomerata alga species was identified in the Hazon Burn. Green algae, especially Cladophora species are generally considered as the best bioindicator of aquatic body contamination by nutrients as well as by heavy metals.
Clodophora glomerata is deep or dull green to brown colors, tough filaments in mats or masses.

Navicula sp. was found in the Hazon Burn sediment samples. The margin-size is from 30 to 100 µm long. This diatom species is found in cool streams, widespread but not usually common, which is reported to be sensitive to moderate pollution (Cox, 1996).

In the area, according to physical features, one moss species was identified, *Cryphaea lamyana*. The literature reports that *C.lamyana* is mainly found on rocks besides river in the continental Europe. Hill *et al.* (1994), aptly summarized the information on the British habitats of *C.lamyana* as ‘on tree-trunks and rocks by major rivers, growing in a zone which is just above the normal water level but is frequently flooded.

In Table 4, BAF values of the algae samples (HB 5, HB 6, HB 7, HB 10) are correlated with uncontaminated Cd, Cr, Ni, Pb BAF values from Chemielewska & Medued (2001). Particularly, Cd (306.6); Cr (723); Cu (4089); Ni (740) and Pb (944) values seem to be enriched in sample HB 7. Figure 7 shows that as the concentrations of these elements decrease in the surface waters, their abundance is increased in sediment and algae. BAF values have proved that algae and moss samples much better accumulate heavy metals than the reed stems, although concentrations of these elements are lower in samples HB 5, HB 6, HB 7, HB 10 than those in the recharge water (S 6). If climate conditions and the river morphologies are suitable for algae development (e.g., smooth topography, long river morphology , slow flow and temperatures a little higher than that at the vicinity of sample HB 7), they can easily accumulate the heavy metals. In this study, it was observed that Fe, Mn, Al, Zn, Si, Cr and Cu can be considerably accumulated by the algae. Fe and Mn have the highest concentrations in the water samples of HB 5, HB 6 and HB 9 due to seepage waters. Fe and Mn values are also high the algae and moss samples at the same locations. This indicates that as the element concentrations increase in water, much more increase is observed in the algae and moss (Table 5). Mouvet (1985) discussed the advantages of mosses in term of heavy metal pollution, as mosses are easily sampled and identified and are abundant and widespread. They are generally tolerant of high levels of pollutants and metals concentrations in moss tissues and correlate strongly with concentrations in water (Mason, 1991).

The reed stem sample has accumulated much more Zn and Cr than the others . They must have also accumulated the other elements in their root. Cr values are lower in sediments than those in the reed stem. This indicates that Cr has accumulated in the reed stem.

5. CONCLUSIONS

The passive treatment system and marine sediments are the source of high SO_4 and Cl concentrations which are supposed to decrease background level.

Secondly, the wetland and seepage waters at different locations have significant impact on both groundwater and surface waters and, in order to solve this problem, new measures must be taken. Thirdly, low Eh and high conductivity values indicate that the Hazon Burn is associated with large quantity of suspended matter. High ionic strength and ionic charge have decreased the activity coefficients. High clay mineral compositions may adsorb the heavy metals but especially fine-size clay minerals (-75 μ) may be the reason of contamination of the surface waters. Lastly, high PO_4 and heavy metal concentrations could be expected in surface waters but they must be accumulated from the different algae species.

Acknowledgement

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Figure Captions

Fig. 1. Location map of the study area and sampling locations of the Whittle coalfield area, northern UK.

Fig. 2. Stratigraphic section of the Lower Carboniferous coal bearing strata in the Shilbottle Coalfield, Northumberland (Johnson, 1992, Younger 2004).

Fig. 3 Distribution of the major and trace elements along the Hazon Burn river water and at the upstream - downstream River Conquet.

Fig. 4 Distribution of the heavy metals contents in the fine (<75 μ m) size fraction and water in the Hazon Burn.

Fig. 5 XRD spectra for the Hazon Burn river sediments in the Whittle coalfield area.

(a) Stream sediment HB 6 180 µm; (b) Stream sediment HB 6 106 µm. a: Ch-chlorite; Mu-muscovite; K-kaolinite; Pl-plagioclase; Q-quartz.

Fig.6 (A) SEM image of sample HB1, 106 µm x500 size fraction sediment sample. Q: euhedral hexagonal quartz crystal to coated carbonate, Py: pyrite, Mu: muscovite; EDS graph of the HB1 106 µm size fraction sediment sample; HB 10, 106 µmX 200. Q= quartz, Ka: kaolinite, Cl: chlorite, si: siderite, Cc: calcite, Py: pyrite and EDS graph of the HB 10, 106 µm.

Fig. 7. Distribution of the element contents of the different media (water, sediment, algae, moss and reed).

Table Caption:

Table 1 Comparison of the major and trace element concentrations of the Hazon Burn and River Conquet river waters and the average of the world river; EEC: European Economic Community ; Av.W.R.W: Average of world river water. G: Guide; *: **: Mandatory ; *** EEC 77/440 surface water criteria; + ; Gibbs (1977) from from Marshall and Fairbridge (1999); italic values have been taken Berner and Berner, (1996) from Marshall and Fairbridge (1999). Bold values have been taken from Krauscopf (1979).
Table 2 Concentration, activity coefficients (y), and activities of the Hazon Burn. Activity coefficients has been calculated from * A= 0.4960 value and –log y= $A*z^2$ *I (Garles ve Christ, 1965, from Akcay, 2002), I: Ionic strength C= conductivity (µS/cm).
Table 3. Comparison of the element contents with NIST and other standart values, *: in percent others in mg/kg. ** WAC173-204-320, ***Krouskopf, 1979.
**** Cairney and Hobson, 1998.
Table 4. Comparison of the trace elements of the Hazon Burn and River Conquet algaes and without pollution green algae. *in µg/L; **from Chemielewska & Medued (2001). EPA-AAP (Environmental Protection Agency- Algal Assay Procedure medium).

Fig 1

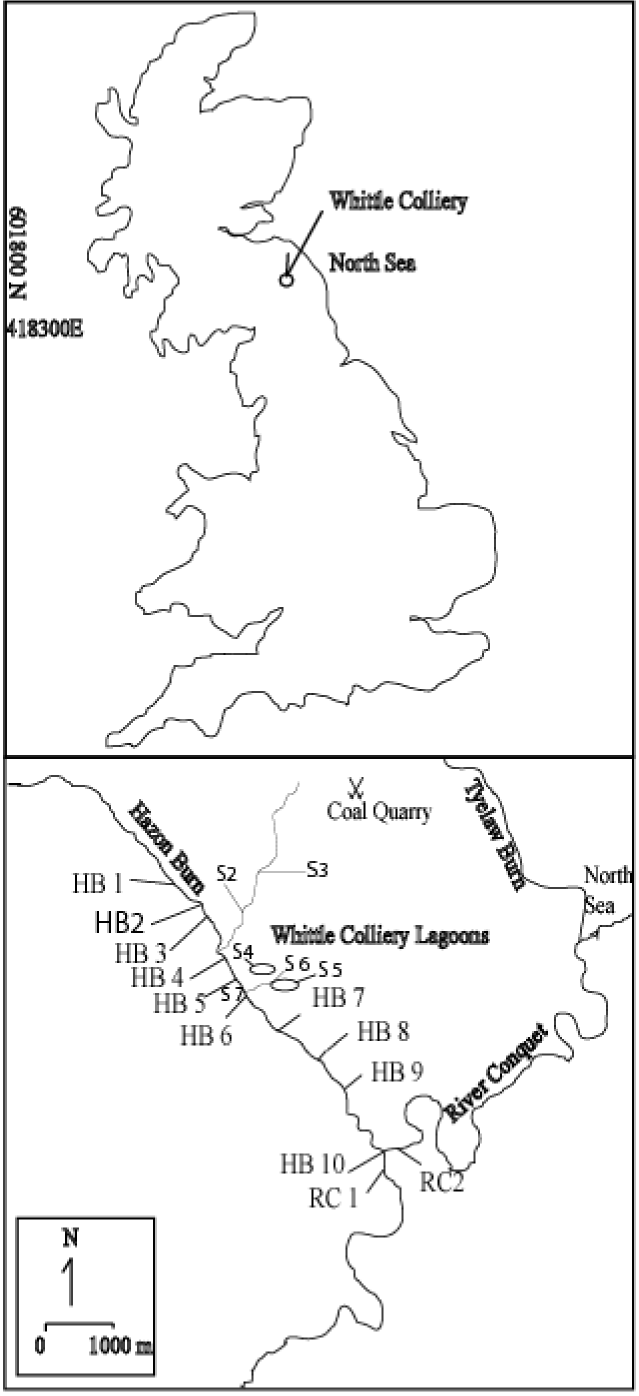

N 008109
418300E
Whittle Colliery
North Sea
Coal Quarry
Hazon Burn
Tyelaw Burn
S2
S3
HB 1
HB2
HB 3
S4
Whittle Colliery Lagoons
S6
S5
HB 4
HB 5
S7
HB 7
HB 6
HB 8
HB 9
North Sea
River Conquet
HB 10
RC 1
RC2
N
0
1000 m

Fig 2

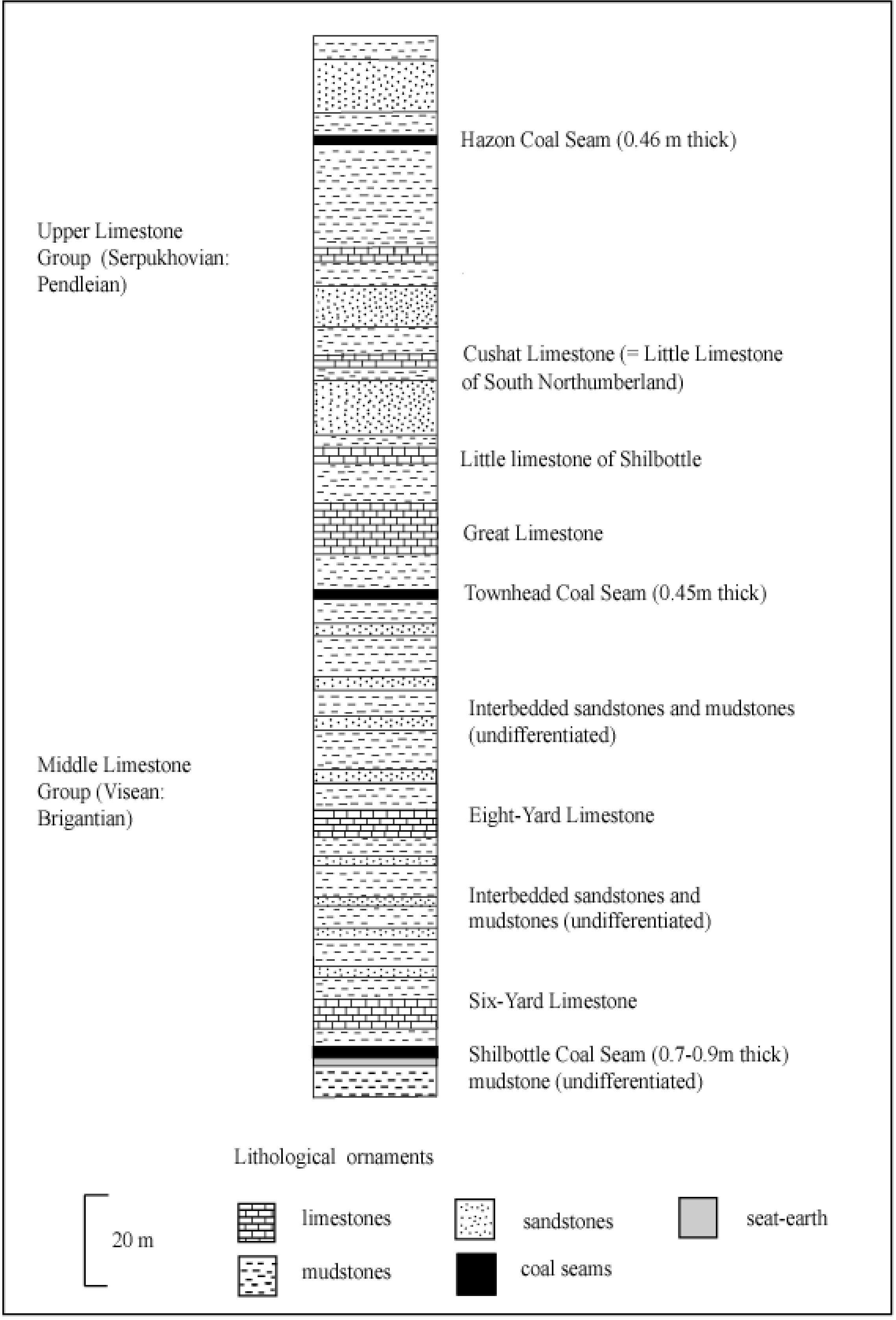

Hazon Coal Seam (0.46 m thick)
Upper Limestone Group (Serpukhovian: Pendleian)
Cushat Limestone (= Little Limestone of South Northumberland)
Little limestone of Shilbottle
Great Limestone
Townhead Coal Seam (0.45m thick)
Interbedded sandstones and mudstones (undifferentiated)
Middle Limestone Group (Visean: Brigantian)
Eight-Yard Limestone
Interbedded sandstones and mudstones (undifferentiated)
Six-Yard Limestone
Shilbottle Coal Seam (0.7-0.9m thick)
mudstone (undifferentiated)
Lithological ornaments
20 m
limestones
mudstones
sandstones
coal seams
seat-earth

Fig.3

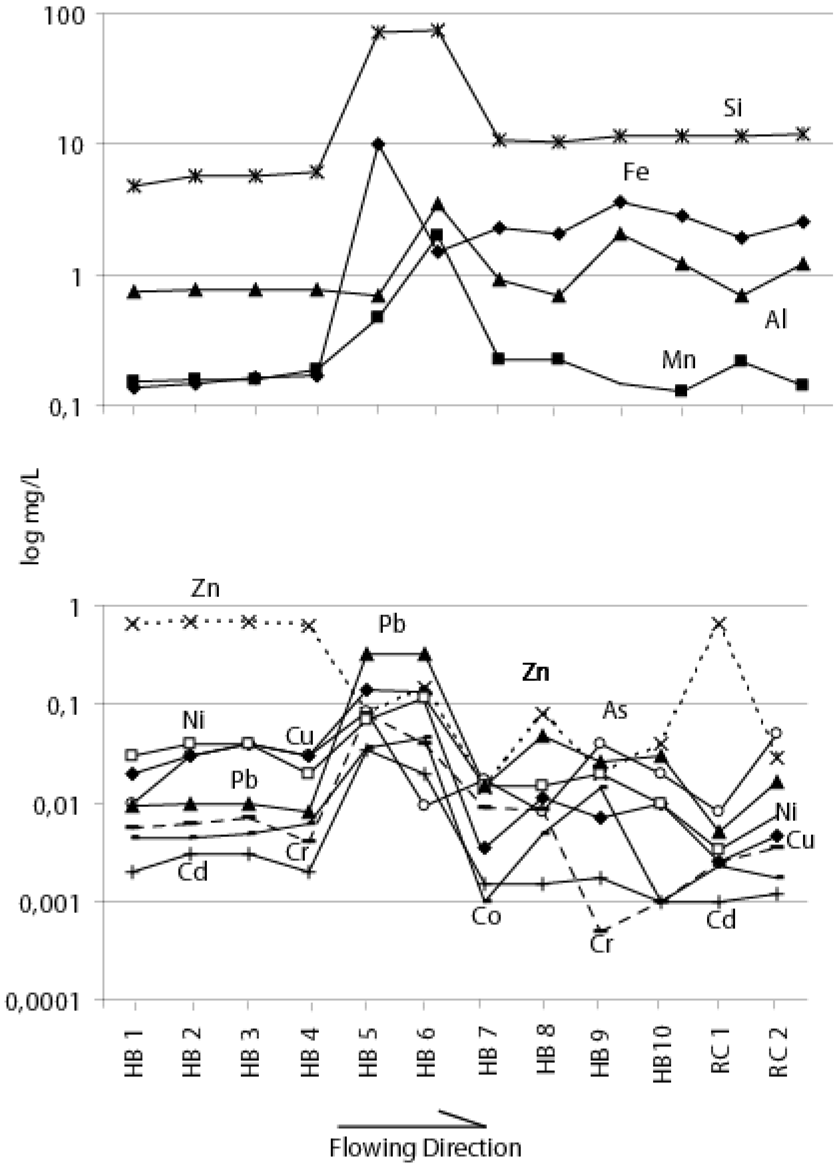
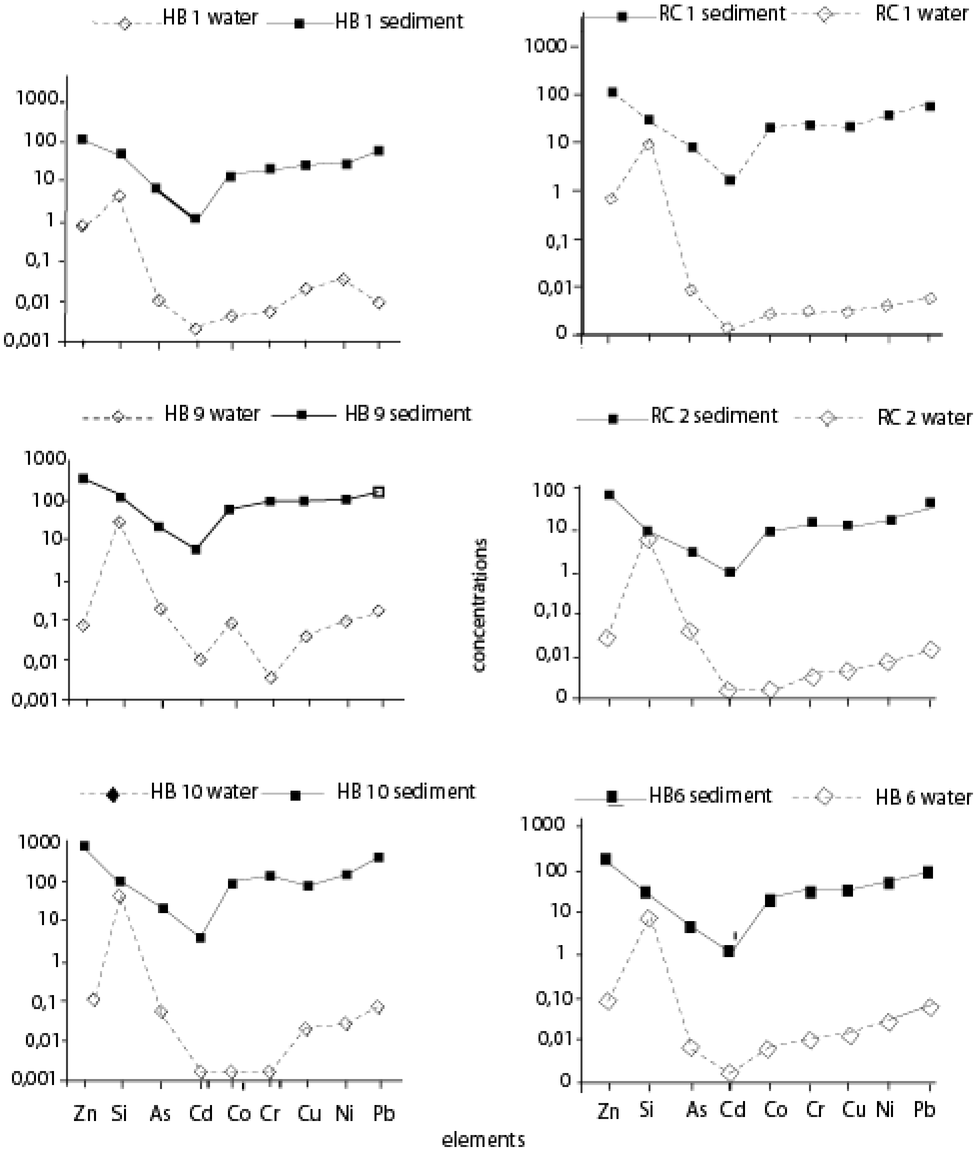

100
10
1
0,1
Si
Fe
Al
Mn
log mg/L
1
0,1
0,01
0,001
0,0001
Zn
Pb
Zn
As
Ni
Cu
Pb
Cr
Cd
Co
Cr
Cd
Ni
Cu
HB 1
HB 2
HB 3
HB 4
HB 5
HB 6
HB 7
HB 8
HB 9
HB10
RC 1
RC 2
Flowing Direction

Fig.4


HB 1 water
HB 1 sediment
1000
100
10
1
0,1
0,01
0,001
RC 1 sediment
RC 1 water
1000
100
10
1
0,1
0,01
0
HB 9 water
HB 9 sediment
RC 2 sediment
RC 2 water
100
10
1
0,10
0,01
0
concentrations
HB 10 water
HB 10 sediment
HB6 sediment
HB 6 water
Zn Si As Cd Co Cr Cu Ni Pb
Zn Si As Cd Co Cr Cu Ni Pb
elements

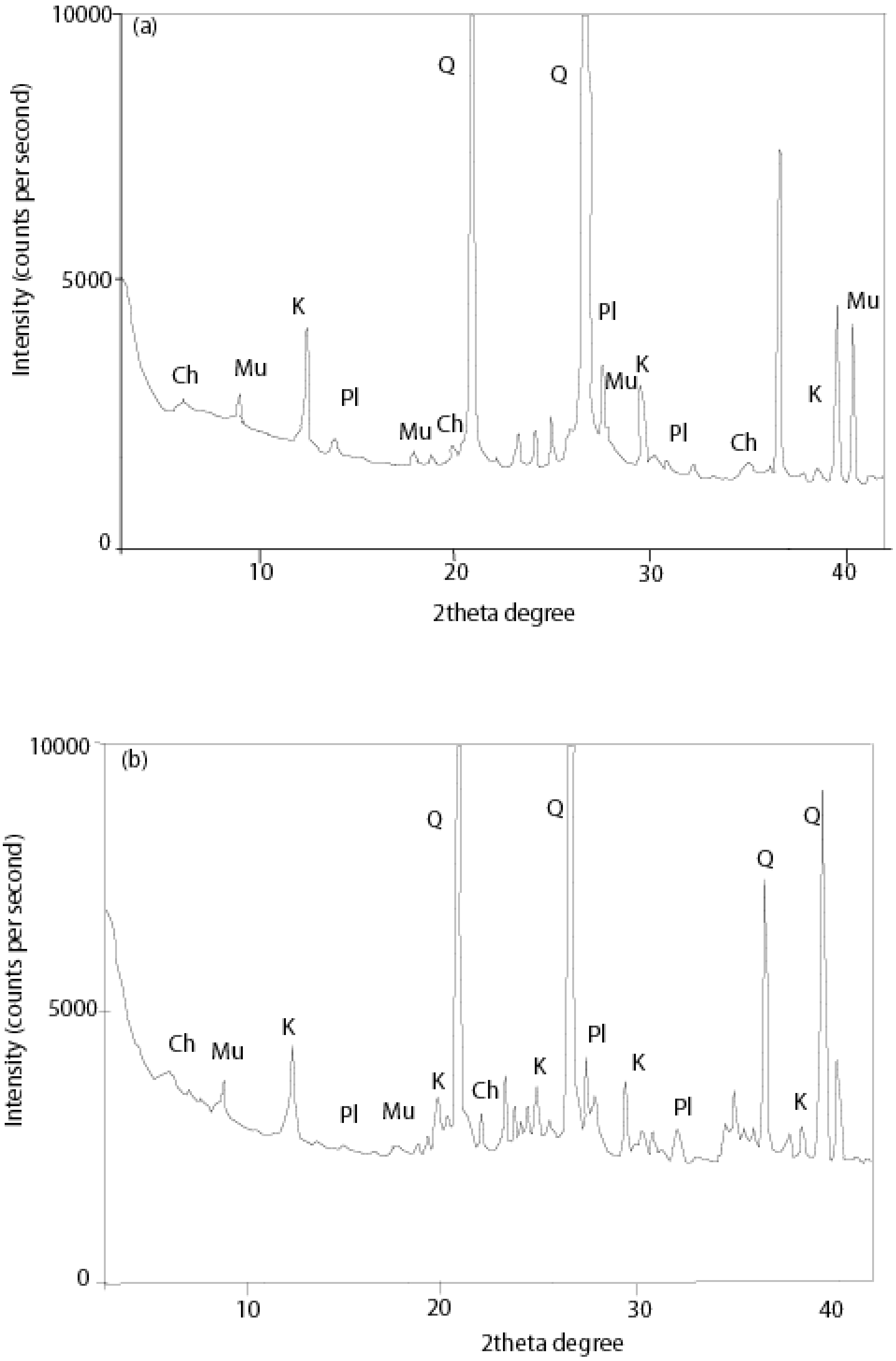
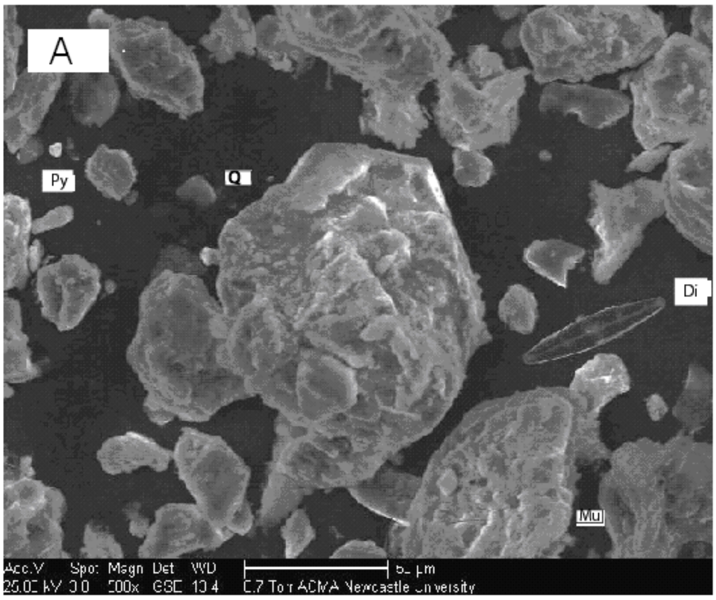
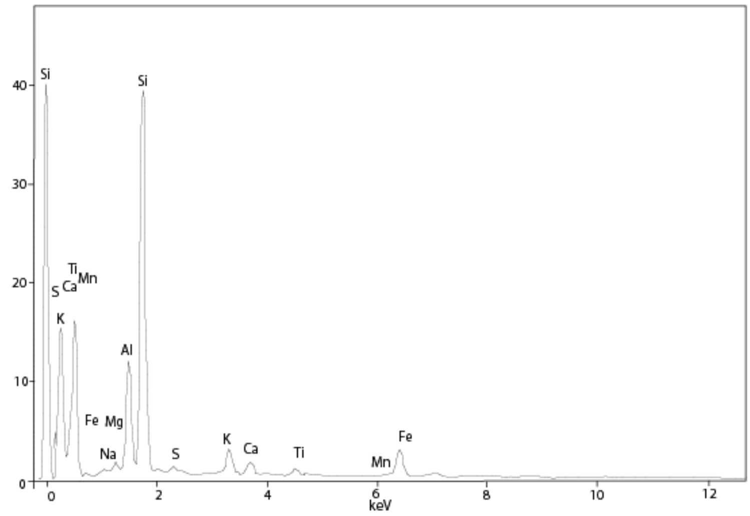

(a)
10000
5000
0
Intensity (counts per second)
Q
Q
Pl
Mu
K
Mu
K
Ch
Mu
Pl
Mu
Ch
Pl
Ch
K
10
20
30
40
2theta degree
(b)
10000
5000
0
Intensity (counts per second)
Q
Q
Q
Q
Pl
K
Ch
Mu
K
K
K
Ch
K
Pl
Mu
Pl
K
10
20
30
40
2theta degree

Fig.5


A
Py
Q
Di
Mu
Acc.V Spot Magn Det WD
50 µm
25.00 kV 3.0 500x GSE 10.4
0.7 Torr ACMA Newcastle University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Si
S
Ca
Ti
Mn
K
Al
Fe
Mg
Na
S
K
Ca
Ti
Mn
Fe
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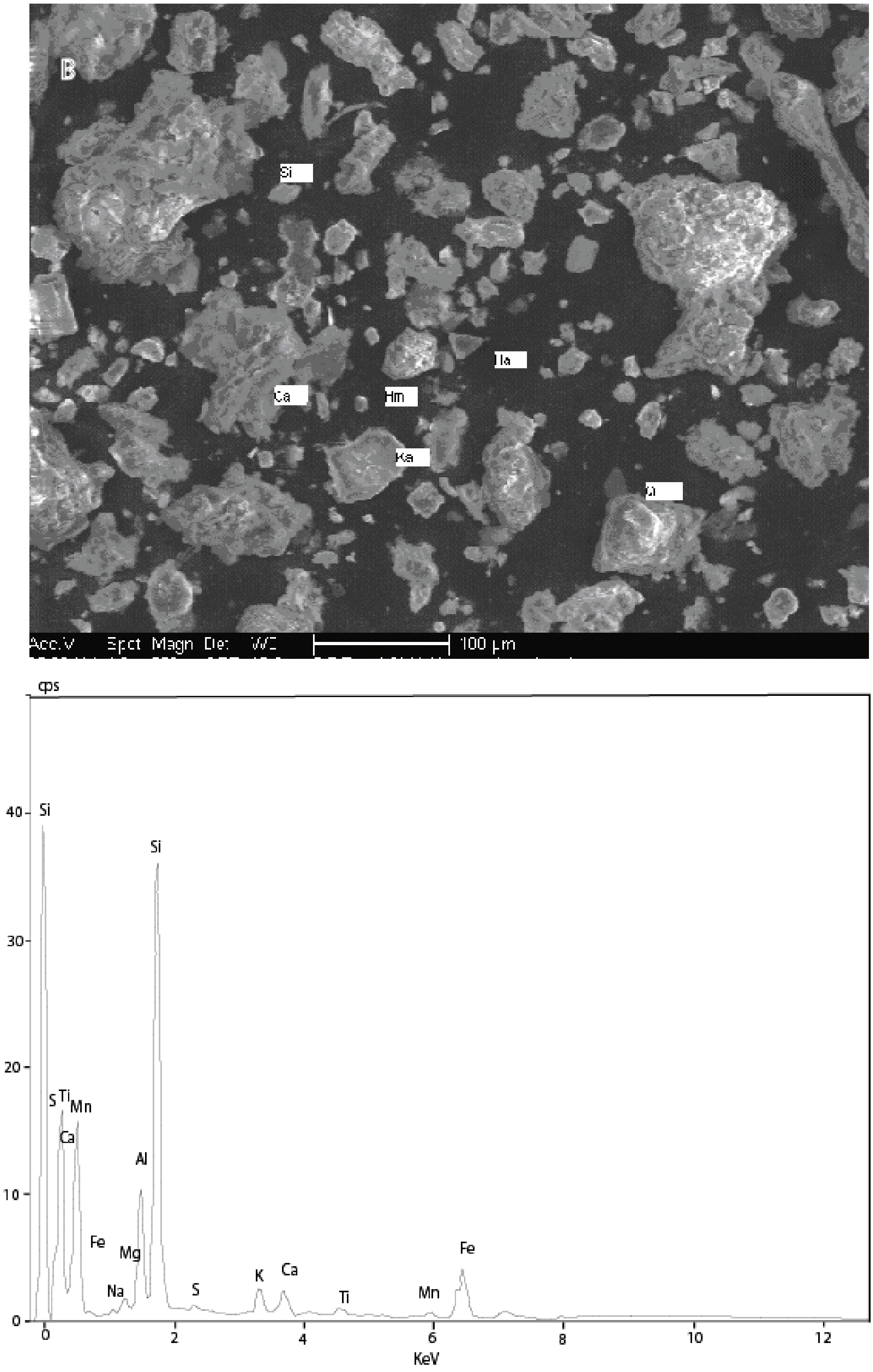
10
20
30
40
0
2
4
6
8
10
12
keV

Fig 6


B
Si
Ia
Ca
Hm
Ka
Q
Acc.V Spot Magn Det WD
100 µm
cps
40
30
20
10
0
Si
Si
S
Ti
Mn
Ca
Al
Fe
Mg
Na
S
K
Ca
Ti
Mn
Fe
0
2
4
6
8
10
12
KeV

Fi 7

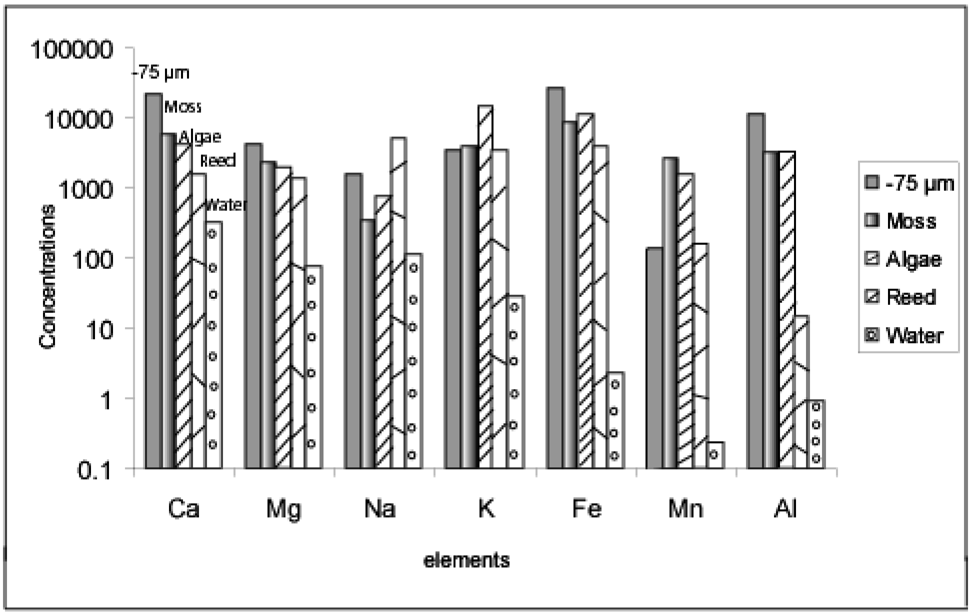

100000
10000
1000
100
10
1
0.1
Concentrations
-75 µm
Moss
Algae
Reed
Water
Ca
Mg
Na
K
Fe
Mn
Al
elements
-75 µm
Moss
Algae
Reed
Water

Table: 1

mgL-1	HB 1	HB 2	HB 3	HB 4	HB 5	HB 6	HB 7	HB 8	HB 9	HB10	*Median*	S.D (σ)	Min	Max	RC 1	RC 2	S 2	S 3	S 4	S 5	S 6	S 7	World average I	World average II
Ca	363	361	365	367	4380	4091.5	306.7	307.65	327.45	306.1	*362*	1600	306.1	4380	150.35	249.05	3106	3050	7008	139000	18707	10734	*13*	**15**
Mg	222.5	221	224	223	1050	4343.5	73.35	73.55	73.25	78.75	*222*	1327	73.25	4343.5	41.1	63.85	446	455	2796	5579	6558	4418	*3.4*	**4.1**
Na	190	189	192	187	2000	1750	115.3	110.6	117.05	106.85	*188*	730	106.85	2000	45.5	82.5	609	589	6208	12406	16640	9709	*5.2*	**6.3**
K	49.6	51	52	65	450	400	24	24.8	23.95	27.75	*50,3*	163	23.95	450	10	19.4	47	43.5	1045	2134	3341	1455	*1.3*	**2.3**
Fe	0.135	0,145	0,162	0,17	10	1.5	2.3	2.1	3.7	2.8	*1.8*	2,99	0.135	10	19	2.55	0.168	3.5	1.6	35	539	41	*0.67**	**0.67**
Mn	0.155	0,157	0,16	0,19	0.475	2	0.225	0.225	0.145	0.13	*0.175*	0,5	0.13	2	0.215	0.14	3	2.6	0.25	5	403	140	0.32^{+}	-
Al	0.75	0,76	0,77	0,77	0.7	3.5	0.92	0.7	2.1	1.2	*0.77*	0,9	0.7	3.5	0.7	1.2	14	1	0.65	21	2.4	5.3	-	**0.4**
Zn	**0.65**	0,68	0,69	0,62	0.08	0.145	0.014	0.08	0.02	0.04	*0.113*	0,3	0.01	0.65	**0.65**	0.028	0.15	0.10	0.18	1.7	1.2	0.3	0.02^{+}	-
Si	4.75	5,75	5,8	6,2	73	76.5	10.85	10.3	11.5	11.5	*10.57*	28,13	4.75	76.5	11.8	12.25	154	151	140	272	251	135	*5.54*	**6.11**
As	0.01	0,03	0,04	0,03	0.085	0.0095	0.017	0.008	0.04	0.02	*0.025*	0,02	0.01	0.085	0.008	0.05	0.04	3.5	0.35	5.4	0.6	0.89	-	-
Cd	0.002	0,003	0,003	0,002	0.035	0.02	0.0015	0.0015	0.00175	0.001	*0.002*	0.01	0.01	0.035	0.001	0.0012	0.035	0.02	0.026	0.5	0.027	0.02	-	-
Co	0.0044	0,0045	0,0049	0,006	0.0365	0.045	0.001	0.00475	0.014	0.001	*0.005*	0.01	0.01	0.045	0.0023	0.0017	0.035	0.04	0.043	0.09	0.04	0.02	0.004^{+}	-
Cr	0.0055	0,006	0,007	0,004	0.08	0.0405	0.009	0.0085	0.0005	0.001	*0.007*	0.02	0.01	0.08	0.0025	0.0035	0.075	8E-05	0.026	0.1	0.06	0.2	0.04^{+}	-
Cu	0.02	0,03	0,04	0,03	0.14	0.135	0.0035	0.0115	0.007	0.01	*0.025*	0.05	0.01	0.14	0.0025	0.0047	0.0225	0.35	0.085	1.49	0.2	0.2	0.06^{+}	-
Ni	0.03	0,04	0,04	0,02	0.07	0.115	0.015	0.015	0.02	0.01	*0.025*	0.03	0.01	0.115	0.0034	0.0075	0.08	0.4	0.07	0.05	0.16	0.03	0.02^{+}	-
Pb	0.0095	0,0097	0,01	0,008	0.32	0.325	0.015	0.047	0.026	0.03	*0.21*	0.12	0.01	0.325	0.005	0.0165	0.225	0.285	0.23	0.33	0.67	0.75	-	-
Cl	326	442	499	241	442	499	241	240	241	252	*289*	114	240	499	91	180	-	-	-	-	-	-	*5.8*	**7.8**
SO4	599	642	712	378	642	712	378	375	374	369	*489*	154	369	712	98	247	-	-	-	-	-	-	*8.3*	**11.2**
NO3	17	10	14.64	-	10	14.64	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	**1**
PO4	<0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Br	0.1	0.01	-	-	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 2

ions	Concentrations mgL-1 (Median)	Mol/kg	zi^2	mi*z^2	log y	y	Activity
Ca^{2+}	327.45	0.008	4	0.032	-0.075	0.84	0.0067
Mg^{2+}	78.75	0.003	4	0.012	-0.075	0.84	0.0025
Na^{1+}	117.05	***0.005***	1	0.005	-0.018	***0.95***	***0.0047***
K^{1+}	27.75	***0.0002***	1	0.0002	-0.018	***0.95***	***0.00019***
Fe^{2+}	2.3	0.00004	4	0.00016	-0.075	0.84	0.000034
Mn^{2+}	0.23	0.000004	4	0.000016	-0.075	0.84	0.0000034
Al^{3+}	0.92	0.000003	6	0.000018	-0.11	0.77	0.0000023
Zn^{2+}	0.08	0.000001	4	0.000004	-0.075	0.84	0.00000084
Si^{2+}	11.5	0.00004	4	0.00016	-0.075	0.84	0.000034
			9	0.000002	-0.17		
As^{3+}	0.02	$2.7*10^{-7}$		4		0.67	0.00000018
Cd^{2+}	0.002	$1.7*10^{-7}$	4	$6.8*10^{-7}$	-0.075	0.84	0.00000014
Co^{2+}	0.004	$6.77*10^{-8}$	4	2.71E-07	-0.075	0.84	0.000000057
Cr^{2+}	0.01	$1.91*10^{-7}$	4	7.64E-07	-0.075	0.84	0.00000016
Cu^{1+}	0.01	$1.5*10^{-6}$	1	1.5E-06	-0.11	0.67	0.0000010
Ni^{2+}	0.02	$3.38*10^{-7}$	4	1.35E-06	-0.075	0.84	0.00000028
Pb^{2+}	0.03	$1.45*10^{-7}$	4	5.8E-07	-0.075	0.84	0.00000012
SO_4^{2-}	378	***0.004***	4	0.016	-0.075	0.84	***0.0034***
Cl^{1-}	252	0.007	1	0.007	-0.11	0.77	0.0054
NO_3^{1-}	14.64	0.004	1	0.004	-0.11	0.77	0.0031
PO_4^{3-}	0.1	0.000001	9	0.000009	-0.17	0.67	0.00000067
Br^{1-}	0.085	0.000001	1	0.000001	-0.11	0.77	0.00000077
		Add(mi*zi^2)	0.076				
Eh	0.098						
pH	8.32	I=	0.038				
		A=	0.4960				
C	788,26		*				
T	11.9 ^{0}C						

Table 3

Element	Size fraction Average of mg/kg -75 µ	-106 µ	-150 µ	-180 µ	NIST values SRM-2704	****Sediment intervent on value mg/kg	** standard Quality mg/kg	**Impact zone max Level-mg/kg	***Average of crust mg/kg
Ca	21450	5850	5250	4960	2.6*	-	-	-	41000
Mg	4159	3200	3150	2800	1.2*	-	-	-	23000
Na	1535	1000	975	862	0.55*	-	-	-	24000
K	3594	2869	2635	2465	2.00*	-	-	-	21000
Fe	27300	23900	22675	22462	4.11*	-	-	-	54000
Mn	139	44.5	39.25	37.34	555	-	-	-	1000
Al	11100	9284	8937	8794	6.11*	-	-	-	81000
Zn	126.03	100.08	75.82	67.16	438	720	410	960	70
Si	27.244	17.298	12.01	14.42	-	-	-	-	28000
As	**5.613**	**6.573**	**3.47**	**3.47**	23.4	55	57	93	1.8
Cd	**1.111**	**0.936**	**0.576**	**0.667**	3.45	12	5.1	6.7	0.15
Co	**16.262**	12.785	7.24	8.267	14	240	-	-	22
Cr	18.404	15.083	8.04	11.97	135	380	260	270	100
Cu	20.384	17.63	15.785	19.46	98.6	190	390	390	50
Ni	27.154	22.45	12.117	14.45	44	210	-	-	75
Pb	48.926	44.79	26.239	38.29	161	530	450	530	12.5

Table: 4

Element	Moss Samples Median mg/L	Algae samples Median mg/L	Reed stem mg/L	EPA-AAP mg/L	Metal content in algal biomass g/kg **	BAF in algae**	OECD mg/L	HB 6 BAF	HB 5 BAF	HB 10 BAF	HB 7 BAF	HB 9 Moss BAF	S2 Moss BAF	S3 Moss BAF	S6 Reed BAF
Ca	5908.62	64149.05	1626.50	1.20	-	-	4.905	12.79	17.76	74.70	247.66	16.51	4.84	1.94	0.09
Mg	2328.21	1951.62	1375.64	2.65	-	-	2.913	0.46	2.89	15.60	25.67	46.50	5.22	4.23	0.21
Na	344.65	756.90	5054.71	11.0	-	-	13.704	0.59	0.57	2.47	4.24	2.94	1.05	0.44	0.30
K	4052.99	14676.22	3490.21	0.469	-	-	-	54.24	49.5	44.79	**318.96**	259	83.32	93.17	1.04
Fe	***8733***	***11295.90***	***4016.70***	-	-	-	0.017	**8153**	**1425**	**4298**	**4505**	**505**	**125014**	**2495.14**	7.45
Mn	***2628***	***1542.97***	***153.29***	1.57*	-	-	0.115	594	**2692**	**22297**	**8031**	**10944**	**1642.03**	**1010.77**	0.38
Al	3296	3298.19	14.67	-	-	-	-	896	**5538**	**4945**	**1964**	368	**392.19**	**3296.00**	6.11
Zn	40.27	62.32	31.02	-	-	-	-	351	682	1041	**5009**	**3305**	**268.48**	**400.98**	25.85
Si	94.56	238.05	88.63	-	-	-	-	1.68	1.51	33.78	32.53	6.42	0.61	0.70	0.35
As	4.73	4.42	2.72	-	-	-	-	357	83.18	460	304	118.18	151.20	1.19	4.53
Cd	0.68	0.45	0.12	-	1.7	200	-	**22.5**	**12.57**	**287**	**306.6**	71.45	27.25	34.03	4.47
Co	6.97	6.75	0.30	0.35*	-	-	-	94.88	155	2070	7920	**401.77**	268.62	174.32	7.55
Cr	6.29	5.40	1.79	-	1.7	210	-	**130**	**68.25**	**485**	**723**	1.02	116.39	**78622**	29.90
Cu	10.02	12.32	1.32	0.004*	-	-	-	76.59	58	**3403**	**4089**	10.02	**473.31**	27.76	6.60
Ni	8.73	9.21	0.33	-	15.6	486	-	**76.36**	**143.14**	**541**	**740**	240.35	132.13	21.82	2.04
Pb	6.81	4.90	3.04	-	7.9	351	-	**14.89**	**15.53**	**87.02**	**944**	184	31.97	24.33	4.53

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PROTECTION OF MARBLE USING BIODEGRADABLE POLYMERS

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The deterioration of historic buildings and monuments constructed by marble has been accelerated in the past century due to the effect of air pollution. The main pollutant responsible for this deterioration is sulphur dioxide (SO_2) which reacts with marble composed primarily of calcite ($CaCO_3$) and converts it into moderately soluble gypsum ($CaSO_4 . 2 H_2O$).

In this study, the possibilities of slowing down the SO_2-marble reactions were investigated by using some bio-degradable polymers; zein and polyhydroxybutryate (PHB) as protective coatings on marble surfaces. For this purpose, marble slabs were coated with these these polymers and then they were exposed at nearly 8 ppm SO_2 concentration at 100 % relative humidity conditions together with uncoated ones in a reaction chamber for several days.
The extent of reaction was determined by leaching gypsum in deionized water and then determining sulphate content by ion chromatography. The efficiency of polymer treatments will be expressed as comparing the gypsum crust thickness of the treated and untreated marble slabs. It was found that PHB treatment provided 50 % reduction in the marble – SO_2 reaction.

1. Introduction

The deterioration of marble that has been widely used in the historic buildings was a slow process until the level of air pollution increased due to heavy urbanization and industrialization. The main pollutant which affects the marble structure is primarily sulphur dioxide. Sulphur dioxide reacts with marble composed primarily of calcite ($CaCO_3$) and converts it into calcium sulphite hemihydrate ($CaSO_3 . \frac{1}{2} H_2O$) (Eqs.1) [1-3]. In the presence of water, calcium sulphite hemihydrate is not a stable product and rapidly converted to gypsum ($CaSO_4 .2 H_2O$) (Eqs.2). Gypsum is moderately soluble and occupies more volume than calcite. As a result, the marble surfaces are eroded in rain-washed areas and disintegrated in sheltered places.

$$CaCO_3 + SO_2 + \tfrac{1}{2} H_2O \rightarrow CaSO_3 . \tfrac{1}{2} H_2O + CO_2 \qquad (1)$$

$$CaSO_3 . \tfrac{1}{2} H_2O + \tfrac{1}{2} O_2 \rightarrow CaSO_4 . 2H_2O \qquad (2)$$

In order to inhibit and/or decrease the SO_2-calcite reaction, various precautions have been proposed. The common method used to inhibit gypsum formation was coating of stone surfaces by synthetic polymers [3-6]. Hence, most of the coated marble surfaces were more deteriorated than those of the uncoated ones due to the SO_2 absorption, and the entrapment of water vapour by polymers [3].

Although the other most common one has been converting the formed gypsum back to calcite by the use of carbonate solution, it is not as effective as expected because of poor adhesion of formed calcite crystals to the original stone surfaces [7].

Furthermore, researchers have studied on the possible ways of slowing down the SO_2-calcite reaction by producing less reactive substrate on the marble surface by using some water soluble organic and inorganic compounds such as oleate, oxalate and phosphate ions [8-10]. It is reported that oxalate and oleate anions produce less reactive calcium oxalate and calcium oleate substrate and provide significant protection to marble exposed only in sheltered places [9].

In this study, the effects of some bio-degradable polymers on marble-SO_2 reaction were investigated. Properties of biodegradable polymers fulfil the principles generally accepted by the International Conservation Community since they are reversible, degradable and allow new treatment of the material to be protected [11,12]. Although many synthetic polymers were tested and used to protect the marble surfaces from air pollution, bio-degradable polymers have not yet been tested for this purpose.

As previously noted that SO_2 reacts with calcite in the presence of water. It is known that some biodegradable polymers have good barrier properties against moisture and water vapour. Hence, by using these types of polymers on the marble surface, it is possible to slow down the gypsum formation. In this study, two different types of biodegradable polymers, zein, and PHB were investigated as a coating agent for preventing gypsum formation on marble surfaces in laboratory conditions. Degree of protection has been established by comparing thickness of gypsum crust for coated and uncoated marble surfaces.

2. Materials, methods and calculations

2.1. Preparation of marble samples and coating with polymers

In this study, Marmara marble was selected to investigate the degree of protection obtained by zein and PHB on the marble-SO_2 reaction. Rectangular plates (nearly 2.8x1.6x0.6 cm) were cut from a large block of Marmara marble and polished with 400-grit silicon carbide powder. The samples were then cleaned in an ultrasonic bath with distilled water, dried at 105 °C and cooled in a desiccator.

Zein solution was prepared at concentration of 35 % (by weight) using ethanol and water as a solvent. Solution of PHB was prepared at concentration of 5 % using the chloroform as a solvent. The marble slabs were then coated with these solutions by dip-coating procedure at room temperature and allowed to dry at 50 °C in an oven for 24 hours.

2.2. Experimental set up

The marble slabss were exposed in a dynamic 8 ppm SO_2-enriched atmosphere at room temperature and at 100 % relative humidity for 35 days in a reactor which was a modified 10 L desiccator [9]. The samples were placed in the desiccator only after the water had been equilibrated with the given concentration of gas. The samples were tied to a glass stand by nylon threads. The maximum number of samples was exposed at a time in order to maintain a constant concentration of SO_2 in the reactor were four.

2.3. Experimental methods

The degree of protection obtained by polymers was determined by leaching the gypsum in deionised water and then determining sulphate ion concentration by ion chromatography. Some quantity of calcium sulphide hemihydrate was formed together with gypsum in the course of exposure. The sulphite was converted to sulphate by adding H_2O_2 in deionised water [9]. Analysis were carried out on a Dionex Model ion chromatography.

Characterization of the microstructures and morphologies of coated and uncoated marble samples before and after exposure to SO_2 were examined by using a Philips XL-30-SFEG model scanning electron microscope (SEM).

2.4. Determination of the thickness of gypsum crust on marble surface

The thickness of the gypsum crust after each period of SO_2 exposure was determined by the following equation (Eqn 3) [3].

$$\delta_p = \frac{W_p}{A\rho_p} \qquad (3)$$

Where,

δ_p = crust thickness (cm),

W_p = weight of the product, gypsum (g)

ρ_p = density (g/cm^3) of gypsum, 2.32

A = surface area of the sample, cm^2

W_p , the weight of the gypsum, can be obtained by mass balance from the weight of SO_4^{2-} ions (W_A), obtained by leaching these in known volume (l) of water from the exposed sample and measuring their concentration (ppm) by ion chromatography.

3. Results and Discussion

Marble slabs, uncoated, coated with zein and PHB polymers were exposed in a reaction chamber for 35 days. The thickness of gypsum crust formed on marble surface were calculated and plotted at some intervals for 35 days (Fig.1,2). Comparison of the thickness of zein and uncoated marble plates shows that zein polymers accelerated the Marble-SO_2 reaction (Fig. 1). This acceleration can be explained by high permeability of SO_2 and water vapour by zein polymer. On the other hand, PHB reduced the reactivity of marble – SO_2 reaction by nearly 50 % (Fig.2). This significant protection can be explained by hindering the SO_2 and water vapor penetration through marble.

Unexposed Marmara marble composed of mainly fine calcite crystals (Fig. 3a). SEM analysis of zein and PHB coated marble samples showed that they were adhered strongly and distributed uniformly on marble surfaces (Fig. 3b,c).

During the period of 35 days exposure, long prismatic gypsum crystals were observed on uncoated marble plates (Fig. 3 d). On coated plates, due to the effects of SO_2 and water vapour, micro holes were observed on zein polymer and they became larger and larger with exposure time. During this period, gypsum crystals were grown behind the polymers and crystallize on the surface (Fig.3 e,f).

4. Conclusions

Sulphur dioxide reacts with calcite in marble and produces gypsum which is much more soluble than calcite and causes erosion of the marble surface.

In this study, the possibilities of slowing down the SO_2-marble reactions were investigated by using zein and PHB as protective coatings on marble surfaces. The use of PHB polymers on marble surfaces provided significant protection up to 50 percentage respectively. Hence PHB polymer seems to be applicable coating agents in reducing gypsum formation on marble surface in a polluted environment.

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FIGURES

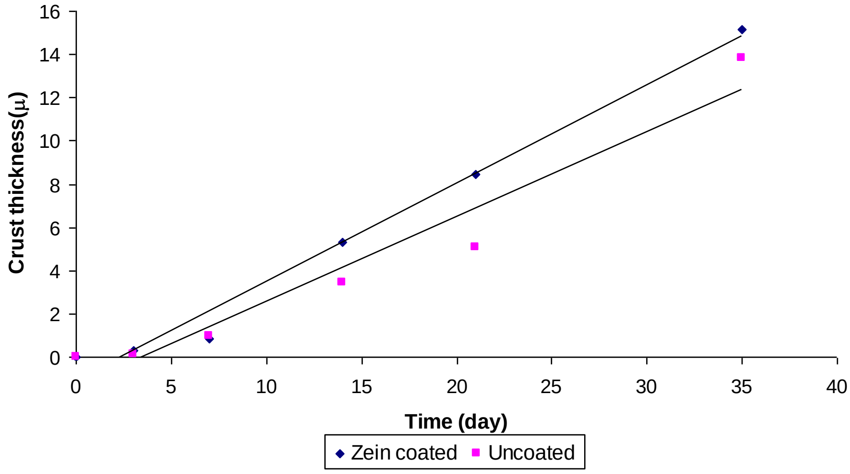

Figure 1. The thickness of gypsum crust on marble plates with and without zein polymer

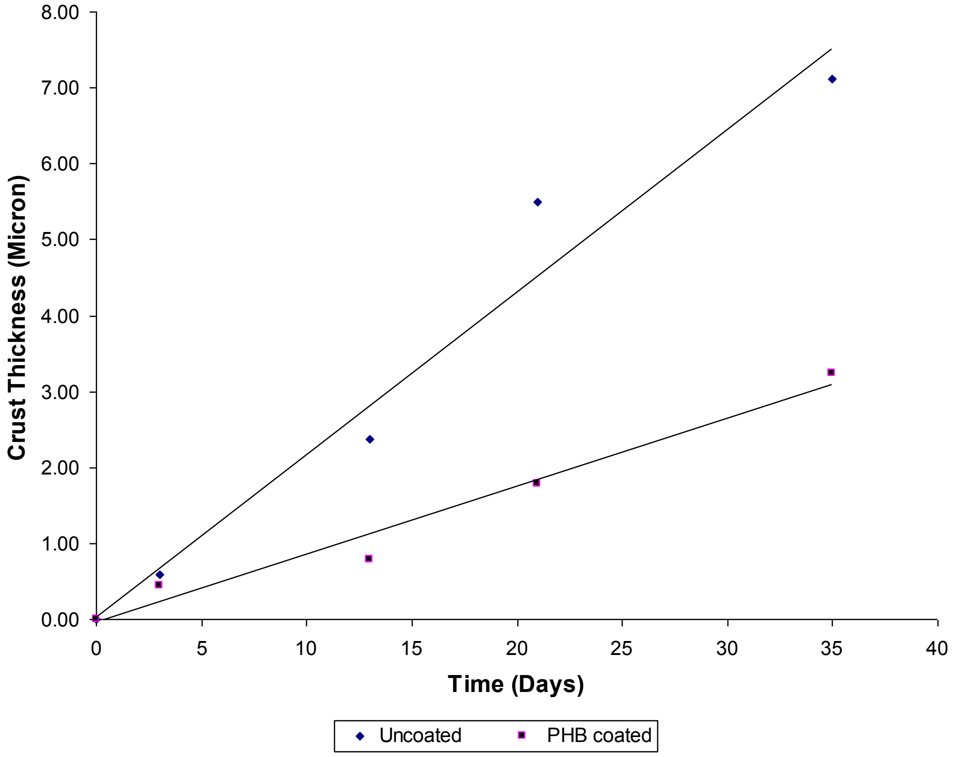

Figure 2. The thickness of gypsum crust on marble plates with and without PHB

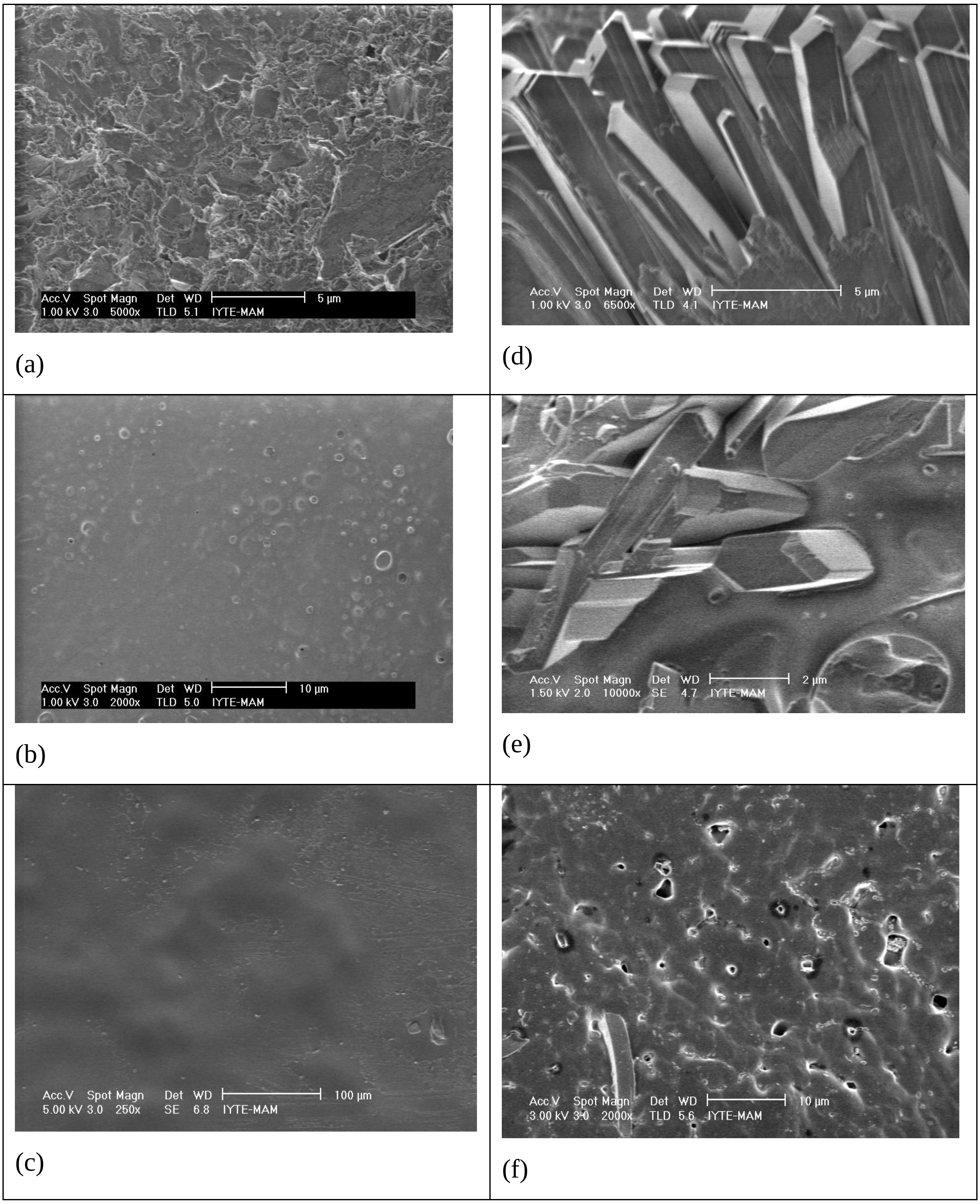

Figure 3. SEM view of fine calcite crystals of unexposed marble (a), zein coated (b) and PHB coated (c) marble surfaces, gypsum crystals on exposed uncoated marble (d) and coated with zein (e) and PHB (f) polymers

SOLID WASTE MANAGEMENT AT THE SOUTH-EASTERN BLACK SEA COASTLINE

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In the Black Sea region of Turkey, most of the municipal and industrial solid wastes, mixed with hospital and hazardous wastes, are dumped on the nearest lowlands and river valleys or into the sea. The impact of riverside and seashore dumping of solid wastes adds significantly to problems arising from sewage and industry on the Black Sea coast.
Increasing amount of solid waste arising from municipalities and other sources and its consequent disposal has been one of the major environmental problems in Turkey. In the Black Sea region of Turkey, all of the municipal and industrial solid wastes mixed with hospital and hazardous wastes are dumped to the nearest lowlands and river valleys or directly into the sea. Appropriate integrated solid waste management systems are needed to prevent this area which has many precise environmental privileges.

This region is short of appropriate land filling sites for the disposal of solid wastes. Usable land is scarce and valuable with very high costs. Trabzon, as the major city in the area, is representative of this region in terms of solid waste characteristics and practices.
In this study, applied planning, management and related environmental problems of solid waste disposal along the South-eastern Black Sea coastline are presented.

Keywords: Solid Waste, Landfill, Waste Management, Metal Toxicity, Black Sea, Turkey

1. Introduction

The Turkish Black Sea coast is 1695 km long, extending from Bulgarian border in the west to the Georgia border in the east. Black Sea coasts constitute 20% of the total coastlines of Turkey. Generally, the Black Sea coastal zone of Turkey may be defined as similar to a typical Pasific coastal area. High mountains parallel to beaches that are not far from the sea are typical properties of this type of morphology. Thus there are not many curves or bays along the coastline. Rocky cliffs exist in many places resulting from wave erosion. Between small sandy beaches, alluvial deltas are present. Plains are found at the river deltas. Geologically, the majority of the zone is defined as Pondid, a geo-tectonic definition which is very common in Turkey. There are 26 main river basins in Turkey, 8 of which are in the Black Sea zone. Additionally, the eastern Black Sea river basin covers the area between Ordu and Artvin, including many small rivers coming from the mountains parallel to the coast.

Excluding Istanbul, the remaining fourteen provinces along the Black sea coast have a total area of 92 198 km^2 and a total population estimated at 8 072 979 in 1990. There are 420 municipalities in the Black Sea Region. Two of them are greater municipalities (Samsun and Izmit). Eighty of these municipalities have populations of over 10 000 people. The region extends over a very large area and shows differences of both nature and population. Based on these differences, the region may be divided into three parts namely, eastern Black Sea region (starting from the boundary of Georgia to the city of Ordu), the central Black Sea region (in between the cities of Ordu and Samsun) and the western Black Sea region (from the city of Sinop to the Marmara regional boundary). The topography of the region has a profound influence on the distribution of the population and thus pollution sources along the coast. The Pontic Mountains that extend along the coastline rise sharply as high as 3000m within 30 km of the shore and do not allow for the development of large cities along the coast. Mountains are also an obstacle for transportation routes which link the region to the rest of the country. Because of the topography and isolated nature of the region, the fairly small population live in small settlements rather than large cities. Climatically, the Black Sea region shows differences between the coastal and inland areas. In areas directly on the coast, an almost oceanic climate is observed. In winter, it is rainy and temperate with the exception of Samsun area. Annual rainfall is more than 1000 mm along the coastline. In this coastal area, it is hot and humid in summer, yet temperate in winter. On the other hand, the inland part of the region is under the effect of continental climate which is less rainy. It is very cold and snowy in winter, hot and mild is summer. Although the rainy season is fall along the coast, it is spring inland. The difference between the coastline and inland climates affects the distribution of vegetation. All of the wetlands in the region are under special protection due to their rare flora and fauna. There are a number of registered natural and archaeological sites in the Black Sea region excluding Istanbul. Thirty-seven of these are natural sites, 2 are urban and natural, 241 are archeological, 36 are urban sites, 1 historical, 2 historical and urban, and 14 archeological and natural registered sites. Twenty-one wildlife protection areas have been founded to protect various threatened species. Turkey’s richest forestry areas are found along the northern slope of the mountains along the Black Sea coastline. In terms of non renewable sources, e.g., minerals (iron ,copper, lead, zinc, manganese etc.) the Black Sea region is fairly well-endowed. No single form of economic activity is dominant throughout the region. Agriculture is the main activity in the eastern part of the Black Sea. The coastal cities generally produce important commercial products, including Turkey's entire tea production and 75% of its hazel nut production. Corn and tobacco are the region's other major farm products. The central Black Sea region shows the agricultural characteristics of central Anatolia. In this part of the region, grain (wheat and corn), tobacco and sugar beets are the major commercial crops. In addition heavy industry has been developed in Karabük-Zonguldak-Ereğli. There are 8 major ports.

2. Solid Waste Management at the South-Eastern Black Sea Region

Most of the cities in this area dispose of their solid wastes directly into the shallow coastal sea waters. Existing heavy industry in this area (e.g. Cayeli Bakir copper mine establishment near Rize city) also dispose of inorganic toxic materials either directly into coastal waters or to the deep anoxic strata via their outfall systems (Fig 1). Solid wastes with their high organic and inorganic strength and quantities are major polluting substances in comparison with the wastewaters. Considerable part of the coastal waters along the south-eastern Black Sea from Samsun to Rize have been officially declared as heavily polluted and restricted sites for recreation and fishing. Direct waste disposal into the sea and waste fillings along the sea shore after a rough manual separation are the applied disposal processes of solid wastes. At this land scarce area, municipalities prefer filling the seashore along the coastline with MSW, to gain some expanded land sites towards the sea. By these fillings water depths have reached to 10m along the coastline, forcing serious coastline protecting measures to be taken. The Black Sea is one of the best examples of a highly stratified inland sea, and has the world's largest anoxic zone (90% of the water column). There is a permanent pycnocline at depths from 35-150 m (Ivanov et al. 2001), due to surface freshwater outflowing from many large rivers, and deeper saline water inflowing through the Bosphorus Strait (Sorokin 2002, Izdar and Murray, 1991). This pycnocline limits exchanges between surface and deep water, but is the most active zone of the sea in terms of oceanographic characteristics. Pollutant loadings to the Black Sea have been described by Zeri et al. (2000), and Tuncer et al. (1998). Rivers and industries along the Turkish coastline were identified as significant sources of Cu and Zn (SUMAE 1990). This is also the existing case in most of the southern Black Sea cities in Turkey (Table 1).

Table 1. Waste disposal applications in the southeastern Black Sea cities in Turkey.

Name of the City	Hopa	Rize	Trabzon	Giresun	Ordu	Samsun	Bafra	Sinop
Population	31,464	50,521	142,000	55,887	80,828	240,674	53,482	23,000
Quantity of Wastewater (x10^3m^3/d)	32	51	142	56	81	241	54	24
Quantity of Solid Wastes (x10^3kg/d)	2	30	200	80	70	450	100	5
Wastewater Treatment Plant	Absent	Absent	Absent	Absent	Absent	Absent	Absent	Absent
Solid Wastes Treatment Plant	Absent	Absent	Absent	Absent	Absent	Absent	Absent	Absent
Wastewater Disposal Method	Disposal to the Sea	Sea Outfall	Sea Outfall	Sea Outfall	Sea Outfall	Disposal to the Sea	Disposal to the Sea	Disposal to the Sea
Solid Waste Disposal Method	Seperation Land&Sea Disposal	Seperation	Seperation Land&Sea Disposal	Seperation	Seperation	Land Disposal	Seperation	Seperation Land&Sea Disposal
Problem of Finding Storage site for Solid Wastes	Serious	Serious	Serious	Serious	Serious	Sufficient Site	Sufficient Site	Serious
Solid Wastes Analysis Report	Absent	Absent	Exist	Absent	Absent	Absent	Absent	Exist
Wastewater Collection Network Adequacy	Not Sufficient	Sufficient	Not Sufficient	Sufficient	Sufficient	Not Sufficient	Not Sufficient	Not Sufficient
Pollution of Rivers	Not Serious	Serious	Serious	Not Serious	Not Serious	Not Serious	Not Serious	Not Serious
Pollution Along the Coastline	Serious	Serious	Serious	Serious	Serious	Serious	Serious	Serious
Sea Pollution	Serious	Serious	Serious	Serious	Serious	Serious	Serious	Serious

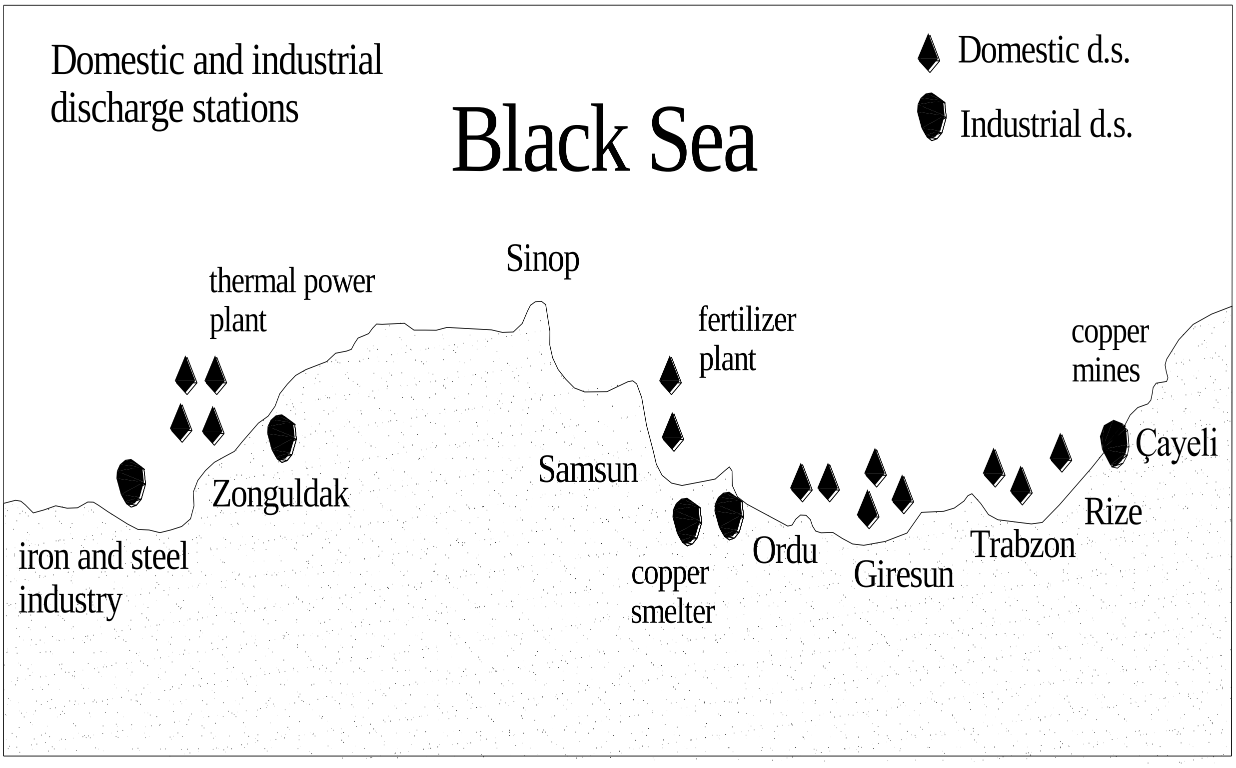
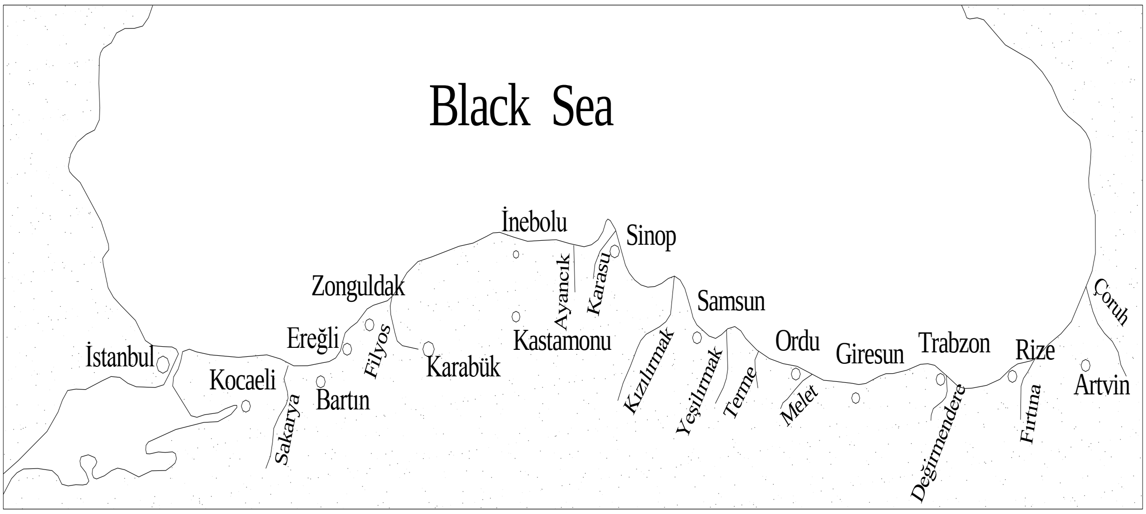


Fig.1. Waste discharging settlements at the South-Eastern Black Sea coast.



The shallow waters of the south coast of the Black Sea have been substantially affected by solid wastes and industrial and sewage discharges (Tuncer et al 1998, Mee and Topping 1998), plus inflows of nutrient chemicals such as nitrogen and phosphorus. There are five large industrial developments along the coast (Fig 1). There is an iron and steel complex (with a treatment plant) and a 600 MW thermal power plant near the city of Zonguldak A fertilizer plant and a copper smelter are located near Samsun, neither with treatment plants. The Cayeli Bakir Copper mine establishment near Rize has an outfall (STP) system discharging its waste at the 250m sea depth. There is substantial information about the overall oceanography of the Black Sea, and its current environmental state (Bakan 2000).

Trabzon as the major city in the area and Gumushane can represent this region in terms of solid waste characteristic (Table 2&3 and 4). This region is in short of appropriate landfilling sites for the disposal of solid wastes. Usable land is scarce and valuable with very high costs. Although the debatable suitability of some present landfilling sites in this area (Fig 2), attempts could not be successful to use them because of the received hard rejections from the people living nearby places. Although prohibited by law, unavoidable sea fillings with solid wastes along the coastline and direct sea disposal applications of the solid wastes have produced many unbearably risky environmental conditions (Berkun et al 2005).

Copper mining is the most important industrial activity in the southeastern part of the region, having serious polluting potential with submarine tailings placements in the Black Sea environment (e.g. Cayeli-copper Bakir mine). SUMAE (1990) indicated the existence of more than 0.1 mg/l copper concentrations in the southern Black Sea coastal waters.

Fig. 2. Schematic description of the proposed waste transport ways along the Black Sea coast of Turkey

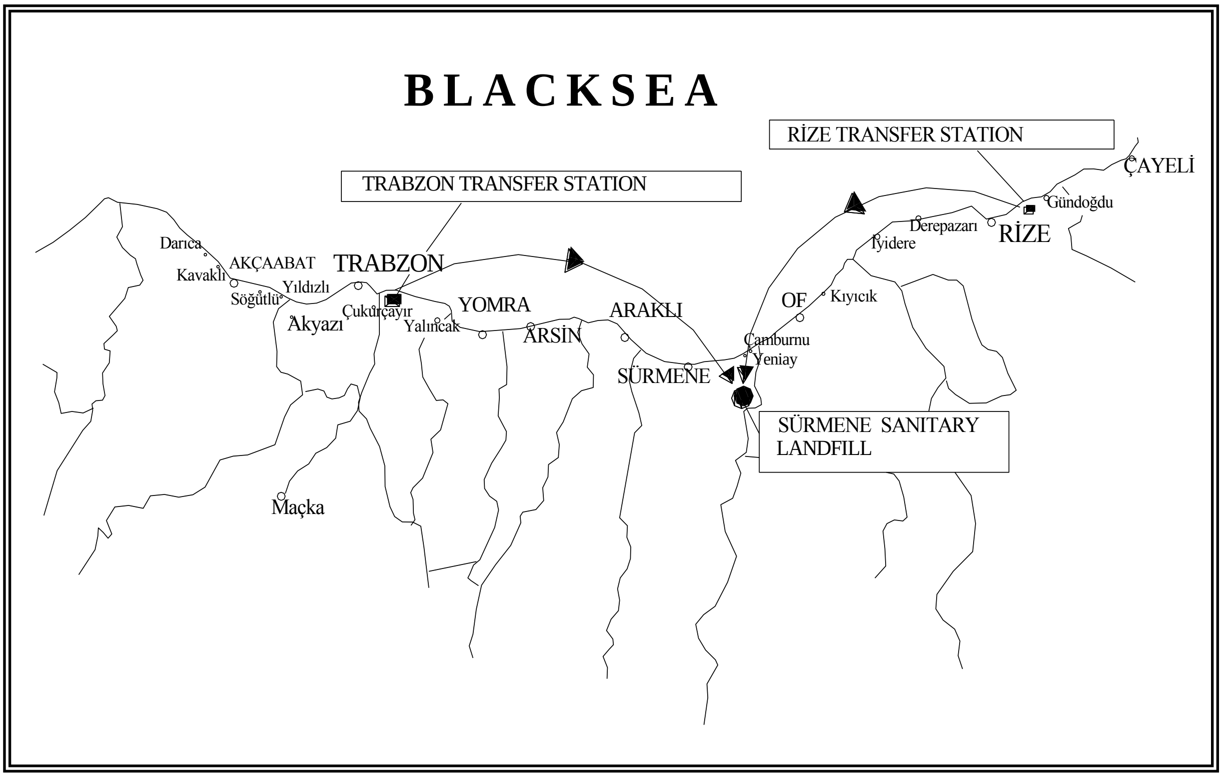


Table 2. Trabzon city's solid waste physical composition.

Metarial	% by weight (mean)	Standart Deviation
Paper - cartoon	6.08	4.68
Metal	51	0.41
Glass	80	0.70
Plastics	89	0.71
Textile	1.30	1.23
Ash	4.87	3.69
Organics	57.46	14.24
Other	28.1	15.94

Table 3. Trabzon city’s solid waste characteristics in comparison with other major cities in Turkey (Basturk 1981, Uluatam et al. 1984, Alyanak 1987)

City	p^H	C %	N %	C/N Ratio	Water Content %	L.cal Value kj/kg
Trabzon	6.32	35.12	0.51	68.50	76.25	1703
İstanbul	7.99	21.32	0.84	34.00	47.60	3773
Ankara	4.94	24.42	1.61	15.28	76.42	460
İzmir	6.94	25.50	1.20	27.50	50.25	1042

Table 4. Gumushane city's solid waste physical composition (Bayram 2005)

Meterial	Winter - Spring		Summer - Autumn	
	% by weight (mean)	Standart Deviation	% by weight (mean)	Standart Deviation
Paper - cartoon	7.1	3.0	12.5	5.8
Metal	1.7	2.0	1.5	1.2
Glass	2.4	1.1	4.2	1.7
Plastics	6.5	3.4	9.3	2.8
Textile	1.3	2.8	1.4	1.0
Ash	46.1	15.6	5.2	11.2
Organics	21.2	8.5	38.1	9.9
Other	13.7	8.0	27.8	12.8

3. Conclusions

The solid waste control regulation is applied properly in the stages of collection and transportation, but the main problem is preparation of the sanitary landfills and rehabilitation of the open dumps because of insufficient financing. On the other hand, in some parts of the metropolitan cities, the Medical Solid Waste Control Regulation is properly and efficiently applied by the cooperation of the healthcare institutions and the municipalities.

As the major city in the Southeastern Black Sea region, Trabzon's solid wastes have high organic carbon and low nitrogen content resulting unsuitably high C/N ratio for composting. This ratio is higher than the other metropolitan cities. Calorific values of the wastes of this city indicated an insufficient incinerating capacity with a high water content. So the landfilling followed with sufficient seperation and recovery seems as the most eligible waste disposal method. An appropriate composting technology can also be applied alternatively if solid waste characteristics are suitably adjusted for composting.

Transporting of the solid wastes to some central main storage areas at this region seems a difficult and costly task because of the hard topographic structure of the region. An integrated solid waste management program should urgently be prepared and applied to handle the solid wastes of the whole southeastern Black Sea region or by some regional separations efficiently. Besides metropolitan cities, integrated waste management applications did not seem eligible due to the mostly financial handicaps of the weak municipalities and the expected public shared investments in these low income areas.

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UTILIZATION OF THE RESIDUAL BRINES OF WATER DEMINERALIZERS

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Utilization of the residual brines of water demineralizers is one of the actual issues of water processing. Overflow brines of water demineralizers contain concentrated components of influent water.

In order to perfect the water demineralizers ecologically by the example of Caspian wather we had previously developed the method of overflow brines utilization basing upon substitution of the division stage of $NaCl – Na_2SO_4 – H_2O$ system because division of the pure chloride system simplifies the processing technology.

The purpose of these investigation was identification of possibility and effectiveness of application of this utilization method of mineralized waters varying from Caspian one.
The viewed utilization method is realized in such way: upon softening link the wather passes for desalination where besides the desalinated water residual brines also occur and get into crystallizer for processing with calcium – bearing solution got in the technological cycle where oversaturation on is achieved. Subsequently gypsum precipitates and gets into the filtering device and the mother solution in the precipitation tank is processed with lime milk. The magnesium hydroxide deposit gets filtrated and the residual solution ($CaCl_2$+NaCl) evaporates till 400 g/l. At this concentration the main part of NaCl gets crystallized and upon separation of NaCl crystals part of $CaCl_2$ with NaCl admixture gets stirred with the utilized brines for its desulfatization.

The specific feature of this technology is recirculation of a part of $CaCl_2$ into utilized brine. By the example of Caspian wather the thechnical and economic efficiency of offered thechnology is substantiated and the optimal unit discharge $CaCl_2$ is determined equal to 0,3-0,4 m^3/m^3 where a deep desulfatization (97-98 %) is gained. The residual concentration of sulfate – ion while processing of Caspian wather concentrates was 7-10 mg/equ/l.

This work covers a wide class of mineralized waters where the main soluble tasks included determination of the desulfatization stage and the optimal unit discharge of $CaCl_2$. The analytical investigations were realized in salt containing degree of 6-24 g/l with hardness from 20 to 60 mg – equ/l and shares of sulfate –ions in anion composition 0,1÷0,5. Absence of bicarbonate ions in the utilized brines was suggested. Salt – containing of the residual brines of water demineralizers entering for utilization regardless of the initial composition was accepted equal to 60 q/l. The concentration of recirculated brine $CaCl_2$ was 7500 mg – equ/l cwith few admixture of sodium chloride (200 mg – equ/l). The discharge unit of calcium chloride varied within 0,2÷0,5 m^3/m^3.

The accounting method based upon determination of the quantity of gypsum dropped from oversaturated solutions and identification of the balanced ion concentrations.

The pervious investigations testified that the most significant impact on the residual sulfate – ion composition is of the initial concentration of sulfate – ions.

The balanced residual calcium and sulfate – ion concentrations were determined from the following form:

$$C_{CaSO_4} = C_{SO_4^{-2}} - \left\{ \frac{C_{Ca^{2+}} + C_{SO_4^{2-}}}{2} - \sqrt{\left(\frac{C_{Ca^{2+}} + C_{SO_4^{2-}}}{2} \right)} - \left(C_{Ca^{2+}} \cdot C_{SO_4^{2-}} - \frac{f^2}{S_p} \right) \right\}$$

Hereby $C_{Ca}{}^{2+}$, $C_{SO_4^{2-}}$ - is concentration of the appropriate components, q – ion/l; f – ion activity coefficient; S_p – solubility product. Calcium sulfate solubility product was accepted as $4 \cdot 10^{-5}$ at the temperature 20-25^{0}C.

Considering the results of the preliminary accounts the technological restrictions for the desulfatization depth in order to exlude contamination of magnesium hydroxide with gypsum and promotion to scaling – free mode of the evaporator system in these investigations only the sulfate – ion concentrations were modified. The gained results as well as the ion composition of the processed mineralized waters are specified in the table.

The analysis of the gained results specified that the residual sulfate – ion concentrations while concentrates processing is 2-10 mg – equ/l.

From the technical and economic considerations selections of the optimal discharge unit of the calcium – bearing solution is necessary because as its increase both the capital and the unit discharges get higher.

But at the lower values of $CaCl_2$ discharge the needed desulfatization depth and getting pure MgO isn t achieved. For these investigations the optimal value of the $CaCl_2$ unit discharge (as specified in the table) is on the level of 0,4 m^3/m^3. Higher than this value modification of the $CaCl_2$ unit discharge insignificantly impacts on the residual sulfate – ion concentrations. The desulfatization depth is 97-78 %. The analysis testifies that the weak impact of the ion compositions of the utilized brines on the indices of desulfatization process can be explained with the high concentrations of the used $CaCl_2$ solution.

Thus, the investigations of the viewed class of mineralized waters discovered the optimal unit discharge $CaCl_2$ necessary for deep desulfatization of the water demineralizers concentrates. The investigation results significantly expand the opportunity of the known method of residual brines utilization and can be applied during projection of the economically and ecologically perfect technological water processing schemes allowing get chemical products of commercial quality simultaneously with desalinated water.

Table 1

Investigation results

Water types	Ion composition of the utilized brine, mg – equ/l					Residual sulfate – ion concentrations, mg-equ/l			
	Na^+	Ca^{2+}	Mg^{2+}	$Ca_{SO_4^{2-}}$	Cl^-	Volume of the recirculated $CaCl_2$ m^3/m^3			
						0,2	0,3	0,4	0,5
I	800	40	160	200	800	8	5	3	3
	800	80	120	200	800	7	5	3	3
	800	120	80	200	800	7	5	3	3
	800	40	160	400	600	9	6	4	2
	800	80	120	400	600	9	5	4	2
	800	120	80	400	600	8	5	3	2
	800	40	160	600	400	10	7	4	3
	800	80	120	600	400	10	6	4	3
	800	120	80	600	400	10	6	4	3
II	700	60	240	200	800	7	5	3	3
	700	150	150	200	800	7	5	3	3
	700	60	240	400	600	9	5	4	3
	700	150	150	400	600	8	6	4	3
	700	60	240	600	400	10	6	4	3
	700	150	150	600	400	10	6	4	3
III	600	80	320	200	800	7	5	3	3
	600	200	200	200	800	7	4	4	2
	600	80	320	400	600	9	6	4	3
	600	200	200	400	600	8	5	3	2
	600	80	320	600	400	10	6	4	3
	600	200	200	600	400	10	5	4	3
IV	800	50	150	100	900	7	4	3	2
	800	50	150	300	700	8	5	3	2
	800	50	150	500	500	10	5	4	3
	600	100	300	100	900	7	4	3	2
	600	100	300	300	700	8	5	3	2
	600	100	300	500	500	9	6	4	2

BIODEGRADATION OF AZO DYES

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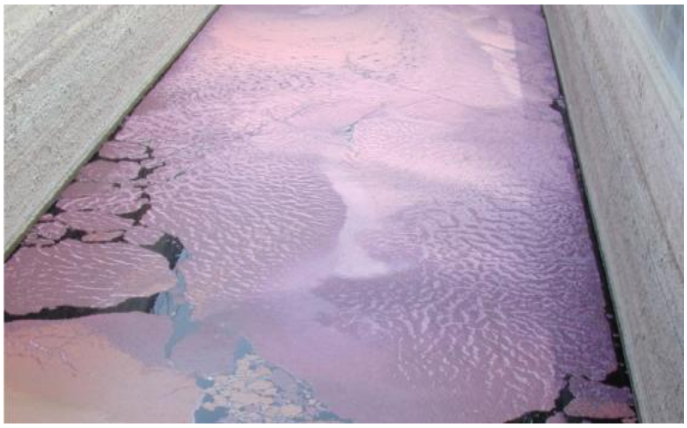
Aim

The aim of this study was to evaluate the potential of using white rot fungi for degradation of 7 azo dyes used in textile industries.

Why are textile waste waters problematic?

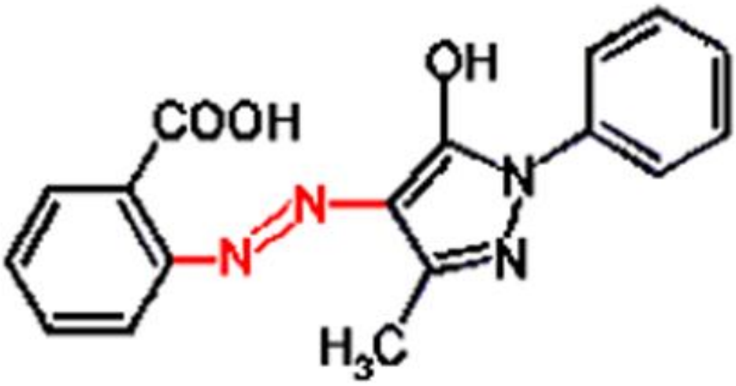
- When processing textiles considerable amounts of water and chemicals are used.
- Dyes are designed to resist water, light and chemicals and this makes them very persistent to biological degradation.
- Current chemical treatment methods are expensive or produce large amounts of solid waste.



Dye wastewater

Azo Dyes

- Azo dyes is the largest group of synthetic dyes and they are characterized by a nitrogen-nitrogen double bond.
- Cleavage of the azo bond results in decolourization of the compound.



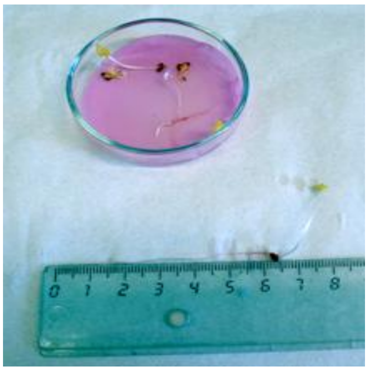
Example of the structure of an azo dye, with the azo bond in red.

How can white rot fungi be used to degrade dyes?

- In the nature white rot fungi degrade lignin, a component of wood, using extra cellular enzymes.
- Since the enzyme systems are non-specific the fungi can be used to degrade many persistent pollutants such as synthetic dyes.

Toxicity tests

Toxicity test were conducted using:



- Activated sludge (respiration test)
- *Lipedium sativum* seeds (germination test)

Toxicity at 500 mg/l.

	% respiratory inhibition	**% growth inhibition root**	**% growth inhibition stem**
Remazol Brilliant Yellow 3GL	0	13 ± 30	-14.0 ± 17
Remazol Yellow RR	15 ± 2	29 ± 30	-7.4 ± 20
Remazol Red RR	15 ± 0	40 ± 20	-17 ± 20
Remazol Blue RR	27 ± 6	0.8 ± 10	-7.0 ± 10
Yellow FN-2R	16 ± 5	19 ± 20	-1.9 ± 10
Red FN-2BL	23 ± 10	17 ± 20	-8.8 ± 10
Blue FN-R	78 ± 4	49 ± 20	-20 ± 30

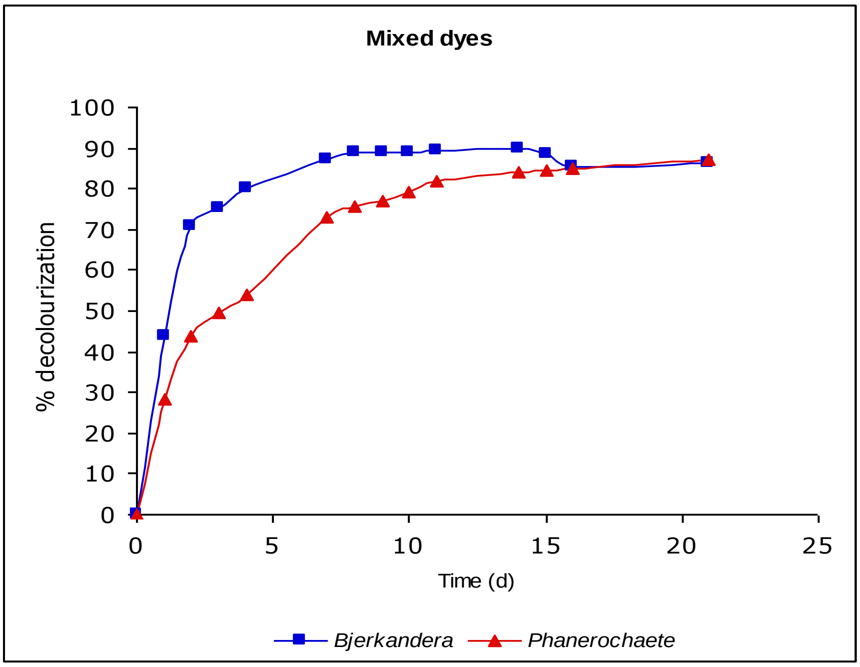
Degradation tests

- Bottles with 100 mg dye/l and 20 g malt extract/l were inoculated with *Trametes versicolor*, *Bjerkandera* sp. or *Phanerochaete chrysosporium.*
- A decolourization of 80-100% was achieved in 2 - 6 days depending on dye and fungi.

Degradation test

- A mixture of the dyes was decolourized by 90 % of both *Phanerochaete* and *Bjerkandera* sp.

- The absorbance at 280 nm was reduced by 90% suggesting the aromatic structures of the dyes were degraded.



Decolourization of a mixture of the dyes

Conclusions

➢ Both *Bjerkandera* sp. and *Phanerochaete Chrysosporium* were capable to decolourize and degrade the selected dyes.

➢ Fungal treatment represents an interesting and cost efficient alternative for the treatment of textile wastewaters.

PLANT SPECIES OF CMC MINING WASTE AREA AND HEAVY METAL ACCUMULATION

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CMC (Cyprus Mining Corporation) operated copper mine and associated facilities in Lefke-Gemikonagi until 1974. After CMC left the Cyprus Island, it left behind widespread piles of tailing deposits exposed to the environment, resulting in pollution of surrounding area with hazardous waste, including heavy metals. In our previous study, we have determined Cu, Fe, Ni, Pb concentrations in soil and in some naturally growing plant species such as *Acacia cyanophylla*, *Asparagus* sp., *Atriplex semibaccata, Juncus* sp., *Phagnalon rupestre, Pistacia terebinthus*, *Polygonum equisetiforme*, *Tragopogon sinuatus* around one selected copper flotation tailing pond (#11B). Heavy metal accumulations, particularly Cu and Fe, have been found high in the above ground parts of *Acacia, Atriplex* and *Juncus*. We have assumed that *Atriplex, Acacia* and *Juncus* may be thought as bioindicator, hyperaccumulator and tolerant species, which may be used for phytoremediation to recover the contaminated CMC area.

In this study, we aimed to determine the other naturally growing plant species from all around the CMC area and heavy metal accumulations (Cu, Fe, Ni, Cd, Pb) in these plant species to detect the degree of pollution, hyperaccumulation and tolerance. Plant species of the mining waste were determined as: *Erodium gruinum*, *Polygonum* sp., *Pistacia lentiscus*, *Prasium majum, Erodium malacoides, Malva nicaensis, Aethiorhiza bulbosa, Sonchus oleraceus, Inula viscosa, Oxalis pes-caprae, Senecio vulgaris, Serapias vomeracia, Lantana camara* and *Cupressus* sp.. Among these species, the highest Cu concentrations were detected in *Erodium gruinum* (74,77 mgkg^{-1}dw) and *Oxalis pes-caprae* (68,08 mgkg^{-1}dw); Fe in *Erodium malacoides* (765,4 mgkg^{-1}dw) and *Oxalis pes-caprae* (696,7 mgkg^{-1}dw); Ni in *Pistacia lentiscus* (31,16 mgkg^{-1}dw); Cd in *Erodium gruinum* (46,68 mgkg^{-1}dw) and *Erodium malacoides* (69,98 mgkg^{-1}dw); Pb in *Erodium gruinum* (0,065 mgkg^{-1}dw) and *Cupressus* sp. (0,135 mgkg^{-1}dw). *Erodium* spp. and *Oxalis* sp. seem quite tolerant as well as they have accumulated high levels of heavy metals, particularly Cu and Fe, which are found in the range of excessive or toxic concentrations (Cu: 20-100 mgkg^{-1}dw; Fe: >300-500 mgkg^{-1}dw) for plants.

Introduction

CMC (Cyprus Mining Corporation) operated copper mine and associated facilities in Lefke-Gemikonagi until 1974. After CMC left the Cyprus Island, it also left behind widespread piles of tailing deposits exposed to the environment, resulting in pollution of surrounding area with hazardous waste, including heavy metals. In our previous study, we determined Cu, Fe, Ni, Pb concentrations in soil and in some plant species **(*Acacia cyanophylla*, *Asparagus* sp., *Atriplex semibaccata*, *Juncus* sp., *Phagnalon rupestre*, *Pistacia terebinthus*, *Polygonum equisetiforme*, *Tragopogon sinuatus*)** around #11B copper flotation tailing pond (Baycu et al., 2005). In this current study, we aimed to determine the other naturally growing plant species from all around the CMC area and heavy metal concentrations (Cu, Fe, Ni, Cd, Pb) in those plants to detect the degree of pollution, accumulation and tolerance.

Materials and Methods

Plant sampling:

Naturally growing plants species of CMC area were collected by S.Guran (Ecological Garden, Gonyeli) and they were identified by Prof.Dr.K.Alpinar from Istanbul University, Pharmaceutical Botany Dept..

Heavy metal determinations:

Plant samples were dried and wet-digested with HNO_3 (Sastre et al., 2002, modified). The obtained suspensions were filtered, diluted and final solutions were analyzed for Cu, Fe, Ni, Cd, Pb using flame AAS. The results were calculated on dry weight basis (mg kg^{-1} dw).

Table 1.

Some of the plant species of CMC area and heavy metal accumulation (mg kg^{-1} dw).

No.	Plant Species	Cu	Fe	Ni	Cd	Pb
1	*Aethiorhiza bulbosa*	9,295	127,915	0,68	0,82	0,035
2	*Cupressus sp.*	20,24	536,5	1,875	3,48	0,135
3	*Erodium gruinum (L.) L'Hérit.*	74,765	236,415	14,25	46,68	0,065
4	*Erodium malacoides*	12,795	765,35	1,795	69,98	0,08
5	*Inula viscosa Ait.*	21,41	652,1	2,105	5,11	0,045
6	*Lantana camara*	1,435	59,945	1,365	1,63	0,015
7	*Malva nicaensis All.*	11,72	377,375	2,01	5,35	0,055
8	*Oxalis pes-caprae L.*	68,075	696,7	4,685	27,9	0,01
9	*Pistacia lentiscus*	3,09	517,6	31,155	11,875	0,015
10	*Polygonum sp.*	16,89	192,905	0,49	16,64	0,01
11	*Prasium majum L.*	9,4	413,51	0,26	0,31	0,035
12	*Senecio vulgaris*	183,7	542,9	5,515	19,61	0,045
13	*Serapias vomeracia*	14,59	588,5	1,645	3,43	0,01
14	*Sonchus oleraceus*	5,265	604,05	0,9	0,17	0,04

Results

Plant species of the mining waste were determined as:
Aethiorhiza bulbosa, Cupressus* sp., *Erodium gruinum, Erodium malacoides, Inula viscosa, Lantana camara, Malva nicaensis, Oxalis pes-caprae, Pistacia lentiscus, Polygonum* sp., *Prasium majum, Senecio vulgaris, Serapias vomeracia, Sonchus oleraceus (Table 1).

Among these species:
The highest Cu concentrations were detected in ***Erodium gruinum*** (74,77 mgkg^{-1}dw) and ***Oxalis pes-caprae*** (68,08 mgkg^{-1}dw); Fe in ***Erodium malacoides*** (765,4 mgkg^{-1}dw) and ***Oxalis pes-caprae*** (696,7 mgkg^{-1}dw); Ni in ***Pistacia lentiscus*** (31,16 mgkg^{-1}dw); Cd in ***Erodium gruinum*** (46,68 mgkg^{-1}dw) and ***Erodium malacoides*** (69,98 mgkg^{-1}dw); Pb in ***Erodium gruinum*** (0,065 mgkg^{-1}dw) and ***Cupressus* sp.** (0,135 mgkg^{-1}dw).

Conclusion

***Erodium* spp**. and ***Oxalis* sp.** seem quite tolerant as well as they have accumulated high levels of heavy metals, particularly Cu and Fe, which are found in the range of excessive or toxic concentrations (Cu: 20-100 mgkg^{-1}dw; Fe: >300-500 mgkg^{-1}dw) for plants (Kabata-Pendias & Pendias, 1986).

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GALVANIC WASTE WATER TREATMENT WITH CHELATING MACROPOROUS COPOLYMER AT STATIC AND DYNAMIC CONDITIONS

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Galvanic wastewaters contain hydroxides, hydrate oxides and metal salts (chromium, nickel, zinc, cadmium, tin, lead, copper, etc.) used in finishing operations, which present environmental hazard. The processes for separation and recovery of metals from wastewaters include: precipitation, adsorption and biosorption, electrowinning, electrocoagulation, membrane separation, solvent extraction and ion exchange [1,2]. The removal of heavy metals with chelating copolymers, consisting of crosslinked copolymer (solid support) and functional group (ligand) with N, O, S and P atoms capable for coordinating different metal ions, is very convenient and simple process, reduced only to filtration as the regeneration step [3].

In this study, four samples of PGME with different specific pore area and pore diameter, were synthesized by suspension copolymerization and functionalized with ethylene diamine, diethylene triamine and triethylene tetramine. The static and dynamic experiments were applied to quantify the influence of porosity of copolymer samples and type of the attached ligand on capacity and selectivity of amino-functionalized PGME for Cu(II), Ni(II) and Zn(II) sorption from single- and multicomponent galvanic solution. Two parameters mass transfer Thomas model was applied for describing the adsorption process in the column. The rapid sorption and high sorption capacities make amino-functionalized PGME perspective for the galvanic wastewater treatment.

INTRODUCTION

Galvanic wastewaters contain many chemical compounds like hydroxides, hydrate oxides and metal salts used in finishing operations (chromium, nickel, zinc, cadmium, tin, lead, copper, etc.) which present environmental hazard. The processes for separation and recovery of metals from wastewaters include: precipitation, adsorption and biosorption, electrowinning, electrocoagulation, cementation, membrane separation solvent extraction and ion exchange [1,2]. The removal of heavy metals with chelating copolymers, which consist of crosslinked copolymer (solid support) and functional group (ligand) with N, O, S and P atoms capable for coordinating of different metal ions, is very convenient and simple process, reduced only to filtration as the regeneration step [3].

Also, the process neither produces waste materials, nor generates secondary pollutants, which makes it very attractive from the ecological point of view.

Macroporous copolymers with desired functional groups could be obtained by copolymerization of monomers that already contain selective functional groups, or by additional modification of synthesized macroporous copolymer. Crosslinked macroporous poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) [abbreviated PGME] is convenient for chemical modification due to the presence of reactive epoxy group in GMA molecule [4]. The reaction with amines yields hydrophilic amino-fictionalized copolymers with high selectivity, capacity and sorption rate, as well as mechanical and chemical stability.

In this study, four samples of PGME with different porosity (specific pore area and pore diameter) were synthesized by suspension copolymerization and additionaly functionalized via ring-opening reaction of pendant epoxy groups with ethylene diamine, diethylene triamine and triethylene tetramine. The experiments under static and dynamic conditions were applied to quantify the influence of porosity of copolymer samples (specific surface area and pore diameter) and type of the ligand attached to PGME on capacity, breakthrough time and selectivity of amino-functionalized PGME. Static experiments showed rapid sorption of heavy metal ions, with the sorption half time of approximately 5 min, while the maximum sorption was reached within 30 minutes.

Further, amino-functionalized macroporous PGME poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) [abbreviated PGME] was tested for Cu(II) sorption from single component solution as well as Cu(II), Ni(II) and Zn(II) sorption from galvanic solution.
The two parameters mass transfer Thomas model was applied to describe the breakthrough curves obtained in column experiments.

The rapid sorption, high sorption capacities and easy regeneration make amino-functionalized PGME perspective for the galvanic wastewater treatment.

EXPERIMENTAL

Preparation of PGME

Four samples of macroporous PGME with different porosity parameters were prepared by a radical suspension copolymerisation in the presence of inert component, as described elsewhere [5]. In the labels of copolymer samples, letter S designate suspension copolymerization, G and E stand for monomers (GMA and EGDMA). The first number in a sample labels stands for the share of aliphatic alcohol in the inert component (w/w) and the second one for the number of C-atoms in the aliphatic alcohol. The copolymerization was carried out at 70 ^{0}C for 2 h and at 80 ^{0}C for 6 h with a stirring rate of 200 rpm. After completion of the reaction, the copolymer particles were washed with water and ethanol, then kept in ethanol for 12 h and dried in vacuum at 40 ^{0}C. The resulting crosslinked beads were sieved and purified by Soxhlet extraction with ethanol. Fractions with average particle diameter (D) in the range 0.15-0.50 mm were used in subsequent reactions.

Functionalization of PGME with ethylene diamine

Four grams of poly(GMA-*co*-EGDMA) (samples SGE-10/12, SGE-20/14 and SGE-20/16), 10.0 g of ethylene diamine and 100 cm^3 of toluene was left at room temperature for 24 h. The reaction mixture was heated at 80 ^0C for 6 h. Modified samples were filtered, washed with ethanol, dried and labeled as SGE-10/12-en, SGE-20/14 and SGE-20/16- en (additional lable -en designate sample modified with ethylene diamine).

Functionalization of PGME with diethylene triamine
A mixture of 3.6 g of poly(GMA-*co*-EGDMA) (sample SGE-10/16), 15.7 g of diethylene triamine and 100 cm^3 of toluene was left at room temperature for 24 h, then heated at 80 ^0C for 6 h. Modified sample was filtered, washed with ethanol, dried and labeled as SGE-10/16-deta (additional lable -deta designate sample modified with diethylene triamine).

Functionalization of PGME with triethylene tetramine
A mixture of 5.0 g of poly(GMA-*co*-EGDMA), 7.75 g of triethylene tetramine and 30 cm^3 of toluene was left at room temperature for 24 h, then heated at 80 ^0C for 6 h. Modified samples was filtered, washed with ethanol, dried and labeled as SGE-10/16-teta (additional lable -teta designate sample modified with triethylene tetramine).

- The pore size distributions of initial and amino-functionalised samples were determined by mercury porosimetry (Carlo Erba 2000, software Milestone 200).
- The concentration of metals was determined by atomic absorption spectrometry (AAS, SpektrAA Varian Instruments).

Metal-uptake and regeneration experiments

Sorption of heavy metal ions was investigated in static and dynamic experiments, at room temperature.

Static experiments

- Determination of Cu(II) sorption rate: 0.5 g of copolymer was contacted with 50 cm^3 of metal salt solution (0.05 M). At appropriate times, 1 cm^3 of aliquots were removed and diluted to 100 cm^3. The remaining solutions were kept for AAS analysis.
- Determination of Zn(II), Cu(II) and Ni(II) sorption rate: 0.5 g of copolymer was contacted with 50 cm^3 of galvanic solution which contained: 1.79 $mmoldm^{-3}$ of Ni(II), 0.86 $mmoldm^{-3}$ of Cu(II) and 0,007 $mmoldm^{-3}$ of Zn (II) ions (at pH 4.5). At appropriate times, 1 cm^3 of aliquots were removed and diluted to 100 cm^3. The remaining solutions were kept for AAS analysis.

- The amount of metal ions sorbed onto unit mass of macroporous copolymer beads (sorption capacity, mmol/g) was calculated by using the following expression:

$$Q = \frac{(C_0 - C) \times V}{m} \qquad (1)$$

where C_0 and C are the concentrations of the metal ions in the initial solution and in the aqueous phase after treatment for certain period of time, respectively (in $mmoldm^{-3}$), V is the volume of the aqueous phase (in dm^3) and m is the amount of the poly(GMA-*co*-EGDMA) amino-functionalized beads used for the experiment (in g).

Dynamic experiments

A total of 2.8 g of amino-functionalized PGME sample was placed in a glass column (inner diameter of 20 mm, length of 300 mm). The solutions [a) single component, 62.5 $mmoldm^{-3}$ Cu(II) solution or b) galvanic solution with initial concentration of 1.79 $mmoldm^{-3}$ of Ni(II), 0.86 $mmoldm^{-3}$ of Cu(II) and 0,007 $mmoldm^{-3}$ of Zn (II) ions] were passed through column at flow rate of 5 cm^3min^{-1}, at pH 4.5. The concentrations of metal ions were determined as described above.

RESULTS AND DISCUSSION

Kinetics

One of the most important properties of the chelating polymers for potential application is the rate of establishing of the equilibrium metal sorption. For this purpose, sorption rate for Cu(II) ions on PGME samples functionalized with ethylene diamine, diethylene triamine and triethylene tetramine was determined. The results are presented in Figure 1. Porosity parameters (values of specific pore volume, V_S, and pore diameter that corresponds to half of the pore volume, $d_{V/2}$ and specific surface area, S_{Hg}) were calculated from data collected by mercury porosimetry as described in the literature [6,7].

Table 1. Porosity parameters of initial and amino-functionalized poly(GMA-co-EGDMA) samples.

Sample	S_{Hg}, m^2/g	V_S, cm^3/g	$d_{V/2}$, nm
SGE-10/12-en	70	1.18	42
SGE-10/16-en	55	0.65	31
SGE-10/16-deta	50	0.66	29
SGE-10/16-teta	53	0.61	30

Non-competitive sorption from single-component Cu(II) solution

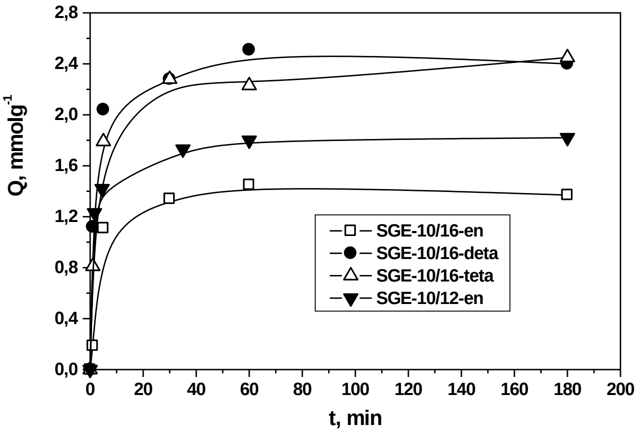


Fig. 1. Sorption of Cu(II) ions vs. time, on amino-functionalized PGME samples (metal ions initial concentration 0.05 moldm^{-3}, pH = 4).

- Sorption of Cu(II) ions was very rapid. Namely, amino-functionalized PGME samples sorbed approximately 80 % and 90 % of Cu(II) ions after 5 and 30 minutes, respectively.
- The high initial rate for Cu(II) uptake suggests that the sorption process occurs predominantly at the surface of the highly crosslinked amino-functionalized beads [8]. Also, hydrophilicity of the macroporous copolymer facilitates the interaction of the copolymer with the solution, as well as the coordination of the metal ions due to the presence of heteroatoms (N and O) [9].
- The sorption half time, $t_{1/2}$, defined as the time required to reach 50% of the total sorption capacity, was of the order of 1 min.
- The sample SGE-10/16-en showed somewhat slower sorption, with $t_{1/2}$ value of 5 min.

The effect of the type of amino-ligand

- Maximum sorption capacity of amino-functionalized PGME depends on the type of the ligand (See Fig. 1). Namely, the maximum capacites for Cu(II) ions on SGE-10/16-deta and SGE-10/16-teta are 1.75 times higher then for SGE-10/16-en. It seems that further improvement in sorption kinetics was not achieved by functionalization with triethylene tetramine, since no difference in maximum sorption capacities between samples SGE-10/16-deta and SGE-10/16-teta was observed.

The effect of porosity parameters

- Porosity parameters also affect the sorption rate and capacity of Cu(II) ions on PGME functionalized with ethylene diamine. The maximum Cu(II) sorption capacity for SGE-10/12-en is 1.3 times higher than for SGE-10/16-en (See Table 1).

Competitive sorption from multi-component Ni(II), Cu(II) and Zn(II) galvanic solution

- The sorption of Ni(II) and Cu(II) ions from multicomponent galvanic solution, under static conditions on sample SGE-10/12-en is rapid (Fig. 2), with $t_{1/2}$ values of 0.5 and 2 min, respectively. However, Zn(II) sorption is considerably slower, with $t_{1/2}$ of 10 min.
- Maximum sorption capacities, after 180 minutes were 0.39 mmolg^{-1}; 0.34 mmolg^{-1} and 0.035 mmolg^{-1}, for Ni(II), Cu(II) and Zn(II) ions, respectively.
- Although SGE-10/12-en has apparently highest capacity for Ni(II) ions, the actual amount of sorbed Ni (II) ions is twice lower than that of Cu(II) ions. The amount of sorbed Zn(II) ions is negligible, as previously reported [4].

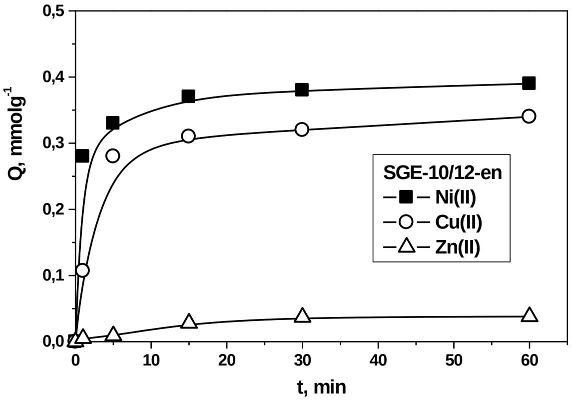


Fig. 2. Sorption rate of Ni(II), Cu(II) and Zn(II) ions on SGE-10/12-en (metal concentration in galvanic solution: 1.79 mmoldm^{-3} of Ni (II); 0.86 mmoldm^{-3} of Cu(II) and 0.007 mmoldm^{-3} of Zn (II) ions, pH 4.5).

Dynamic experiments

In order to examine potential application of PGME-en samples in hydrometallurgy, sorption studies were carried out under dynamic conditions. Data were treated with Thomas model, one of the commonly used methods in column performance theory [10]:

$$\ln\left(\frac{C_0}{C}-1\right)=\frac{k_T q_0 W}{Q}-\frac{k_T C_0}{Q}V_{out} \qquad (2)$$

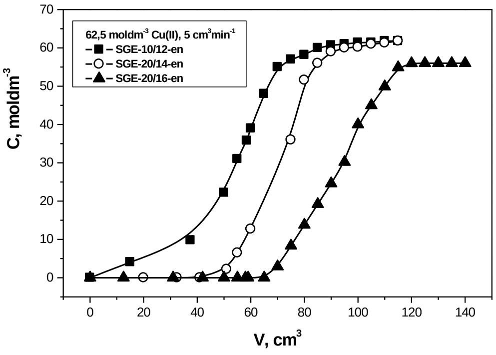
where C_0 is the inlet metal concentration (molm^{-3}), C the outlet concentration at time t (molm^{-3}), k_T is the Thomas rate constant (m^{3}mol^{-1}min^{-1}), Q the volumetric flow rate (m^{3}mol^{-1}), q_0 the maximum copolymer phase concentration of metals equivalent to an equilibrium liquid concentration of C_0 (molkg^{-1}), W the amount of copolymer in column (kg) and V_{out} is the effluent volume.

The kinetic parameter k_T and the exchange capacity q_0 was determined from a plot $\ln\left[(C_0/C)-1\right]$ versus t at a given flow rate and initial concentration:

$$\ln\left(\frac{C_0}{C}-1\right)=k\left(-t\right) \qquad (3)$$

Non-competitive sorption from single-component Cu(II) solution

Figure 3. shows the breakthrough curves of Cu(II) passing through PGME samples with different porosity functionalized with ethylene diamine.



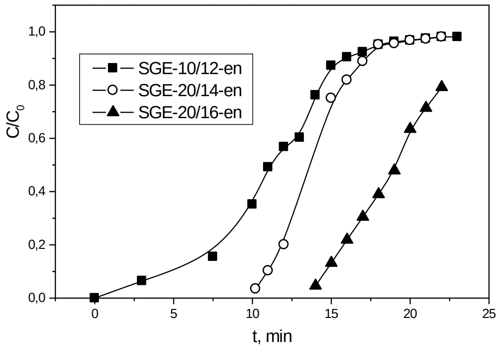


Fig. 3. Breakthrough curves of Cu(II) through the column packed with SGE-10/12-en, SGE-20/14-en and SGE-20/16-en (metal concentration: 62.5 mmoldm^{-3} of Cu(II), pH 4.5, volumetric flow 5 cm^{3}min^{-1}).

- Breakthrough curves for samples with higher specific surface area (SGE-10/12-en and SGE-20/14-en) are sharper then for SGE-20/16-en.
- The break points (the point at which $C/C_0 = 0.05$) were slower when specific surface area of amino-functionalized PGME decreases.

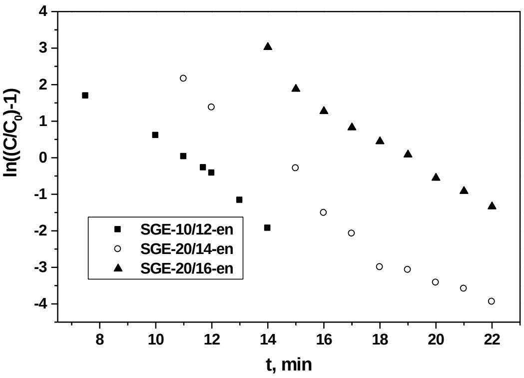


Fig. 4. Typical plot for determination of the Thomas parameters (the solution conditions and flow rate were the same as described in Fig.3).

Table 2. Thomas parameters calculated for Cu (II) sorption and specific surface area for PGME-en samples.

Sample	S_{Hg}, m^2/g	Break point, min	$k_T \cdot 10^{-3}$, m^{3}mol^{-1}min^{-1}	τ, min
SGE-10/12-en	70.0	2.11	6.47	10.7
SGE-20/14-en	48.6	10.5	9.78	14.4
SGE-20/16-en	19.8	14.2	8.00	19.0

- The value of k_T decreases with the increase of specific surface area.
- The values of τ (time when $C = C_0/2$) are acceptable for practical application.

Competitive sorption from multi-component Ni(II), Cu(II) and Zn(II) galvanic solution

Figure 4 shows the breakthrough curves of Ni(II), Cu(II) and Zn(II) ions passing through through the column packed with SGE-10/12-en.

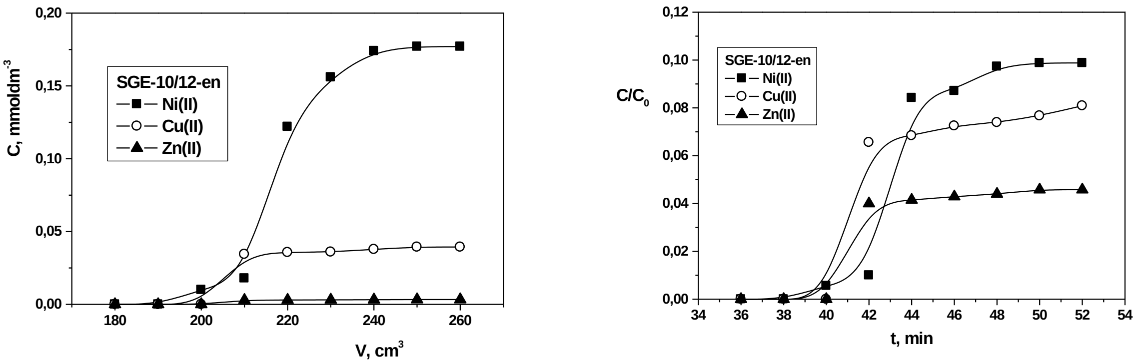


Fig. 4. Breakthrough curves of Ni(II), Cu(II) and Zn(II) ions through the column packed with SGE-10/12-en (metal concentration: 1.79 mmoldm^{-3} of Ni (II); 0.86 mmoldm^{-3} of Cu(II) and 0.007 mmoldm^{-3} of Zn (II) ions, pH 4.5; volumetric flow 5 cm^{3}min^{-1}).

- Breakthrough curves for Cu(II) sorption is somewhat sharper than for Ni(II) and Zn(II).
- PGME-en has higher capacity for Ni(II) ions (0.18 mmoldm^{-3}) then for Cu(II) ions (0.070 mmoldm^{-3}), with insignificant amount of sorbed Zn(II) ions (0,003 mmoldm^{-3}).
- The value of k_T decreases with the increase of specific surface area.
- The values of τ (time when $C = C_0/2$) are slow for practical application.

Table 3. Thomas parameters calculated for Ni(II), Cu(II) and Zn(II) sorption, calculated by Thomas model and specific surface area for SGE-10/12-en.

Metal ions	$k_T \cdot 10^{-3}$, m^{3}mol^{-1}min^{-1}	τ, min
Ni(II)	0.300	48.7
Cu(II)	0.0198	238.0
Zn(II)	0.230	391.7

- The obtained results demonstrate the strong selectivity of used chelating copolymer for Cu(II) over other metals.
- The rapid sorption and high sorption capacities make amino-functionalized PGME perspective for the galvanic wastewater treatment.
- However, further optimisation of porosity and ligand chelating characterictics is needed in order to develop selective and efficient sorbent for galvanic solution treatment.

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THEORETICAL SUBSTANITATION OF PROCESS OF RECTIFICATION OF OIL-POLLUTED SOIL.

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The ways and methods of mechanical, chemical and physico-chemical influence making sense for elaboration of technology on rectification of oil-polluted soil, based on washing of oil contaminant by means of water, concentrated in remote, hydrophobic sites of pores and capillaries of aggregated structure of the soil have been theoretically proved. Set of used ways and methods as a whole is defined by the necessity to provide water, as oil washing agent on rectified surfaces of soil minerals, with conditions favorable for it, as well as maximum access to oil-contaminant, allocated in difficult to access areas in pores and capillaries.

Washing process represents a complex of compound effects with a big variety and nature of contamination in composition, in different nature of washed surfaces and variety of changes in physico-chemical characteristics of cleansers. In works [1-3] general conceptions about role of moistening and adhesion in washing effect are presented and physical and chemical analyses of powers, forming on three-phase interface in the system “detergent-washed surface-oil pollution” has been carried out. Quantitative link of the energy of process, i.e. mechanical work required for rectification with basic physico-chemical characteristics of detergents and washed surfaces has been shown. In [4] on the base of thermodynamic analyses of changes in free energy of the system “solid surface-oil contamination-washing solution” relevant equation for quantitative evaluation of the mechanical work, required for entirely separation of contamination from washed surface and its disintegration into drop state has been derived. In [5] relevant equations related to mechanical work on separation of remaining of oil contamination from solid surface had been derived, the role of emulsification and moistening in complex process of washing effect was theoretically substantiated. Results of numerous investigations, drawn conclusions and technical substantiations known up to present time, are connected with the study of processes of washing of oil contaminants from textile fabric and polished metal surface, wash of bituminous sands, or the processes of displacement of oil from oil-saturated sands during deep-laid oil production under the conditions of high pressures and temperatures.

Although rectification of oil-polluted soil through wash of oil contaminant from surfaces of mineral particles through its wash by water solution is in compliance with the basic rules of known processes, however specific characteristics of investigated objects, i.e. oil-polluted soil with a variety of minerals and characteristics in its composition, as well as necessity to carry out the washing process in spare, mild conditions with regard to temperature and pressure for preserving its viability, requires special approaches in solving the put by problem and special analyses during the optimization of the process as a whole.

Before pollution takes place oil-polluted soils consist mainly of polydisperse, poly-mineral and hydrophilic particles with intermediate pores and capillaries partially or fully thick with oil contaminant. Oil covers separated mineral particles, penetrates into spaces between them, or settles on separate aggregates, formed by these particles, penetrating their pores and capillaries. Inside the aggregated structure contains immobilized in structural net liquid phase (oil and water) with heterogeneous allocation of phases in the volume.

Numerous investigations prove an aligning effect of solid surface of minerals on the interface layer of liquid that covers them [6-8]. Adhesion of liquid is caused by molecular interaction, which appears on interface of phases “liquid-solids”, adhesive interaction between liquid and soil phases is allocated on a short distance into the depth of liquid, measured by molecular sizes. As the layer of liquid is removed from solid surface the adhesive interaction decreases, giving its place to cohesive interaction [9]. With consideration of the above-mentioned during the pollution of soil by petrol its active components, such as organic acids, phenols, pitches, pyrobitumen and others, being adsorbed on the surface of minerals that compose the soil, form boundary layer with firm molecular bond. This thin layer of oil being under the influence of minerals has irregular characteristics with conservative values of density and viscosity in comparison to oil contained in the volume, and which in its turn, interacting with the surface of minerals, waterproofs it. Water-repelled mineral particles irreversibly coagulate as a result of partial adsorption of stabilizing hydrate cover from their surface. Oil-polluted soil, stratified on water surface during sedimentation analyses, does not sink, and due to its hydrophobic property floats on surface. Thus, appearance of boarding adsorption layer on the surface of minerals is connected with adsorption of surfactant substances constituting a component part of oil. A thickness of adsorption boarding layer in this case is many times less than thickness of the layer of oil covering [10-11], formed through increment of its volume by oily layers with peculiar natural characteristics (unlike adsorption boarding layer). Changes of characteristics of oil layer covering mineral particles will depend on terms of soil pollution. The longer this term is, the more significantly will change the composition and characteristics of oil contaminating the soil under influence of environment and climatic conditions [12-13].

The above-mentioned ways and methods of mechanical, chemical and physico-chemical effects have been resulted from the above-stated nature of oil-polluted soil and characteristics of oil contaminant, covering the surface of minerals that form the soil, in the form of film of boundary layer with firm molecular bond and oil layer stratified on it. These ways and methods constitute the essence of eliminated technology for rectification of oil-polluted soil, based on water wash of oil contaminant concentrated in hydrophobic areas of pores and capillaries of the aggregated soil structure that are difficult of access.

The set of applied ways and methods in the whole is determined by necessity during clearing of mineral surface of the soil to provide water, as oil-sweeper agent, favorable conditions as well as maximum access to oil contaminant contained in suppressed and difficult to access areas of pores and capillaries. With this purpose in the process of preparation of the soil to rectification it is necessary to combine chemical, physico-chemical and mechanical effects, the main goal of which is to peptize all fine particles and create conditions for entire separation of all particles of the soil and release of components of sand, dust, clay and colloids from aggregate and micro-aggregate states.

For access of water into hydrophobic capillaries and pores of oily rock a certain back pressure, pressurization pressure must be overcome [14]:

$P_{pre} = (1/r_1 + 1/r_2) \cdot \sigma_{12} \cdot \cos\theta$, where

r_1 and r_2 – are radius of water pore and drop correspondingly; σ_{12} – surface tension on the boarder of two immiscible liquids (oil-water); θ – contact angle of moistening; P_{pre} – pressurizing pressure.

The smaller the pores where drops contain residual oil are, the more pressure gradient for their displacement by water is demanded. For rectification of oil-polluted soil (in non gradient pressure conditions) displacement of residual oil from small pores becomes impossible because of their inaccessibility for displacing water. Thus, the degree of destruction of the system of pores and capillaries in the aggregated structure of oil-polluted soil can be reviewed as criteria of effectiveness of influence on disperse system in the process of oil wash, and destruction limit may be reviewed as optimal level of these effects. The put by problem is solved through usage of complex methods of combined chemical, physico-chemical and mechanical effects on structured disperse systems of mineral particles of the soil. When oil-polluted soil possesses equal chemico-mineralogical composition the effectiveness of its rectification has to rise with the increase of dispersibility of mineral particles of the soil. Methods of increase of dispersibility are connected with influence on different powers, linking mineral particles into unified system of structured formations, such as coagulation, condensation-crystallization and mixed-coagulated-crystallized macro-and micro aggregates [15]. To make possible realization of mass exchanged processes during the influence of organic solvent and washing water solution on oil stick allocated on surface, it is necessary to destroy the structure and all aggregates from particles with their entire disconnection (splitting all bonds, contacts) and release liquid phase immobilized and irregularly allocated in the volume from structural net. During intensive mechanical effects the strength cohesion between particles breaks, using for this purpose effects of adsorptive reduction of strength of the structure in presence of surfactant environment ("Rebiner effect") [16]. At the same time aggregates on initial particles destroy and structural bonds break. In this case watering of the surface of particles will be realized not under the control of capillary suction, but in consequence of diffusion processes and, thus making possible significant increase of bound water and increase particles' hydrophily. The character of water distribution depends not only on adsorption characteristics of the surfaces of solid phase, but also on its dispersibility as well as evenness of reciprocal distribution of liquid and solid phases in micro – macro volumes of the system.

In the process of rectification of oil-polluted soil through washing of the surface of mineral particles by water solution, hydrophysics of particles of the soil serve as determining process, as during the displacement of oil by water the surface of particles transfers from mosaic with presence of hydrophilic and hydrophobic areas under common hydrophoby of the system into whole hydrophilic.

As an example for chemical method of effect on oil-polluted soil may serve displacement of Ca and Mg ions from exchangeable complex of clay minerals and their replacement to Na^+ ions, that leads to dispersion of waterproof and veritable aggregates, sintered by calcium and magnum. Increase of pH environment of suspension of the soil up to 8,0-8,5 resulting in recharge of electropositive hydrates of Al and Fe oxides leads to destruction of isoelectric aggregates, formed by them jointly with electronegative particles, such as silica and clay minerals.

Besides, in order to achieve high washing degree of oil-polluted soil organic solvent is added in water system. The main role of the latest is to weak coagulated bonds between waterproofing mineral particles of the soil. By diluting oil layer covering minerals organic solvent significantly reduces viscosity of this oil as well as significantly reduces interfacial surface tension on the oil-water boarder, increasing the effectiveness of rectification of oil-polluted soil.

By using chemical, physico-chemical and mechanical methods of influence on the oil-polluted soil along with the increase of dispersibility of mineral particles, entire and equal reallocation of different phases and components in microvolumes of the system, i.e. its homogenetive limit is achieved. At the same time disperse environment as well as disperse phase, participating in these processes, undergo changes.

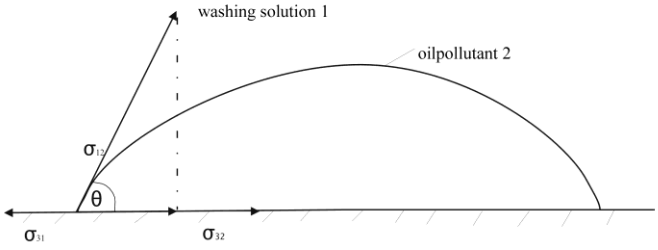
The sizes of mineral particles of the soil and ratio between volumetric content of constituents change. Oil is continuously diluted by organic solvent and transfers into the volume of washing water solution. Surface of grinded minerals rectified form oil undergo hydrophysics by oil displacing water. Water capsules formed on the surface of particles are the factors of stabilization and prevent particles from aggregation.

Thus, parallel to rectification of oil, the hydrophysics of surfaces of the dispersed particles is achieved while oil contaminant is retained by washing system that prevents repeated stick of removed oil drops to purified surface (resorption). Prevention of resorption of oil drops on purified surface is solved by special additions to washing water solution.

Washing effect of water runs in three-phase water-soil-oil contaminant boarder and is controlled by superficial powers.

Washing ability of water depends on the value of surface tension on “oil-water” boarder σ_1 and contact angle θ of moistening on “oil-solid” boarder. Insertion of active additions surfactant (SAS) and wetting agents into washing water reduces interface surface tension σ_{12}, promoting the penetration of water solution SAS into oil volume, dispersing it with formation of drops, and reducing contact angle of moistening θ, ensuring separation (tear off) of oil drops from polluted surface. As a result of adsorption SAS oil layer emulsifies and in this case separation of oil drops by water stream becomes possible.

Picture 1 represents the scheme of the balanced state of the oil covering the surface of mineral particle in detergent.



Pic.1. Scheme of the balanced state of the oil covering the surface of mineral particle in detergent.

θ – balanced contact angle of moistening; σ_{31}, σ_{32}, σ_{12} – interface surface tension on boarder "solid surface – detergent, solid surface – oil, detergent – oil".

Balanced state of covering oil on three-phase boarder "detergent (1) – covering oil (2) – solid surface (3)" is described with famous thermodynamic equation of Yung:

$\sigma_{31} - \sigma_{32} = \sigma_{12} \cdot \cos\theta$, where

σ_{31}, σ_{32}, σ_{12} – interface surface tension on boarder "solid surface – detergent, solid surface – oil, detergent – oil" correspondingly. θ- balanced contact angle of moistening.

Separation of oil contaminant may be carried out only by forced dispersion on washed surface.

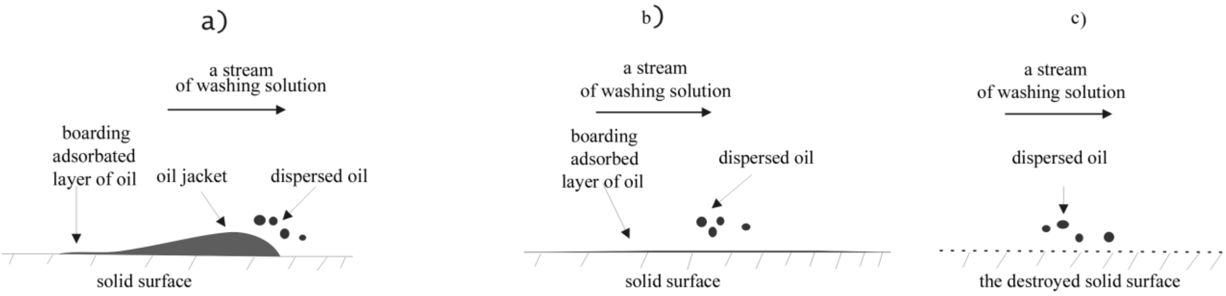
General energy that is required to spend for separation of oil contaminant from solid surface may be divided into physico-chemical work, that is the result of intermolecular interaction of detergent during adsorption on three-phase boarder, resulting the stick oil to assemble in the form of drops that fix on the surface with a certain contact angle of moistening, and also into additional mechanical work necessary for coalescence and complete separation of these drops from the surface[17]. Degree of dispersion of oil contaminant into the state of drops in the process of its rectification from the surface of minerals will depend on surplus of mechanical work influenced on washing system over the work of adhesion as well as of emulsive ability of washing solution.

A stream of moving liquid has mechanical influence on stick layer. Mechanical influence of washing stream is shown in the form of tangential force, directed at a tangent to stick layer and dynamic force, which operates in its butt-end. Besides, mechanical influence of the stream, molecular-surface processes, such as adhesive interaction and moistening of contacting phases also influence on stick of layer.

Increase of the effectiveness of wash can be reached due to strengthening of molecular-surfactants influence of the stream. The more effective detergent, water solution of surfactant substances are, the less necessary is to insert additional mechanical work into washing systems. Mechanical efforts of the stream in the form of tangential force and in the form of dynamic force of the stream have the influence on thin films when molecular-surface effects running on boarders have already prepared separate oily particles of the film for their separation [18].

The above-mentioned rules, related to wash of the surface of mineral particles of oil-polluted soil covered with oil, laid in the basis of rectification technology eliminated by National Academy of Sciences of Azerbaijan Special Design Engineering Office on Complex Treatment of Mineral Raw (SDEO CTMR ANAS). Mechanism of multi-stage process may be represented by different transformations in water washing stream during joint chemical, physico-chemical and mechanical effects on suspension, consisting from oil-polluted soil, organic solvent and washing water with SAS and other active additions.

The following transformations take place in case of the above-mentioned effects, pic. 2:



Pic. 2. The model of elementary acts of washing effect of the stream of detergent during the adhesion of disperse system: a – coalescence separation of oil drops from oil layer cover; b – entire separation of oil drops and layer; c – mechanical separation of rectified surface with grinded mineral particles together with the film of strongly linked active components of oil and dispersion of its liquid part until drop state is achieved.

The structure of the soil and all aggregates from mineral particles destroy as a result of their complete disconnection, thus providing water and organic solvent with free access to the oil, contaminating surfaces of these particles.

Under mechanical influence of the stream of detergent, consisting of water solution of SAS and organic solvent, the surface layer of the oil covering minerals, rarefy with reduction of viscosity due to dilution caused by solvent and breaks to droplets, that are ready for their next coalescent separation under their transfer into washing stream in the form of superfine emulsion, pic 2a. In this case mechanical work is spent on destruction of aggregates, consisting of mineral particles, as well as on dispersion of oil and on overcoming of cohesion forces. Organic solvent and active additions reduce surface tension of water on the boarder with oil σ_{12}, promoting penetration of water solution into the surface volume of oil that covers minerals. As a result of adsorption of SAS oil layer is emulsified and thus makes possible the drag-out of oil drops by washing stream.

This stage completes wash of oil that covers minerals so long as the strongly linked boarder layer of the adsorbed active components of the oil become bear, pic. 2b. For breaking the strongly linked boarder layer by washing solution jointly with organic solvent it is necessary to destroy mineral particles.

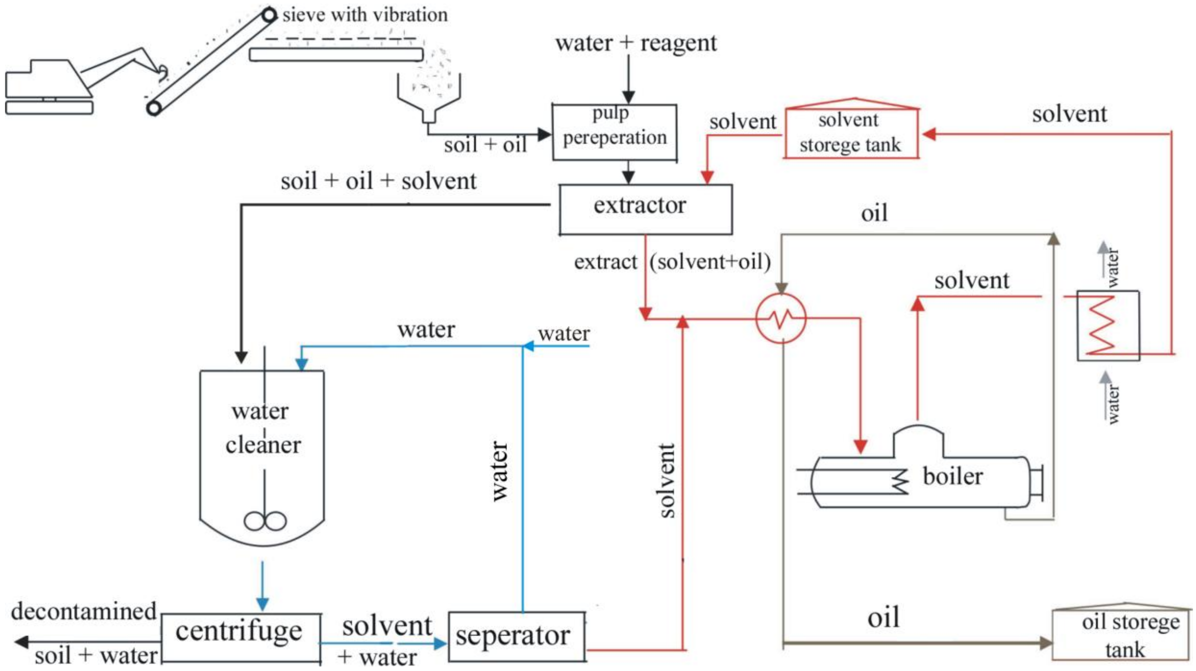
Under the mechanical influence of the stream of washing solution, consisting of water solution of SAS and organic solvent, a thin film of boarder layer becomes thinner due to its wash from the surface by organic solvent of active components and breaks, being accompanied by decomposition of mineral particles.

As a result of break of the thin film of boarder layer, liquid part of the boarder layer splits into droplets, that are ready for their next adsorption and entire separation, with their transmission into the stream in the form of superfine emulsion and thus complete rectification of the surface of minerals is achieved, pic. 2c.

In this case mechanical work is spent on decomposition of mineral particles, dispersion of oil film until the drop state is achieved and overcoming of adhesion forces.

Technology elaborated in SDEO CTMR of ANAS is intended for extraction of oil from oil-polluted soil, oil-slimes and tar sands; for their return of rectified soil to household turnover; for enhancement of ecological situation of mining, transportation and oil processing regions. The basis of the technology constitutes wash of oil from the surface of grinded rock by means of water and participation of organic solvent in the medium of water solution of SAS and active components under the temperature of 40-50 ^{0}C, with the following separation of mineral and organic (solvent) phases. The process of rectification, (pic. 3) consists of the following main stages: extraction of oil from oily rock in extractor, separation of phases in stripper, regeneration of solvent in evaporator, collection of separated oil and rectified (refined) soil. The task put by is solved through rational distribution of material streams in the process of rectification, that lies in the idea that main part of oil contaminant of the soil is extracted in excavator in the form of extract (oil in solvent), from which later by the method of single evaporation oil separates in evaporator and collects in collector, and solvent returns to recycle. After extraction the soil refined from oil entirely (completely) is refined by the stream of washing solution in splitter from remaining of solvent, which returns to recycle, while the refined soil returns to dump.

The elaborated technology was tested in co-operation with State Oil Company of Azerbaijan Republic in 1996 and TACIS Programme in 2001 in the framework of the project EAZ 9801 of European Union. Testing in the frame of EAZ 9801 project had been carried out with direct participation of «BECIP-FRANLAB» and French Oil Institute. It was settled, that the technology for refining of oil-polluted soil ensures high degree of oil extraction from different rock (not less than 98-99%) with any characteristics of organic and mineral phases; ensures environmentally appropriate technology providing non-waste industry with the use of partially returnable technological water. Researched carried out by our side showed that the most rational direction for the use of the residual oil, extracted from oil-polluted soil of Absheron peninsula, lies through the ways of thermal influence, and it maybe used as oil fuel, that is in compliance with State Standard 10585-99. Satisfactory similarity of its technical requirements with those of bunker fuel that has characteristics of the residual oil was also shown.



Pic. 3. Fundamental technological scheme on rectification of oil-polluted soil.

According to calculations of specialists from TACIS Programme and Oil Institute of France expenses for refining of 1 ton of oily ground with the use of elaborated technology for plant with output of 100 t/h amount ~15,0 $ USD.

On the base of this technology establishment of mobile plant for liquidation of accidental consequences in oil pipes, during oil transportation by railway, etc., is possible. In case of necessity stationary plants for rectification of oil-polluted soil with output of 5, 10, 30 and more tons of processed soil per hour may be built up.

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THE USE OF PURIFICATION SLUDGE OF PAPER INDUSTRY IN AGRICULTURE

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In this study, the effect of Seka Izmit Waste Water Purification Plant's purification sludge on plant productive, and the accumulation of heavy metals on land and plants were investigated.

In order to accomplish this study, 5 different samples were prepared from different composition of purification sludge and soil. Horsebean was planted on these mixtures in green house conditions, and the improvements of plants, and heavy metals polution on the plants and the mixtures were examined.

In this study there were two main purposes. The first one was examining the use of purification sludge at agiculture's land improvements by considering the ratio of plant nutrition elements, and the second one was investigating the effect of heavy metals on plant productive and soil polution including the measurement of necessary parameters.

1.1. Material

In this research, the final purification sludge of Seka-Izmit Waste Water Purification Plant was used as material. Horsebean plant of Sakarya region was experienced as plant material. The research was conducted in growing period (August-November) in research green house at Sakarya University.

1.2. Method

The research was conducted according to the method which was figured out by Duzgungunes and colleague (1987) [1]. As a result of 3 repetitive arrangement of coincidental parcel experience totally 60 plants were used in this study.

1.2.1. Application and Care Process

After the open air water content of sludge taken from Seka-Izmit was dewatered, the sludge pieces was crunched into soil format, and was put into black bags of 25 cm diameter. 5 seeds were planted into each of these bags and the numbers were given to them. The labeled horsebean bags were placed in the green house in 3 repetetive form. The arrangement of the bags in the green house can be seen in figure 1-1 .

Figure 1-1.The arrangement of the bags in the green house

The A sample which was used for control was prepared as follows; 100% garden soil, 2:1:1(soil+ organic animal fertilizer+perlit)ratio. With the different composition of this mixture and purification sludge of paper industry, the following samples were formed; B(50% garden soil+50%purification sludge), C(75% garden soil+25% purification sludge), D(25% garden soil+75% purification sludge), and the final sample E with 100% purification sludge. The plants were growed in the black bags.

5 seeds were applied to the each 5 different samples(A,B,C,D, and E) in 4.9.2001 by 3 repetetive. In this application, each 5 seeds were well improved chosen, and an extra care was given to the depth of planting of the seeds, and they were watered immediately.

The technical and cultural activities such as watering were applied regularly and in time for the improvement of roots, the parts above the soil and sowing grass of the seeds. The watering process just started after sowing and it continued usually with 1 day intervals according to the need of the plants. The spray method was used in watering. The watering of the plants in the black bags continued till the water overflew from the bags, and the watering was done in time by considering the moisture of the soil. By the end of the plants green house improvement, all cultural activites stopped in December-January. After horsebean completed its growth, the unrooting of the plants took place. The unrooting was done by hand in lab conditions with an extra care. Every unrooted plant was labeled, and counted, weighted and morphologically measured as it was considered in the research. It is found out that samples shall be taken several times during the season in order to be completely succesful at the analysis of the plants. It is expressed that samples can be taken at the beginning of the season, in the middle of the season, before the harvest or during the harvest.

The images of the horsebean in the green house, which completed its improvement, can be seen in Figure 1.2.

Figure 1-2 Horsebean in the green house

1.2.2. Morphological Measurement

After seedling plants, whose number was decreased by thin out in the bags, finished its improvement, leaf samples that are taken from each combination are given a ball shape, and they were transferred to the lab.

1.2.3. Main measurements, counting, weighting, and evaluations

The classical measuring, counting, and weighting methods were used to the samples which were unrooted and washed with care. In order to figure out the differences between the applications, the following main measuring, counting, weighting and evaluations to the plant samples were performed.

Leaf wet weight(g)- Leaf dry weight(g)- Leaf amount(number)- Plant stem diameter(mm)-Plant lenght(cm)-Plant root lenght(cm)

1.2.4. Analitic Solutions

After dissolving of the soil and plant samples, the amount of heavy metals Cu, Cr, Ni, Pb, Zn, Fe, Mn and Cd in the 180 solution black glasses(a glass is 100 ml) was measured by the help of atomic absorption equipment. The results were presented at each different graphs for horsebean type, samples, and elements.

2. Experimental Studies

2.1.Morphological Measurement
Morphological measurements were performed to follow the horsebean plant improvement

2.1.1. The wet weight of horsebean leaves

***Even in the first try, sample A presented the best wet weight, in the followings tries sample C and D were the best. It was observed that sewage sludge has positive effect on the plant improvement period.

2.1.2. The dry weight of horsebean leaves

***Even in the first try, sample A presented the best dry weight, in the following tries sample C was the best one.In the improvement period, all samples gave the similar measurement. The sewage sludge is especially usefull at this period.

2.1.3. Horsebean plant lenght

***In 4 tries, horsebean plant showed the best result at sample C. It had even higher value than sample A which was 100% plant soil. In the other samples, horsebean continued its improvement. Even at 100% purification sludge, it presented 24,6; 34,0; 44,1; 55,3 cm values respectively which was really good.

2.1.4. Horsebean Leaf Number

***In all tries, sample C presented the best value. The addition of purification sludge to the soil displayed a positive effect for horsebean. 25 % purification sludge especially affected the increase of leaf number.

2.1.5. Horsebean root length

***Sample C presented the best value for the horsebean root length. Other soil samples with purification sludge and sample E (100% purification sample)showed sufficient values.

2.1.6. Horsebean stem diameter

***Even sample C had the best value, the other samples presented also close values. The best value is 2,5 cm, whereas the worst value was 1,8 cm. Horsebean plant unlike corn plant did not show too much decrease in stem diameter at soils with purification sludges.

2.2. The effect of purification sludge to the plant growth/improvement

The improvement of horsebean plant which was planted in the soil with purification sludge was observed by measuring several parameters For this purpose plant wet weights, plant dry weight, plant length, leaf number, root length, stem diameter were measured with intervals. The improvement of unrooted plants according to the sample types are displayed in Fig 2.1)

Figure 2-1 The improvement of unrooted plants

The followings are observed after the analysis of the measurements

2.2.1. Plant wet weight

Even though horsebean performed the best growth in samples C and D(75% purification sludge) after sample A, all samples displayed good result in improvement period .)

2.2.2. Plant dry weight

Plant dry weight showed paralel result with plant wet weight which was expected.

2.2.3. Plant lenght

Horsebean showed the best result in C sample in all 4 tries. Other purification sludge added soils, and sample E also had a good performance related with plant length

2.2.4. Plant leaf number

The best result was in sample C. 25% purification sludge addition played an increasing effect on plant leaf number

2.2.5. Plant root length

Horsebean gave good result in all samples

2.2.6. Plant stem diameter

Even horsebean displayed the best value in C sample, the other samples also gave good results. No big decrease in stem diameter was observed compared to sample A
Horsebean plant presented the best improvement in prufication sludge added soil. Purification sludge can be used as fertilizer for horsebean growing.

2.3. Analytic measurements

2.3.1. Horsebean plant, Cu; samples and intake-concentration relation

The Cu concentration- intakes graph related with tha data which were collected after analyis of Horsebean in the samples and AAS was shown in Fig 2.2

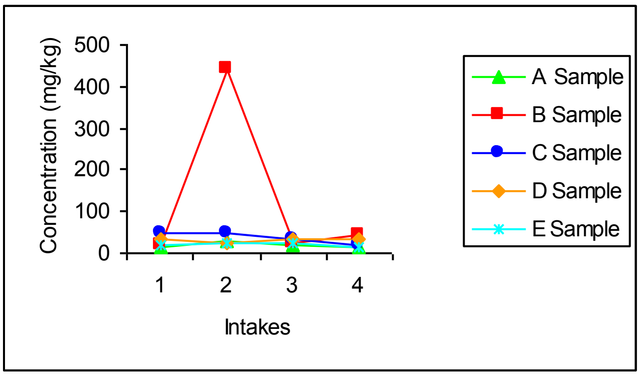


Figure 2-2 The relationship between intake and concentration in the horsebean for Cu

Cantle (1984) figured out in his study, which were related about estimating the amount of elements in food by atomic absorbtion spectometer, that the bottom and top heavy metal limit for vegetables were 0,02-18 mg/kg in his study [2]. In all measurements at the leaves of horsebean in all samples shoed a value higher that top value. The extreme value of sample B at second try can be as a result of experiment error. In other samples Cu intake was similiar. Sample B showed an increasing intake whereas sample C showed a decreasing intake. This can be because of minimum (25%) purification addition of sample C)

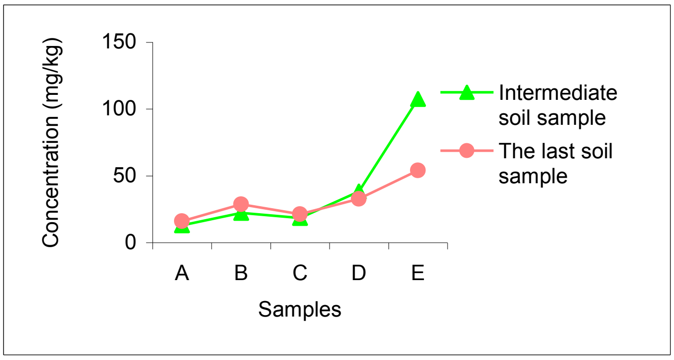


Figure 2.3. The relationship between intake and concentration in the horsebean in the soil for Cu

Accorfing to he limit value of heavy metals table 2.1, copper limit value for Turkey is 50 mg/kg oven dry soil [3]. All samples analysis other than sample E gave a value(mg/kg) smaller than this limit.A little increase of Cu was displayed in the samples except sample D and E.

Table 2.1. Limit value of heavy metals in the soil [3]

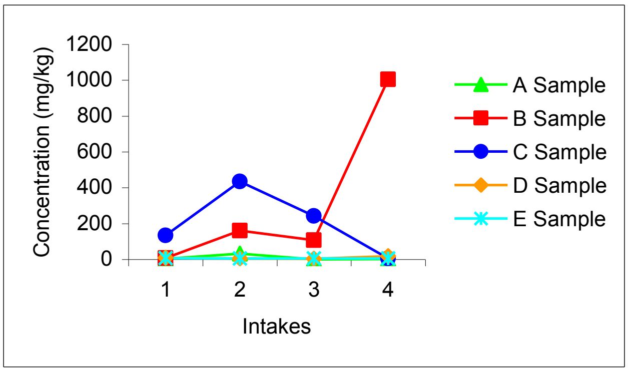
Heavy Metal	pH<6,mg/kg Oven Dry Soil	pH>6, mg/kg Oven Dry Soil
Lead	50**	300**
Cadmium	1**	3**
Chromium	100**	100**
Copper*	50**	140**
Nickel*	30**	75**
Zinc*	150**	300**
Mercury	1**	1.5**

* The ministry limit value can be increased by 50 %, if pH value is greater than 7.

** If it is proven that it doesn't give any harm to human being and environment in lands where fodder plants are grown, these limits value can be exceeded.

2.3.2. Horsebean Plant,Cr; samples and intake-concentration relation

The Cr derişimi – alımlar graph related with tha data which were collected after analyis of horsebean in the samples and AAS was shown in Fig 2.4



Figurel 2.4 The relationship between intake and concentration in the horsebean for Cr

According to table 2.2 which displays acceptable amount of crom heavy metals in plants, the crom heavy metal toxic level is 1-2 mg/kg dry material. [4]. All intakes in sample B and C were over limit According to this, heavy metals in samples A,D and E were not harmful for man and animal health. In samples A, C and E a decreasing Cr intake were observed whereas in samples B and D an increasing Cr was presented.

Table 2.2 Limit value of heavy metals in the plant in Turkey[4]

Element	Limit Value in plants (mg/kg – dry matter)
Cadmium (Cd)	0,3
Lead (Pb)	0,5
Copper (Cu)	15–20
Nickel (Ni)	20–30
Zinc (Zn)	150–200
Chrome (Cr)	1–2
Mercury (Hg)	0,03

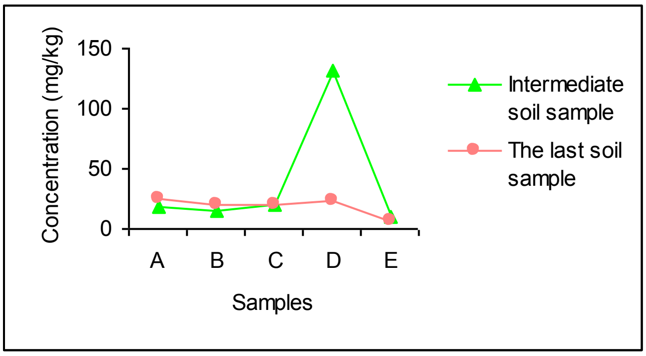


Figure 2.5. The relationship between intake and concentration in the horsebean in the soil for Cr

According to Table 2.1 which displays heavy metal limits in soil, heavy metal crom toxic level in Turkey is 100 mg/kg oven dry soil.[3] Considering this table, all samples other than soil interval sample taken from sample D, presented values lower than this limit. All samples displayed a decrease in Cr intake, whereas last soil specimen of samples A and B showed a little increase.

2.3.3. Horsebean Plant,Ni; samples and intake-concentration relation

The Ni concentration – intakes graph related with the data which were collected after analyis of horsebean in the samples and AAS was shown in Fig 2.6

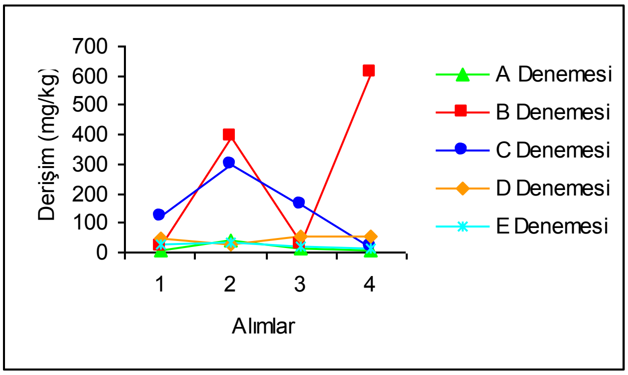


Figure 2.6 The relationship between intake and concentration in the horsebean for Ni

According to Table 2.2, which displays the allowable potential element amount (mg/kg- dry material),the toxic limit level of Ni in Turkey is 20-30 mg/kg- dry material. The measurement results from the leaf specimen of plants in all samples displayed a higher value than this.In samples B and D, there was an increasing Ni intake, whereas in samples C and D there was a decreasing Ni intake.

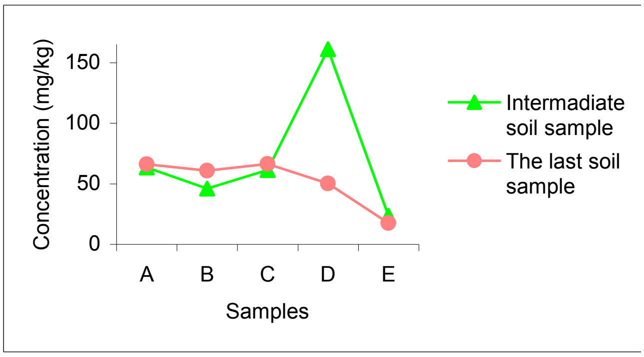
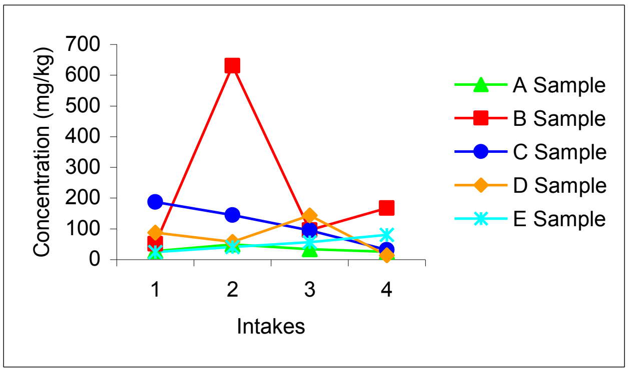


Figure 2.7. The relationship between intake and concentration in the horsebean in the soil for Ni

According to Table 2.1., the heavy element nickel toxic limit value is 30 mg/kg firin dry soil[3].All samples other than sample E displayed a higher value than this.An increasing intake of Ni in samples B and D is parallel with the high decrease in the last specimenn soil of these samples.There was a decreasing intake of Ni in samples C and E. There was not a big Ni decrease in the soil of these samples.)

2.3.4. Horsebean Plant,Pb; samples and intake-concentration relation

The Pb concentration – intakes graph related with the data which were collected after analyis of horsebean in the samples and AAS was shown in Fig 2.8



Figıre 2.8 The relationship between intake and concentration in the horsebean for Pb

According to Table 2.2, the heavy metal element lead limit is 0,5 mg/kg-dry material in Turkey.[4]) Sample B diplayed respectively for 1,2,3 and 4 specimen as 50,4;630,4;95,6;166,9 mg/kg, sample C presented respectively for 1,2, and 3 specimen as 186,5; 144 and 94 mg/kg , sample D gave respectively for 1,2, and 3 specimen as 87,5; 56,8 and 143,3 mg/kg and sample E diplayed respectively for 3 and 4 specimen as 56,2 ve 79,8 mg/kg .All these values are above the limit. In all specimen of A sample, there was similiar Pb intake, whereae in sample B and E there was an increasing intake and in samples C and D there was a decreasing intake. This result is proportional to the amount of purification sludge addition.

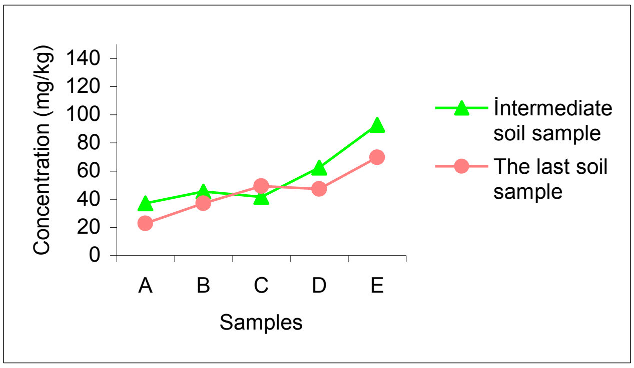


Figure 2.9. The relationship between intake and concentration in the horsebean in the soil for Pb

According to table 2.1, the heavy metal element lead toxic limit is 50 mg/kg oven dry soil in Turkey.[3] In all samples other than sample D and E concentration values (mg/kg) is below this limit. In the last specimens of soil, Pb amount decreased paralel to plant intake. However, it is found in soil with some derisim values.

2.3.5. Horsebean Plant,Zn; samples and intake-concentration relation

The Pb concentration – intakes graph related with tha data which were collected after analyis of horsebean in the samples and AAS was shown in Fig 2.10

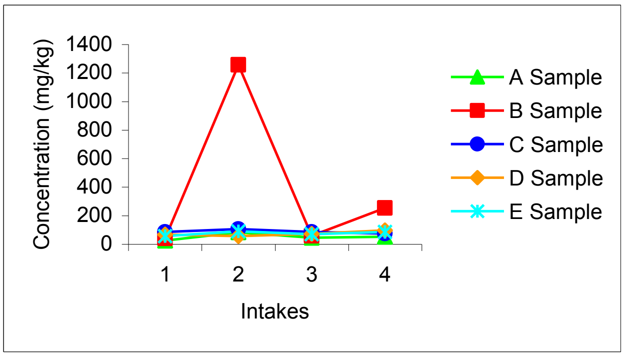


Figure 2.10 The relationship between intake and concentration in the horsebean for Zn

According to table 2.2, the limit value of zinc in Turkey is 150-200 mg/kg.)[4]. As a result of measurements, all samples other than second specimen of sample B, the values were below this limit This over value can be an experimental error. It can be evaluated that heavy metal concentration is not harmful for man and animal health. An increasing intake of Zn by time was generally observed for all samples

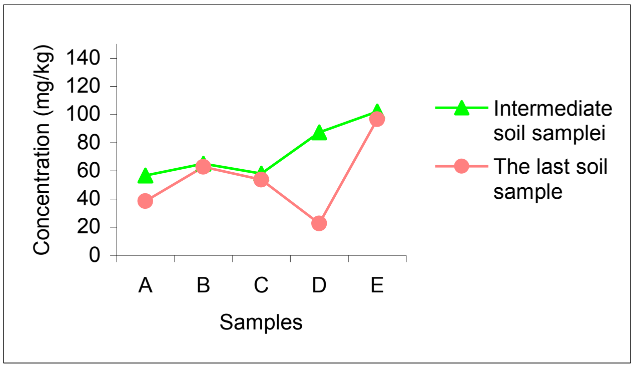


Figure 2.11. The relationship between intake and concentration in the horsebean in the soil for Zn

According to Table 2.1, the heavy metal element zinc toxic level is 150 mg/kg firin dry soil.[3] All values received from the samples were very small compared to this value. Even there was an increasing intake of Zn by time, in all last soil specimens a decreased was observed compared to first soil specimens.

2.3.6. Horsebean Plant,Fe; samples and intake-concentration relation

The Pb concentration – intakes graph related with tha data which were collected after analyis of horsebean in the samples and AAS was shown in Fig 2.12

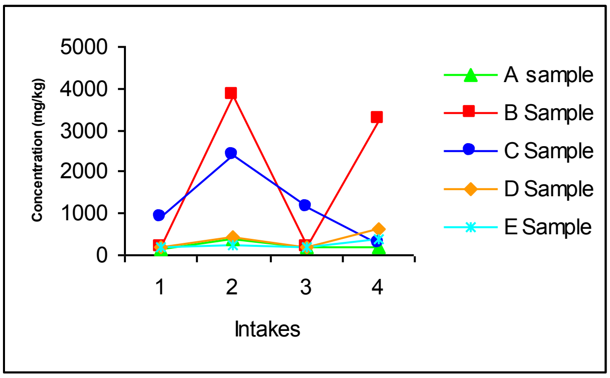


Figure 2.12 The relationship between intake and concentration in the horsebean for Fe

In all samples, horsebean displayed an increasing Fe intake. Fe intake to the plant is in a high values compared to other metals.

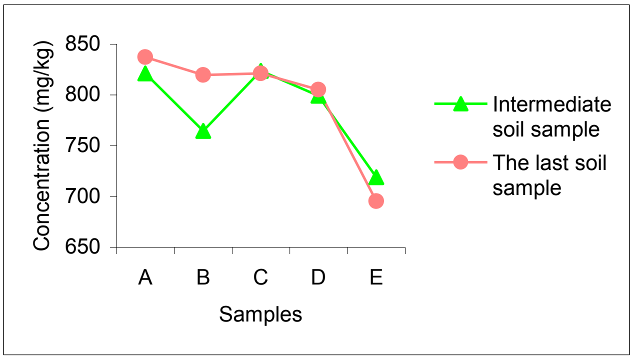


Figure 2.13. The relationship between intake and concentration in the horsebean in the soil for Fe

Even the horsebean showed a great intake of Fe, there was not a big decrease of Fe in soil.

2.3.7. Horsebean Plant,Mn; samples and intake-concentration relation

The Mn concentration – intakes graph related with the data which were collected after analyis of horsebean in the samples and AAS was shown in Fig 2.14

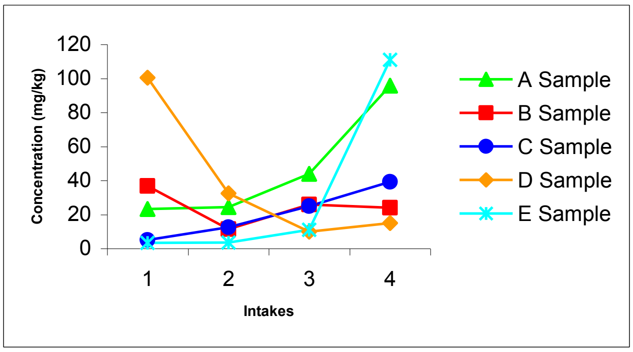


Figure 2.14 The relationship between intake and concentration in the horsebean for Mn

Horsebean displayed an increasing Mn intake in samples A,C,and E whereas it showed a decreasing intake in samples B and D.The Mn intake is very obvious in last specimens of samples A, C and

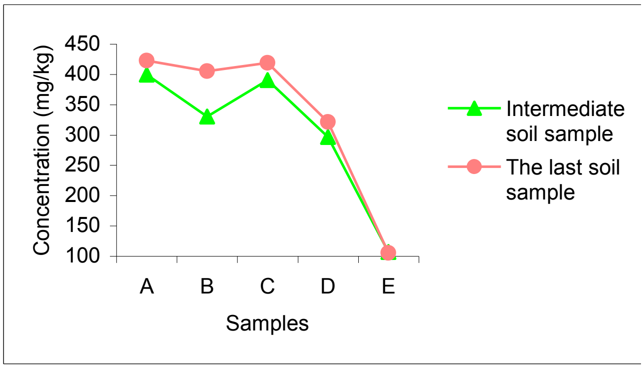


Figure 2.15. The relationship between intake and concentration in the horsebean in the soil for Mn

There was a slight increase of Mn intake in all soil specimens.So Mn accumulation can be mentioned in soil.

2.4. The heavy metal intake in plants which growed in purification sludge added soils

The amount of heavy metal intake in purification sludge added soil was measured by the samples taken from the plants with some intervals.For this purpose, Cu,Cr,Ni,Pb,Zn,Fe,Mn and Cd metals were observed in plant samples by atomic absorption spectometer.

2.4.1. Horsebean Plant

- Horsebean showed an overlimit intake of heavy metals other than Zn, Fe and Mn in all samples)

- Horsebean generally presented an increasing intake of metal by time.)

- As a result of measurement of soil where plant grew, Cu was above limit in sample E, Cr was over limit in the interval sample of E,Ni intake in samples A,B,C, and D was above the limit, and Pb amount in samples D and E was over limit.

- The last specimen of soil displayed generally a small value of heavy metal intake compared to first specimen of soil

Plant showed generally the utmost intake in sample B. The plant improvement in 50% purification sludge was not good enough. Sample E presented a good plant improvement in the fisrt phase of improvement, whereas sample C showed a good plant improvement in the plant growth phase.

RESULTS AND DISCUSSION

- In this study, the effect of purification sludge addition to soil on plant improvements in green house conditions were observed by measuring different parameters. Also the heavy metal intakes of the plants which grew on this purification sludge added soil was measured. The heavy metal amounts in the soil was also studied. The followings are the result of this study:
- When plants are investigated according to their wet and dry weights amount, sample E showed the best result in the first fast growing period following sample A. However, through the improvement period soil with addition performed better results.
- Other than sample A, respectively sample C, B and E performed the best results in plant length. During improvement period, they showed the similiar values.
- The addition of purification sludge to soil had negative effect on plant leaf.
- Horsebean reached to sufficient root length.
- The stem diameter performed sufficient improvement.
- Horsebean showed the best improvement in samples C and D.
- It is considered that horsebean can easily be grown in purification sludge added soil from the point view of plant improvement
- Plants showed Cu, Cr,Ni,Fe, and Mn heavy metals intake over the limits
- Horsebean presented heavy metal intake over the limits except Zn,Fe and Mn.
- Horsebean presented an increasing metal intake
- In the first growing and in the last unrooting period, plants showed heavy metal intakes above the limit except in sample D and E
- In the last soil specimen, the heavy metal intake in horsebean is much lesser. Plants intook the heavy metals to their own.
- Sample C (25%purification sludge added soil)showed acceptable heavy metal values
- Adding purification sludge to soil more than this value caused overlimit values of heavy metals. It is not appropriate to use these plants as nutrition for man and animal.
- It is considered by the increase in the last specimen of soil that adding purification sludge to soil for years can cause accumulation of heavy metals in soil
- This is an initial study about using purification sludge in agriculture. It is considered that it will more appropriate to use purification sludge in garden plants other that nutrition plants. The study can be continued by using purification sludge in garden plants. Since the purification sludge added soil in this study consists fertilizier, the amount of N and P increase with the addition of purification sludge which causes negative effect on plants. This can be reason of poor improvement of plant in samples B and D. The study must be tried with soils without fertilizer.

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DETERMINATION OF SEA POLLUTION IN ALIAĞA BAY, IZMIR, TURKEY: 7-ETHOXYRESORUFIN O-DEETHYLASE (EROD) INDUCTION IN LEAPING MULLET (*LIZA SALIENS*).

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Aquatic environment have been continuously polluted by numerous chemicals and xenobiotics as a result of wide range of industrial and human activities. Pollution of the aquatic environment is a global concern owing to devastating effects of contaminants whose levels are growing at an alarming rate and becomes as a big threat to the health of organisms inhibiting the seas, as well as to human consumers of such organisms. Mainly, as a consequence of industrial activities today's aquatic environment increasingly polluted by persistent organic pollutants (POPs) and also other chemicals and physical agents such as pesticides, polychlorinated biphenyls (PCBs), metals, polycyclic aromatic hydrocarbons (PAHs), radionuclides. The identification of contamination that is harmful to aquatic life is a challenging aspect of aquatic environmental management. Induction of cytochrome P4501A and of its monooxygenase activities, namely arylhydrocarbon hydroxylase (AHH) and 7-ethoxyresorufin O-deethylase (EROD) activities, in fish by these chemicals are the most widely used biochemical measurements in biomonitoring of environmental contaminants. Aliağa Bay, at the west coast of Aegean Sea nearby İzmir, hosting a wide range of industrial activities such as oil-refinery, paper factory, ship-breaking. There is no national documentation or research on determination of pollution resulted from industrial activities in this area. Thus obtained results from this study would be the first information regarding Aliağa Bay. In this study, the degree of induction of cytochrome P4501A-associated EROD activity and immunochemical detection of cytochrome P450 1A in leaping mullet (*Liza saliens*) was used as biomarker for assessment of PAH/PCB type organic pollutants in Aliağa Bay. Mullet caught from different section of the Bay, had approximately 52 times more EROD activity (2389.25 ± 3326.20 pmol/min/mg prot) than the feral fish sampled from clean reference site (46,33 ± 16,18 pmol/min/mg prot) near Foça. The results of this study indicated that Aliağa Bay is highly contaminated with PAH and/or PCB type organic pollutants.

Introduction:

Pollution of the aquatic environment is a global concern owing to devastating effects of contaminants whose levels are growing at an alarming rate and becomes as a big threat to the health of organisms inhibiting the seas, as well as to human consumers of such organisms.

Aliağa Bay at the west coast of Aegean Sea nearby İzmir, hosting a wide range of industrial activities such as oil-refinery, paper factory. However waste of these industrialization, city sewer system are common causes of pollution, also World's fifth biggest ship-breaking area has been located near of this region. There is no national documentation or research on determination of pollution resulted from industrial activities in this area.

Aim:

In this study, the degree of induction of CYP4501A-associated EROD activity in the liver and immunochemical detection of CYP 450 1A1 in leaping mullet (*Lisa saliens*) will be used as biomarker for assessment of PAH/PCB type organic pollutants in Aliağa Bay.

Material and Methods:

Aliağa Bay, is located at 60 km north of İzmir and hosting a large range of industrial activities such as petroleum refinery, ship breaking yard and paper bleaching factories. The refinery, principally serves the regional markets of western Turkey, is one of the biggest of Europe since 1987.

Foça, which is 70 km. north - east of Izmir, a picturesque seaside town, was used as clean reference site.

The Aliağa Bay and Foça are located on the west coast of Turkey, within the borders of İzmir.

Among the bay from the different sites, but mainly from the refinery side, totally 33 leaping mullet (*Liza saliens*) were caught by local fishermen. Liver EROD activities of these fishes have been compared with 27 fishes, caught from clean reference site Foça.

Results:
Fishes were captured and livers were removed and frozen immediately in liquid nitrogen. EROD activity of the mullet liver was determined spectrofluorometrically.

Mullets caught from different sections of the Bay, had approximately 52 times more liver EROD activity (2389.25 ± 3326.20 pmol/min/mg prot) than the feral fish sampled from clean reference site (46,33 ± 16,18 pmol/min/mg prot) near Foça. (p=0.0003)

	n	**Mean of EROD Activity (pmol/min/mg protein)**	**Standart Deviation**
Aliağa Bay	33	2389,25	3326,20
Reference Site	27	46,33	16,18

Table 1: Results of the study summarized.

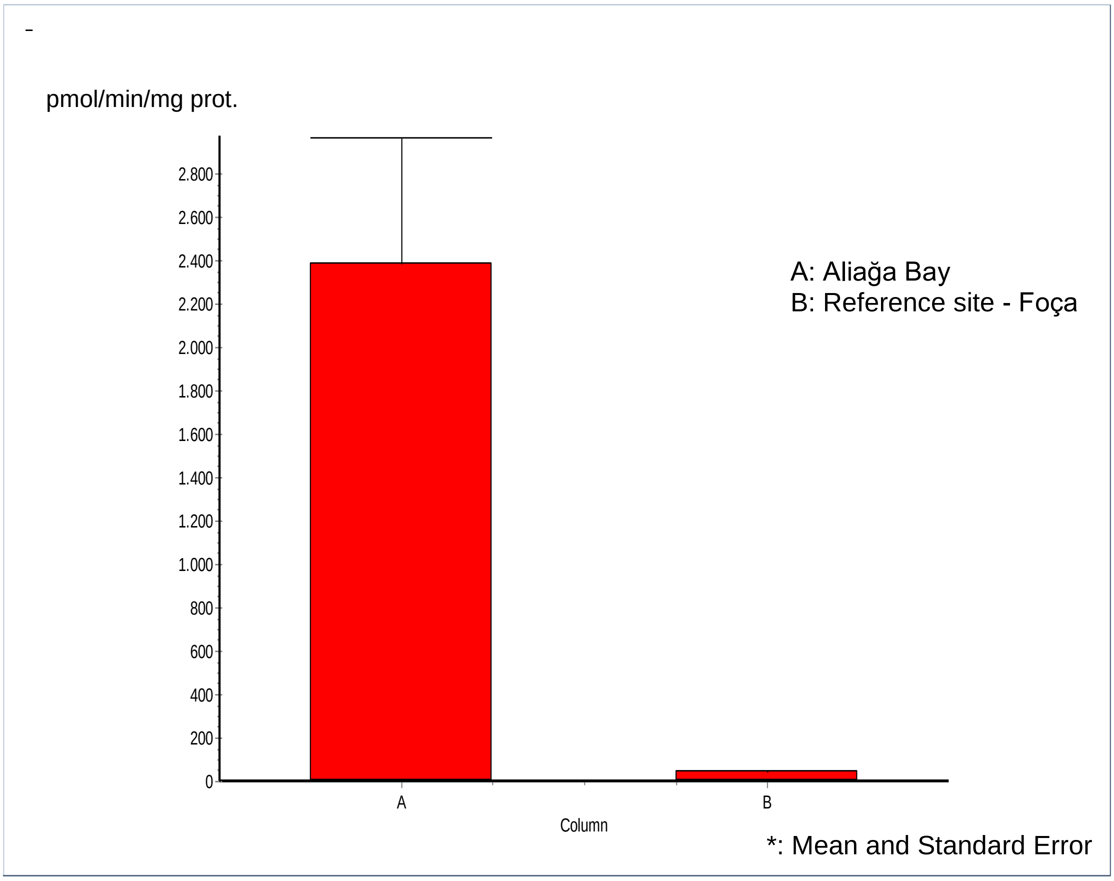

Table 2: Values of Liver EROD Activities of Fishes Caughted from Aliağa Bay and Foça

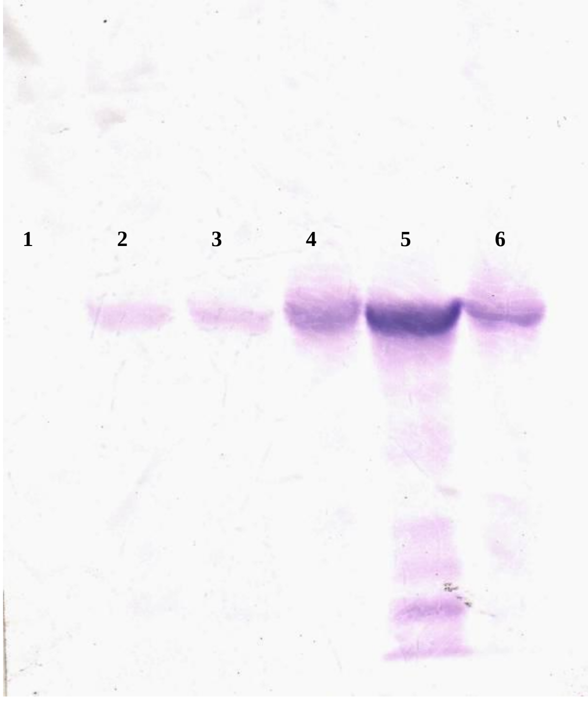

Figure: Immunochemical detection of liver microsomal cytochrome P4501A of mullet caught from different sites within Aliağa Bay by western blotting. The numbers show collection sites. 75 µg microsomal protein was applied to each slot. (1:control)

Discussion:

Because there is no research on determination of pollution in Aliağa Bay, a comparison can not be made within this area. Izmir Bay, which was identified as highly contaminated site before[1], had close results with our study. Highly urbanized and industrial section of the Izmir Bay, showed elevated liver EROD activity with 1293 ± 292 pmol/min/mg which is 62 fold greater with respect to the value at it's reference site(25 ± 9 pmol/min/mg)[1].

Although, detailed qualitative and quantitative analyses of organic chemicals in the waters and sediments of Aliağa Bay are not available, the EROD activity results point out a high contamination of PAH and/or PCB type organic pollutants within Bay, and draw attention to the current situation as an early indication.

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EXAMINATION OF SOME PARAMETERS FOR ECOLOGICAL GROWTH OF MAIZE IN PELIC VERTISOL

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I. Changes in weed population of maize crop under conditions of different fertilization and herbicidal treatment

Some investigations on the primary weed infestation of maize, depending on climatic conditions (Mikova and Stoimenova, 2006) and on the changes of weed population according to the used herbicides (Mikova and Stoimenova, 2006) and types of cultivation (Serafimov, Sabev et all, 2001) were done in Bulgaria.

The aim of this research was study of changes in weed population of maize sowing, depending on the fertilization rates and weed control.

The experiment was conducted from 2002 to 2004 on Pellic Vertisol with pH /H_2O/ of 6,2, total N - 0,24%, total P - 0,08% and humus - 3,43%. Maize hybrid “Kneja”509 was grown in two field crop rotations with cereals. The experiment was carried out after the block method in 4 replications with plot size of 150 m^2 and included: factor A-weed control; a_1-chemical weed control – Lacorn cambi 5500 ml/ha^{-1} (alachlor 33,6%+atrazine 14,4%), a Greek preparation, applied right after sowing, during the first year of the investigation, and Lacorn cambi 5500 ml/ha^{-1}+Atrazine 1600g/ha^{-1} during the next two years; a_2- control (without weeding) and factor B-rates of N fertilization; b_1 – 20 kg/ha^{-1} ; b_2-40 kg/ha^{-1} and b_3 – 80 kg/ha^{-1} a. i. After determination of weed species and the quantitative weed infestation in the variants with a chemical treatment from sowing to the relevant phenological stage: “5-6 leaf”; “9-10 leaf” and “tasseling” of maize, the variants were kept up clean up to the end of growing period by manual weeding. The ploughing (25-30 cm) was done after the harvest of predecessor. Fertilization, according to the values of factor B was performed with the last pre-sowing cultivation. Sowing was done during the first decade of April. The herbicidal treatment was done right after sowing at a consumption of solution 400l/ha^{-1}.

The effect of the herbicides and changes in weed population depending on the fertilization rates were determined in dynamics by the quantitative-weight method, in parcels of 1m^2 (12 replications per variant). The weed dry biomass was determined by drying to the constant weight. Weeding of *Cirsium arvense* (L.) Scop. and *Convolvulis arvensis* L. was not taken into account . During the whole maize growing period these weeds were mechanical removed in intervals of 10-12 days.

Results and discussion

From sowing to the stage “5th -6th leaf” of maize (a period of 47-49 days in the tree years of investigation) the crop was highly infested with by annual dicotyledons, mainly *Hyoscyamus niger* L., *Amaranthus retroflexus* L., *Ranunculus re*pens L., *Sinapis arvensis* L, *Chenopodium album* L. and other annual cereals: *Setaria glauca* (L.) Beauv; *Setaria viridis* (L.) Beauv and *Echinochloa crus-galli* L.

During the stage “5th -6th leaf” of maize in untreated variants in 2002, weed density was very high and varied from 243 pl./m^2 in N$_{20}$ to 263 pl./m^2 in N$_{80}$ /Table 1./. Dicotyledon species determine weed density in all untreated variants. At the lowest fertilization rate they take up 83% of total density and from 72 to 76 % of weed dry biomass. In the same year, during the same crop stage the herbicidal effect of Lacorn cambi 5500 ml/ha^{-1} was relatively well expressed in all fertilized variants –weed density decreased up to 81%.

Table 1. Weed species and quantitative weed infestation in maize sowing (2002)

Variant, weed species	Fertilization rates					
	N$_{20}$		N$_{40}$		N$_{80}$	
	Density	Dry biomass	Density	Dry biomass	Density	Dry biomass
	pl./m^2	g/m^2	pl./m^2	g/m^2	pl./m^2	g/m^2
	From sowing to the stage "5th - 6th leaf" of crop					
Without weed control - cereals	40	1,6	106,7	5,8	100	6
Dicotiledonus	203,3	15,9	140	14,9	163,3	20
Total	243,3	17,5	246,7	20,7	263,3	26
Lacorn cambi 5500ml/ha^{-1} - cerleals	10	0,5	20	1,2	33,3	1,4
Dicotiledonus	35	1,9	43,3	4	36,7	2,6
Total	45	2,4	63,3	5,2	70	4
	From sowing to the stage "9th -10th leaf" of crop					
Without weed control - cereals	100	65,5	43,3	44,9	160	113,1
Dicotiledonus	203,3	353,5	276,7	472,7	163,3	226,6
Total	303,3	419	320	527,6	323,3	339,7
Lacorn cambi 5500ml/ ha^{-1} - cereals	100	42,7	100	26,9	83,3	28,6
Dicotiledonus	3,3	1	16,7	1,2	10	4,6
Total	103,3	43,7	116,7	28,1	93,3	33,2
	From sowing to the stage "tasseling" of crop					
Without weed control - cereals	100	237,2	36,7	162,4	43,3	288,4
Dicotiledonus	170	220,5	66,6	851,1	113,4	262,4
Total	270	457,7	103,3	1013,5	156,7	550,8
Lacorn cambi 5500ml/ ha^{-1} - celeals	20	8,7	13,3	7,7	26,7	14,2
Dicotiledonus	6,7	3,6	0	0	0	0
Total	26,7	12,3	13,3	7,7	26,7	14,2

Close in the same frontiers was the effect of the herbicide with regard to weed dry biomass. From the stage "5th –6th leaf" up to "9 th -10 th leaf" (a period of 37 days) the effect of Lacorn cambi considerably decreased as compared with the first observation. This was particularly well expressed as regards to the dry biomass which increased with nearly 5 times in N_{40} variants and up to 18 times in N_{20}. Appreciable changes in weed population occur in the treated variants. While initial weed infestation was determined by dicotiledon species, the secondary weed infestation was realized by annual cereals, which were nearly 85-86% of total weed density as well up to 98 % of the dry biomass of weed population. In the untreated variants as well as in these with chemical control the dry biomass of weed population greatly increased in comparison with the primary infestation. At these variants the dicotyledonous determined the kind of weed population.

During the stage "tasseling"(55 days after removing of secondary infestation) the late weed infestation in the variants treated with Lacorn cambi is very slight manifested in comparison with primary and secondary infestation. In the variants with higher rates of nitrogen fertilization, the late weed infestation is presented completely by cereal weed.

Because of the relatively short persistency of Lacorn cambi in dose of 5500ml/ ha^{-1} in the next years we added Atrazine in dose 1600g/ha^{-1}. In 2003 and 2004 during the stage "6th-8 th" of maize, the weed density in untreated variants was very high and varied from 740 pl/m^2 in N_{20} fertilized variants to 1117 pl/m^2 in N_{80} variants (Table 2). As contrasted with 2002 in 2003 and 2004 the cereal weeds determined the density of infestation and took up 92-95% from weed dry biomass. During the first 47 days after treatment by Lacorn cambi + Atrazine, the herbicide mixture had a weak effect in the N_{20} and N_{40} fertilized variants. Well manifested herbicidal effect was observed in the N_{80} variants. The data concerning the effect of the herbicides, used in the indicated doses against the primary weed infestation was of interest. In the N_{20} variant the herbicide mixture decreased weed density as well as weed dry biomass of the annual cereal weed by 50%. In N_{40} variant the effectiveness of herbicide mixture decreased in relation to density and dry biomass of cereal weeds, compared to the variants with the low fertilization rate. The weakest effect of the mixture in relation to the density of cereal weeds was observed in the variants with highest rates of fertilization. As a result of frequent rainfall from sowing until stage "9th-10th leaf" (period of about 70 days) in last two years, all treated and control variants were strongly weedy (Table 2). In the interval of 70 days the amount of rainfall was 140 mm as a result of which the efficacy of the mixture Lacorn cambi +Atrazine decreased considerably in comparison with it's effect on primary weed infestation. This was strong manifested in the case of weed dry biomass which increased after the first observation from 22 times in N_{20} and N_{40} variants up to 69 times in N_{80} variants. From "sowing" up to the stage "9th-10th leaf" of maize in the control variants as well in the treated variants the changes in weed polulation were observed. The late spring species *Solanum nigrum* L., *Polygonum convolvulus* L. and *Polygonum aviculare* L. came up. As distinct from other years (1988-2001) weed infestation was realized mainly by annual cereals which took up to 91-96 % from weed density and 88 - 96% from weed dry biomass in the control variants. In the treated variants the situation was 84-90% and 75-85% respectively.

In the stage “tasseling” of maize (88 days after sowing) changes in the weed population species structure in all investigated variants were not observed, most likely because of the full overshadowing of soil surface, more evidentiary manifested at untreated variants. At the same time the highly manifested competition in regard to weed density inside species was apparent. The long period of infestation, rapid weed development up to the stage “9th -10th leaf” , shortage of nourishing substances because of the unbalanced fertilization and high overshadowing were the main reasons for declining of poorly developed weeds. Rainy and cool weather caused their maceration. Owing to these reasons weed density in the treated and untreated variants decreased as compared to the same parameter in the maize stage “9th –10th leaf”. In the next stage “tasseling” the cereal weeds also had a main part in the weed density and weed dry biomass in 2003 and 2004. In untreated variants they determined from 66 to 82% of weed density and from 79 to 92 % of weed dry biomass. Similar situation was observed at the treated variants, where the cereal weeds determined from 67 to 82% of weed density and from 79 to 92% of weed dry biomass according to the fertilization rates.

Table 2. Weed species and quantitative weed infestation in maize sowing (mean for 2003-2004)

Variant, weed species	Fertilization rates					
	N_{20}		N_{40}		N_{80}	
	Density	Dry biomass	Density	Dry biomass	Density	Dry biomass
	pl./m^2	g/m^2	pl./m^2	g/m^2	pl./m^2	g/m^2
	From sowing to the stage "5th - 6th leaf" of crop					
Without weed control - cereals	690	30,8	983,3	47,7	1060,0	647,8
Dicotiledonus	50,0	1,8	70,0	4,3	56,7	43,4
Total	740,0	32,6	1053,3	52,0	1116,7	691,2
Lacorn cambi 5500ml/ha^{-1} + Atrazine1600 g/ha^{-1} cereals	346,7	15,5	293,3	15,2	240,0	6,7
Dicotiledonus	36,7	1,1	20,0	0,5	16,7	0,7
Total	383,4	16,6	113,3	15,7	256,7	7,4
	From sowing to the stage "9th -10th leaf" of crop					
Without weed control - cereals	1443,3	394,9	1576,7	460,8	1373,3	542,1
Dicotiledonus	127,0	55	50	16,1	73,3	28,6
Total	500	364,8	550	342,9	553,3	512,2
	From sowing to the stage "tasseling" of crop					
Without weed control - cereals	760	608,4	346,7	623	253,3	524,5
Dicotiledonus	190	165,3	173,3	56,7	53,3	124,4
Total	950	773,7	520	679,7	306,6	648,9
Lacorn cambi 5500ml/ha^{-1} + Atrazine1600 g/ha^{-1} cerleals	340	422,3	146,7	164,1	116,7	327
Dicotiledonus	93,3	81,2	73,3	125,8	6,7	1,9
Total	433,3	503,5	220	289,9	123,4	328,9

Conclusions

On the 49th day after treatment, a low herbicidal effect of Lacorn cambi in dose of 5500 ml/ha^{-1} (alachlor 1848 g/ha^{-1} a. i. + atrazine 790g/ha^{-1} a. i.) on Pellic Vertisol was observed in reference to weed density. The effect is relatively better as regards to the weed biomass. In cases with higher weed density and weed biomass the herbicidal effect is well manifested.
From 49th to 86th day after treatment , the effect of Lacorn cambi in dose of 5500 ml/ ha^{-1} vastly decreased in comparison with primary infestation. This is most pronounced in the case of weed dry biomass at the fertilized with N_{20} variant. Secondary and late infestation was realized by annual cereal weeds which had a main part of weed density and of the quantity of weed dry biomass at the variants with the highest fertilization rates.

The primary infestation of all variants during the first year of investigation was realized by late annual dicotyledonous - *Hyoscyamus niger* and *Amaranthus retroflexus.*

Addition of Atrazine 1600g/ha^{-1} to Lacorn cambi 5500ml/ ha^{-1} did not increase the effect of herbicide mixture in cases of cool and rainy weather, especially against secondary and late infestation.

In years with more precipitation during maize growing period, cereal weeds had the main part in weed density and weed dry biomass during the primary infestation as well as during the secondary and late infestation.

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DECOLORIZATION OF TEXTILE DYES BY A FILAMENTED FUNGUS *ASPERGILLUS ORYZAE*

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Synthetic dyestuffs are used extensively in textile, paper, printing industries and dye houses. The effluents of these industries are highly colored and the disposal of these wastes into receiving waters causes damage to the environment. They may significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of metals, chlorides, etc. in them. Toxic and genotoxic effects of the textile dyes on organisms suggest the need for remediation of dyes before discharging them into the environment. Biosorption has been continuously studied for the removal of heavy metals and other pollutants from wastewater, so it could be a promising alternative to replace or supplement present dye bearing wastewater treatment processes.

Pellets of a filamented fungus *Aspergillus oryzae* were used in this study for decolorization of Levafix Brillant Blue EB and Cibacron Blue CR which are widespread used dyes in textile industries. 72 hours old pellets were effectively decolorized Cibacron Blue CR and 84 hours old pellets were effectively decolorized Levafix Brillant Blue EB. Spectrophotometric and microscopic examinations of *Aspergillus oryzae* pellets showed that the process involved decolorization through biosorption but not microbial metabolism.

The longevity of this decolorization activity under optimum conditions was investigated in repeated mode by the addition of 250 mg/l of dye in five dosages (50 mg/L each) in the growth medium of *A. oryzae*. The percentage of Cibacron Blue CR decolorization remained high after 5 days operation. This study showed that *Aspergillus oryzae* pellets could effectively be used as an alternative to the traditional physicochemical process.

Key Words; *Decolorization, Biosorption, Aspergillus oryzae, pellet, Cibacron Blue CR, Levafix Brillant Blue EB*

1. INTRODUCTION

The increase in using of cotton, which adds up to nearly half of the world's fiber consumption, has led to substantial growth in the usage of reactive dyes. They represent currently about 20 to 30% of the total market for dyes. Unfortunately, around 30% of the applied reactive dyes are wasted because of the dye hydrolysis in the alkaline dye bath. As a result, dye effluents contain 0.6 to 0.8 g dye/l [1]. As dyes are relatively recalcitrant to biodegradation, dye wastewater is usually treated by physical or chemical treatment processes such as adsorption, membrane-filtration, physicalchemical flocculation combined with flotation, ion exchange, precipitation, and ozonation. However, these technologies are costly, little adaptable to a wide range of dye wastewaters, and usually inefficient in the removal of color, which leads to colored waterways, and public complaints [2, 3]. Color in wastewater is highly visible and affects esthetics, water transparency, and gas solubility in water bodies. Besides the problem of color, there is a general concern that some azo dyes either are toxic or can be modified biologically to toxic or carcinogenic compounds. After releasing them into the aquatic environment, they may be converted into potentially carcinogenic and/or mutagenic amines [1]. The implementation of strict legislation which rules the discharge of colored water combined with an increase awareness of that negative environmental impact of these dyestuffs has resulted in an increasing number of studies on the microbial decolorization of dyes in recent years [4].

Currently, most of the research work deals with the biosorption and bioaccumulation of azo dyes using dead and living fungal biomass [5, 6, 7, 8, 9] In the present investigation, *Aspergillus oryzae* fungal biomass has been used for decoloriztion of two textile dyes, Levafix Brillant Blue EB (LB) and Cibacron Blue CR (CB), which had not been used for the decolorization of textile dyes previously by others.

2. MATERIALS AND METHOD

Chemicals **:** LB and CB anthraquinone-based reactive dyes, were from Çukurova Textile Industry, Turkey. Chemical structures of CB and LB are given in Figure 2.1 and Figure 2.2 respectively. All other chemicals used were of analytical grade

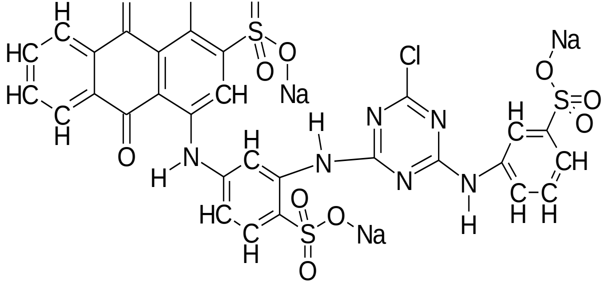

Figure 2.1. Chemical structure of CB (Reactive Blue 235)

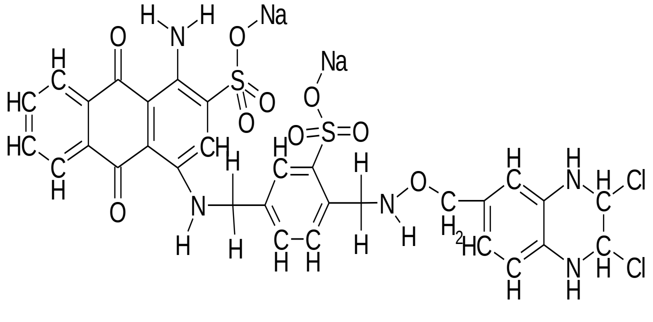

Figure 2.2. Chemical structure of LB (Reactive Blue 29)

Microorganism and culture conditions **:** *Aspergillus oryzae* was used in our study. It was grown from a homogenized spore inoculum to a 250 ml Erlenmeyer flask containing 80 ml medium at 30 $^{\circ}$C with shaking at 150 rpm. The density of the spore suspension was adjusted to give an absorbance of 1,025 at 650 nm, corresponding to about $5x10^7$ spores per ml. The composition of culture medium was: glucose, 10 g l^{-1}; KH_2PO_4, 1 g l^{-1}; $NH_4H_2PO_4$, 1 g l^{-1}; $MgSO_4 \cdot 7H_2O$, 0.5 g l^{-1}; $CaCl_2$, 0.1 g l^{-1} ; pH 5.

Effect of Pellet Age **:** In order to determine effect of pellet age on decolourisation, fungus incubated for different time periods (24, 36, 48, 60, 72, 84, 96 hours). At the end of incubation period dye was added into culture medium at a concentration of 50±3 mg/L. experiments were carried on in shaking incubator (150 rpm) at 30 ^{o}C.

Repeated Experiments **:** Mycelium pellets cultured for 96 h in dye free culture medium for repeated experiments. After cultivation, dye was added into the medium at a concentration of 50±4 mg/L from sterilized stock dye solution. Samples were taken immediately after dye addition to determine initial dye concentration and after 24 hours following dye addition to determine the dye concentration remained in medium. Dye addition was repeated 5 times at 24 hours intervals.

Dye concentration assay **:** Dye concentration was determined spectrophotometrically at 598 nm for LB and 609 nm for CB. All the experiments were carried out in triplicates.

Decolorization efficiency of fungus was determined by using the equality 2.1

$$\text{Decolorization efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \tag{2.1}$$

Decolorization efficiency of fungus in repeated experiments was determined by using the equality 2.2

$$\text{Total decoloriztion efficiency (\%)} = \frac{\sum C_0 - C_t}{\sum C_0} \times 100 \tag{2.2}$$

Where C_0 is the initial dye concentration at the beginning of each cycle and C_t is the dye concentration determined after 24 hours incubation period following dye addition.

3. RESULTS AND DISCUSSION

***Effect of Pellet Age* :** Effect of fungal age on decolorization was determined by adding 50±3 mg/L LB and CB separately to the media of 24, 36, 48, 60, 72, 84 and 96 hours old submerged fungal cultures. Dye concentration remained in the media was determined after 24 hours; decolorization efficiency was calculated and given in Figure 3.1. As shown in Fig. 3.1., after 24 hours following LB addition 20.28 %, 35.26 %, 54.91 %, 63.43 %, 78.88 %, 85.01% and 85.46 % decolorization efficiency was obtained by 24, 36, 48, 60, 72, 84 and 96 hours old fungal pellets respectively. Increasing decolorization efficiency by increasing pellet age is explained by increasing biomass and so adsorption sides. Similarly decolorization efficiency of fungus for CB increased by increasing pellet age as shown on figure 3.1. After 24 hours following CB addition, 49.18 %, 67.13 %, 85.05 %, 88.18 %, 93.59%, 94.66 % and 95.19 % decolorization efficiency was obtained by 24, 36, 48, 60, 72, 84 and 96 hours old fungal pellets respectively. It is also clearly be see from figure 3.1. that 72 hours old pellets were effectively decolorized CB and 84 hours old pellets were effectively decolorized LB.

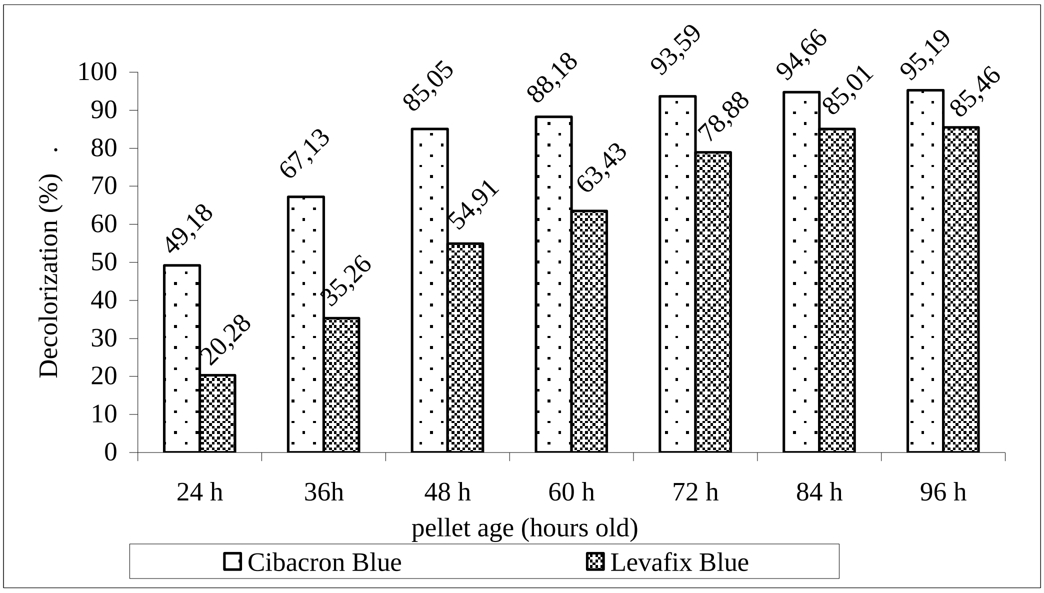

Figure 3.1. Decolorization efficiency of fungus at different pellet ages

In literature, accumulation is indicated to differentiate by fungal age or life stage of organism [10]. It was reported that one day old cells of *Thiothrix* A1 strain was accumulated less Ni and Zn than 2-5 days old cells [11].

Reuse of A. oryzae pellets for decolorization of LB and CB **:** Five graded repeated experiments were done by adding 50±4 mg/L LB and CB at 24 hours intervals to the media where 96 hours old pellets were produced. Initial dye concentration of each stage and dye concentration remained 24 hours after each dye addition were determined and given in Figure 3.2 for LB and in Figure 3.3. for CB.

As shown on figure 3.2. 70 % decolorization efficiency for LB was obtained at second and third stages and decolorization efficiency was apparently decreased at forth stage. Total LB concentration added to the medium at five stages was determined to be 247.65 mg/L and 161.66 mg/L of this dye was found to be removed by *A. oryzae* by biosorption. Overall LB decolorization efficiency was calculated as 65.27 %.

V

IV

II III

I

Figure 3.2. Change in LB concentration during repeated experiments.

As shown on Figure 4.3. at the last stage, CB decolorization efficiency was still high (81,76 %). Total CB concentration added to the medium at five stages was determined to be 246.15 mg/L and 235 mg/L of this dye was found to be removed by *A. oryzae* by biosorption. Overall CB decolorization efficiency was calculated as 95,47 %.

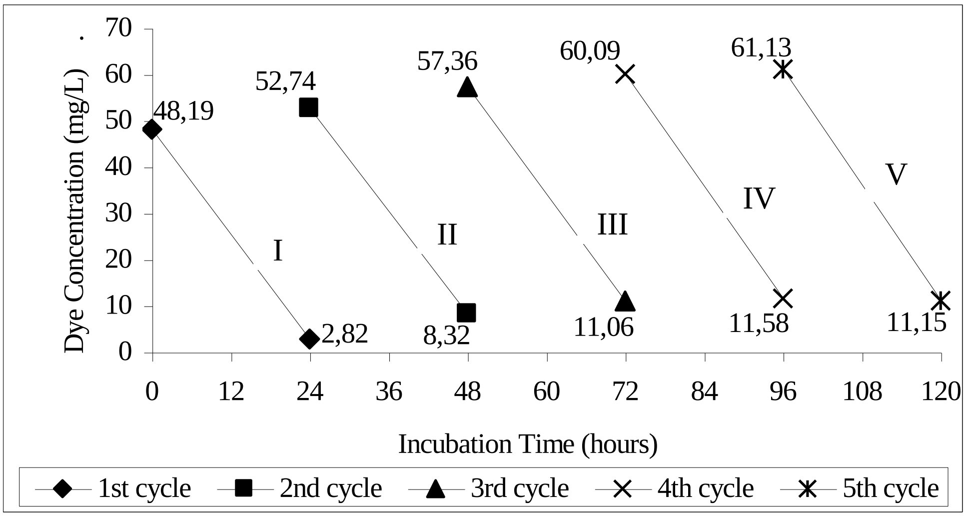

Figure 3.3. Change in CB concentration during repeated experiments.

Repeated experiments showed that, *Aspergillus oryzae* can remove very high concentrations of textile dyes added to the medium by degrees. High concentrations of dyes added to the medium at once, may cause inhibition of metabolic activities, reduction in specific growth rate and reduction in biomass amount i.e. reduction in adsorption sites. By graded addition of textile dyes to the medium, fungus overcome the toxic effects of textile dyes. Inhibition effects of high dye concentrations on microbial metabolism and so on decolorization efficiency emphasized in literature [12, 13, 14, 15, 16].

Differences in dye structures (Figure 3.1.) result in different decolorization efficiency of *A. oryzae* for each dye. Decolorization efficiency of the fungus for CB was higher than LB. As LB decolorization efficiency was lower at the first stage it accumulated in the medium and overall decolorization efficiency of LB significantly dropped. In this part of the study 96 hours old cells that are at the stationary phase of production were used. It is reported in literature that when reproduction of microorganisms is not important, dye structure becomes important [17]. CB is more soluble than LB because CB has three sulphonic acid groups whereas LB contains two sulphonic acid groups. Higher solubility of CB makes it easier to diffuse inside the pellets. LB adsorbed at surface and diffused the pellet regions near to surface at first three stages. After fourth and fifth dye additions decolorization efficiency for LB dropped significantly as its diffusion pellet interiors is not as effective as CB. Different dyes have different molecular structure that makes the fungal decolorization ability to differentiate. It was reported that, minor differences between two dyes originated from electron configuration and charge intensity cases a change in decolorization ability of the same fungus for these dyes [18].

Life cycle of *Aspergillus* genus is shown by figure 3.4. In submerged cultures, hypha of *Aspergillus* sp. comes together to form small ball like structures called pellets which are cream coloured. Cell wall of *Aspergillus* genus is known to made up from chitin and β-Glucan (Figure 3.5. a and 3.5. b respectively) which are known to be effective for adsorption [19, 20]. The coloured pellets shown in figure 3.6. shows adsorption of dye on these adsorption sides.

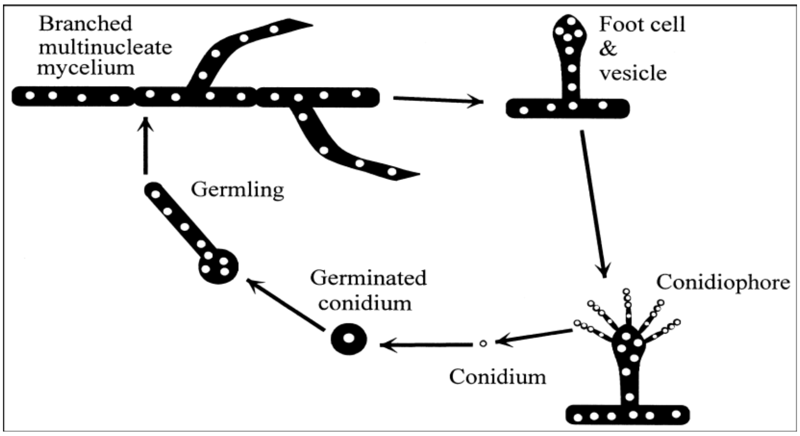

Figure 3.4. The asexual life cycle of *Aspergillus* sp. After dispersal and contact with a suitable substrate, conidia germinate and initiate hyphal growth (the germling stage). Germlings grow to form a branched multinucleate mycelium [21].

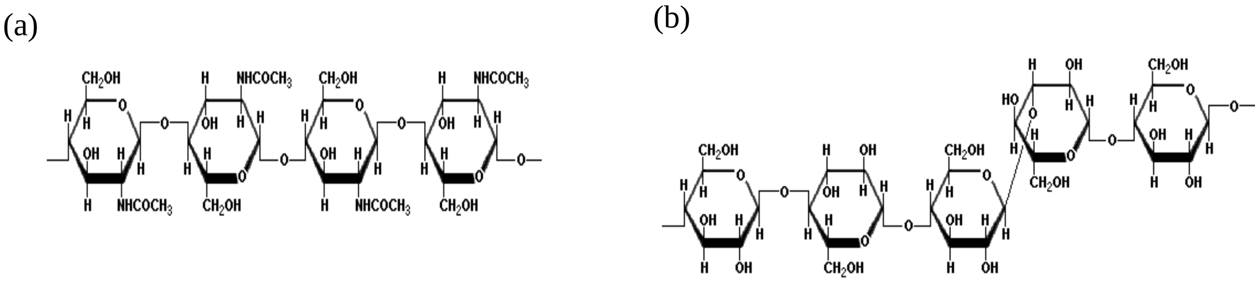

Figure 3.5. Chemical structures of Chitin (a) and β-Glukan (b) present in cell wall structure of *Aspergillus* sp.

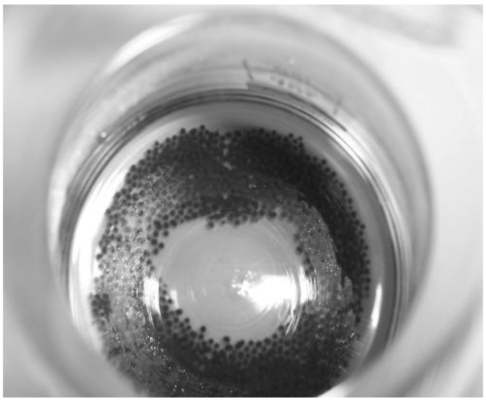

Figure 3.6. Dye adsorbed pellets of *Aspergillus oryzae*.

CONCLUSIONS

- Effective decolorization of CB and LB was achieved by 72 hours and 84 hours old pellets of A. oryzae respectively.
- Spectrophotometric and microscopic examinations of pellets showed that the process involved decolorization through biosorption but not microbial metabolism.
- The longevity of this decolorization activity under optimum conditions was investigated in repeated mode by the addition of 250 mg/l of dye in five dosages (50 mg/L each) in the growth medium of *A. oryzae*. The percentage of Cibacron Blue CR decolorization remained high after 5 days operation.
- This study showed that *Aspergillus oryzae* pellets could effectively be used as an alternative to the traditional physicochemical process.
- Decolorization of dyes with different structures by using *A. oryzae* should be tested and by this way its use in coloured waste water treatment processes could become widespread in future.

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ADSORPTION OF CHROMIUM(VI) BY WOOL

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The aim of this study was removal of low concentrations of chromium(VI) from aqueous solution. As an adsorbent, a natural material wool was used for the removal of chromium(VI). The ability of this natural material to adsorb chromium(VI) ions was investigated using a batch system. The influences of adsorbent dosage, contact time, pH, initial metal concentration and types of adsorbent on the removal were studied. Amount of adsorbed chromium(VI) increased with the decrease in pH value. Adsorption equilibrium was established within 10 min which was well described by the Langmuir and Freundlich adsorption equilibrium. Kinetic data were processed using the intraparticle diffusion model. The experimental results clearly suggested that locally available wool is effective for the removal of low concentrations of chromium(VI) ions from aqueous solutions especially in acidic pH ranges.

Keywords: Wool; heavy metals; chromium(VI); adsorption; wastewater.

1. Introduction

Removal of heavy metals at low concentrations from an aqueous environment is generally difficult. In very low metal concentrations, processes such as chemical precipitation, reverse osmosis and other methods are not adequate and nor sufficient. Adsorption using activated carbon is an effective method for the removal or reduction of heavy metals from wastewaters. However, the process generally has a high cost [1].

The maximum permission limit of chromium in potable water is 50 μg/L in Turkey. The presence of Cr(VI) in drinking water is of great concern as Cr(VI) can lead to liver damage, pulmonary congestion and oedema. Various low cost materials and polymeric adsorbents have recently been reported to be potentially useful in the removal of metal ions from aqueous solution. For example, as a natural polymeric adsorbent, wool has successfully been used for heavy metal removal from aqueous solution [2-12].

In this study, batch adsorption experiments were carried out to evaluate the performance of locally available wool fibers in the removal of Cr(VI) from dilute aqueous solutions. The effect of important factors such as adsorbent concentration, contact time, pH and initial Cr(VI) concentration on Cr(VI) removal is investigated.

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Up to now, researchers have done studies on the adsorption of metals by wool [2-7,9,11,12], but with the exception for Bektas and Balkaya [8], they did not consider the adsorption of low concentration of Cr(VI) in water treatment purposes. Also, in some of these studies, wool samples were subjected to pretreatment in various ways such as soxhlet extraction, modification by polyethylenimine or acidified anhydrous methanol, conditioned with acetic acid etc. In the present study, the wool samples were not subjected to the pretreatment procedures performed by other researchers who studied metal removal using wool [2-7,11,122].

2. Materials and methods

2.1. Wool

Wool from sheep, goat and lamb used in this study were obtained from a commercial firm. The wool samples in loose form, taken from Samsun in Turkey were first cleaned by hand to remove animal and plant debris. They were then washed carefully with detergent and rinsed with tap water. The wool samples were dried for 24 h at 25 ˚C. They were not subjected to any pretreatment, except for washing with detergent.

2.2. Chemicals

The chemicals used were of analytical reagent grade. Aqueous Cr(VI) solutions were prepared by dissolving anhydrous $K_2Cr_2O_7$ in distilled water.

2.3. Adsorption experiments

Batch adsorption experiments were carried out at room temperature by shaking the mixture wool-Cr(VI) solution in erlenmayer flasks at 100 rpm using a horizontal bench shaker (Nüve SL-350) throughout the contact time. Before the experiments, dry wool samples were swollen by immersion in 100 mL distilled water for a few minutes. After blotting excess water between two filter papers, the wet wool samples were put into erlenmayer flasks containing 100 mL Cr(VI) solutions. In this study, a similar experimental method used by Edgar and Simpson [4] and, Balköse and Baltacıoğlu [6] for studying uptake of metal by wool fibers was used.

The Cr(VI) contents in the aqueous solutions were determined spectrophotometrically at 540 nm using diphenyl carbazide as the complexing agent [13]. pHs of the solutions were adjusted to the required value with dilute nitric acid solution, where it was necessary.

Each cycle of adsorption test run was repeated at least twice to ensure the accuracy of the test data collected.

3. Results and discussion

The adsorption of Cr(VI) from dilute aqueous solution on the wool was examined as a function of adsorbent concentration, contact time, pH, initial metal concentration and types of adsorbent. The effect of the size of the wool samples was not taken into account in this study.

3.1. Effect of adsorbent dosage

Firstly, the effect of adsorbent dosage on Cr(VI) adsorption was researched. It was observed that the amount of Cr(VI) adsorbed varies with varying sorbent mass (g). As seen from Fig. 1, Cr(VI) adsorption decreased with the increase of adsorbent dosage. The decrease in amount of Cr(VI) adsorbed (mg/g) with increasing adsorbent mass is because of the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent [14].

3.2. Effect of contact time

The effect of contact time on the amount of Cr(VI) adsorbed is shown in Fig. 2 where the majority of Cr(VI) ions are adsorbed during the first 5 minutes. The amount of Cr(VI) adsorbed increases until 20 min and then remains practically unchanged. The fast rate of uptake of Cr(VI) ions during the first 5 minutes has significant practical importance, as it will facilitate smaller reaction volumes ensuring high efficiency and economy [15]. Balköse and Baltacıoğlu [6] also found similar results for uptake of metal cations (Cu, Zn, Ni) by kıvırcık wool fibers.

3.3. Adsorption kinetics-intraparticle diffusion model

The adsorption of Cr(VI) on the wool, taken from Samsun, Turkey, was analyzed using first order and second order kinetic models. It was seen that since the first and second order kinetic correlation indexes are quite low, it was better not to decide a precise kinetic degree that the adsorption of Cr(VI) species on the wool follows (Table 1).

Table 1. The reaction rate constants

First order kinetic		**Second order kinetic**	
k (h^{-1})	**r**	**k (L mol^{-1} h^{-1})**	**r**
0.0083	0.6569	0.1338	0.7869

R: Correlation coefficient

To fit the experimental data in an intraparticle diffusion plot is the most commonly used technique for identifying the mechanisms involved in the sorption process [14]. In the present paper, the kinetic of adsorption of Cr(VI) ions onto this wool was studied by using intraparticle diffusion equation. The initial rate of the intraparticle diffusion is the following [16-18]:

$$q = f\,(t^{½}) \qquad (1)$$

The rate parameter (K_i) for intraparticle diffusion can be defined as:

$$q = K_i\ t^{½} \qquad (2)$$

where K_i is the intraparticle diffusion rate constant (mg/g $min^{1/2}$).

To determine the intraparticle diffusion rate constant (K_i), q was fitted against $t^{1/2}$ (Fig. 3). The value of K_i was determined as 0.0012 mg/g $min^{1/2}$ from the slope of the plot.

As pointed out by Singh et al [17] and Vadivelan and Kumar [14], in the intraparticle diffusion model the linear plot indicates a rate controlled by the process. The plot of Fig. 3 is of a double nature, an initial curved portion followed by a linear portion and plateau. The initial curved portion is attributed to the boundary layer effect, the final linear portion to the intraparticle diffusion and the plateau to the equilibrium. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion rate constant K_i (mg/g $min^{1/2}$). The intercept of the plot reflects the boundary layer effect. If the intercept is large, the contribution of the surface sorption in the rate-limiting step will be greater.

It can be said that such a double nature or a non-linear relationship confirms that intraparticle diffusion is not a fully operative mechanism for this system. A similar result has been interpreted for adsorption of Cr(VI) on chitin by Sağ and Aktay [19] and Microcystis by Singh et al [17].

The kinetic data were further analyzed using the Boyd kinetic expression in order to predict the actual slow step involved. This kinetic expression predicts the actual slowest step involved in the sorption process for different sorbent sorbate systems [14]. The Boyd kinetic expression is given by [20];

$$F = 1 - (6 / \pi^2) \exp(- Bt) \qquad (3)$$

and

$$F = q / q_0, \qquad (4)$$

where q_0 is the amount of Cr(VI) adsorbed at infinite time (mg/g) and q represents the amount of Cr(VI) adsorbed at any time t (min), F represents the fraction of solute adsorbed at any time t, and Bt is a mathematical function of F.

Substituting Eq. (4) in (3), Eq (3) simplifies to;

$$1- F = (6 / \pi^2) \exp (- Bt) \qquad (5)$$

or

$$Bt = - 0.4977 – \ln (1 – F) \qquad (6)$$

The Bt values at different contact times can be calculated using Eq. (6). The calculated Bt values were plotted against time (t) as shown in Fig. 4. The linearity test of Bt vs t plot was employed to distinguish between the external transport or intraparticle transport controlled adsorption [14,21]. It was observed that at the studied initial Cr(VI) concentration Bt vs. t plot was not linear and do not pass through the origin confirming that the external transport mainly governs the adsorption process [20,22].

3.4. Effect of pH

The range from pH 1.0 to 5.0 was employed in this study. In Fig. 5, the effect of initial pH on the adsorption of Cr(VI) is presented. The amount of Cr(VI) adsorbed increased as the initial pH of the solution decreased. This result is consistent with the finding of Dakiky et al [9] on Cr(VI) removal by wool from sheep. They revealed that wool has a high adsorption capacity in acidic medium. They reported that the optimum pH for removal was found to be 2. Also, various adsorbents such as Sphagnum moss peat [23], Cladophora Crispata [24], phosphate treated sawdust [25], hazelnut shell [26], dried anaerobic activated sludge [27], activated carbon [28], coal [29], persimmon tannin gel [30], Fe-modified steam exploded wheat straw [31] and, activated alumina and activated charcoal [32] have exhibited a high adsorption capacity in acidic medium.

The interaction of Cr(VI) ions with the wool may be primarily electrostatic in nature. Cr(VI) ions, which are anionic nature, do not bind at high pH where the overall wool surface charge is negative, but they do bind at low pH where the wool surface charge is positive [24]. For the present study it can be said that at low pH the wool fibers will bear an overall positive charge originating from protonation of its acidic groups in that the anionic Cr(VI) ions will be electrostatically attracted. At pH values up to 5.0, due to deprotonation of carboxylic groups, the wool fibres build up an increasing negative charge accompanied with a concomitant repulsion towards the Cr(VI) ions. The protonated sites are likely to have taken part in the adsorption process, as revealed by Laurie and Barrachlough [5] for anionic $HgCl_3^-$ and $HgCl_4^{2-}$ and Tabak and Afsin [33] for ammonia and pyridine species. These sites possibly induce the hydrogenation of negative regions of the related species on the wool surface.

The efficient adsorption of Cr(VI) by wool at very low pH values may be explained in terms of ion exchange. Wool keratin has many functional groups, such as carboxylate, amine and amide that are potential binding sites for metal cations [2,6]. The efficient removal of Cr(VI) ions which are anionic in nature in highly acidic solutions may be involved in the exchange of the carboxylate, amine, amide groups with metal ions.

Sorption of heavy metals on inorganic sorbents depends strongly on the pH value. At low pH values (pH<5.0), a variety of inorganic sorbents can not be used efficiently in treatment of waters containing heavy metal ions [34]. Experimental results relating to pH indicated that in contrast to most inorganic sorbents, the wool as a polypeptide loose fibre (a natural polymer) is a suitable sorbent in acidic medium (Fig. 4).

3.5. Effect of initial Cr(VI) concentration

The effect of initial Cr(VI) concentration on the adsorption of Cr(VI) was studied by treating 5 g wool with 100 mL of Cr(VI) solution for 20 min at pH 2.0. Experimental studies were carried out at low Cr(VI) concentrations (0.1-0.9 mg/L) which can be available in drinking water sources (raw waters). With the concentration changes from 0.1 to 0.9 mg/L, the amount of Cr(VI) adsorbed increased from 0.0017–0.0180 mg/g (Fig. 6).

3.6. Cr(VI) uptake depending on kind of fibre

The morphological structure of wool fibers (cuticle, ortho and para cortex, medulla) and functional groups in wool keratin exhibit differences with each other [6]. Since the interaction between fibre and metal depends on the kind of fiber and its chemical nature in addition to the kind of metal and its valance state, the solution concentration, pH, time, temperature etc [6,11], in the lab-scale studies, the variation of Cr(VI) removal for different kinds of wool, respectively two kinds of wool from sheep, wool from lamb and wool from goat were investigated. As illustrated in Fig. 7, the Cr(VI) removal(%) obtained by wool from goat was higher than that by the other wool samples.

3.7. Adsorption isotherm

The equilibrium data obtained were analyzed in the light of Freundlich and Langmuir adsorption isotherms. The values of the Freundlich and Langmuir constants are presented in Table 1. The correlation coefficients (r) for the Freundlich and Langmuir equations were found to be higher than 0.98 (Table 1). Therefore, it can be said that Cr (VI) adsorption onto the wool fits to the Freundlich and Langmuir isotherms.

Freundlich constant 1/n was found as 0.358 for the present system. Considering this data, it can be said that since n>1, the adsorption is favourable [15]. Values of n in the range 2-10 represent good adsorption [35].

The Freundlich constant 1/n is also a measure of the deviation from linearity of the adsorption [36]. If the 1/n>1 or becomes larger (1/n>>1), the adsorption bond becomes weak, but if this value is less than 1 (0.358 for the present system), chemical rather than physical adsorption can be considered dominant. Thus, it can be said that chemical adsorption seems to be dominant when the locally available wool fiber is used for adsorbing Cr(VI) ions [36,37].

Table 1. The values of Freundlich and Langmuir constants [10].

Freundlich model			**Langmuir model**		
K (mg/g)	**n**	**r**	**q_m (mg/g)**	**b (L/mg)**	**r**
0.0398	2.7925	0.9966	0.0178	114.8209	0.9885

r: Correlation coefficient

3.9. Comparison of adsorption capacities of various adsorbents for Cr(VI).

In their previous studies, the current authors [8] studied Cr(VI) removal by the locally available wool from sheep, taken from Agrı, Turkey, at pH 5.4 and wool dosage of 90 g/L and room temperature. They obtained to 88.7% removal for 0.9 mg/L Cr(VI) at room temperature within 30 min. Dakiky et al. [9] obtained 81.3% removal for 100 mg/L Cr(VI) at pH 2 and wool dosage of 16 g/L and 30 °C within 2 h. Direct comparison of our study with other studies is difficult owing to the different applied experimental conditions. The concentration range studied by us was also smaller than the range one can find in literature. However, adsorption capacities of Cr(VI) on various adsorbents such as polymeric, low-cost, and activated carbon are presented in Table 2. The comparison of adsorption capacity values of various polymers [9,19,38] and wool (this study) for Cr(VI) indicates that although the Cr(VI) adsorption by locally available wool is favorable (n>1), it is not a strong adsorbent. However, the adsorption capacity of the wool from sheep is higher than that of various low cost adsorbents such as Cladophora Crispata [24], Seyitomer fly ash [29], soya cake [39], bagasse, fly ash and powdered activated carbon [40].

From the data it can be seen that a high amount of wool was used here (5 g/100mL) as adsorbent, and adsorption capacity of the wool was low. It should be noted that the wools used in this study were original length, not subjected to any pre-treatment like cutting in any size. It can be said that size reduction of adsorbent would increase the adsorption capacity. Also, if temperature optimization was improved, the adsorption capacity will also increase.

Table 2. Previously reported adsorption capacities of various adsorbents for Cr(VI).

Adsorbents	Adsorption capacity (mg/g)	References
Various polymers		
Chitin	28.04	[35]
Fe (II) polymethacrylates	22.26	[38]
Fe(III) polymethacrylates	3.87	[38]
Wool from sheep (sized 1 cm long fibers, 30 °C)	41.15	[9]
Low-cost adsorbents		
Cladophora Crispata	0.02-0.03	[24]
Soya cake	0.00028	[39]
Afsin-Elbistan fly ash	0.0809-0.2949	[29]
Seyitomer fly ash	0.0077-0.2160	[29]
Bagasse	0.0005	[40]
Fly ash	0.001	[40]
Heat activated bauxite	0.52	[41]
Activated carbon		
Powdered activated carbon	0.03	[40]
Wool from sheep, collected from Samsun, Turkey (not sized in specific length, room temperature)	0.04	This study

4. Conclusion

The results obtained in this study showed that the locally available wool fiber can be used as a natural adsorbent for removal of low concentrations of Cr(VI) from aqueous solutions. The initial pH values are crucial for the highest level of Cr(VI) adsorption. The wool fibers which are abundantly available in Turkey at low cost are cost effective adsorbents for removal of low concentrations of Cr(VI).

External transport mainly governs the adsorption process. It can be concluded that Cr(VI) removal by the wool seems to be a practical method from the standpoint of cost for treatment of drinking water sources (raw waters) and dilute industrial wastewater streams. When the waste wools discharged from wool manufacturing process is used for the present system, the relative cost of this material would be lower than that of virgin wool and even much lower than that of synthetic polymer-based materials.

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Fig. 1. Effect of adsorbent mass (g) on Cr (VI) removal (Initial Cr (VI) concentration: 0.70 mg/L; initial pH: 1.0; volume of solution treated: 100 mL; contact time: 45 min).

Fig. 2. Effect of contact time on Cr (VI) removal (Initial Cr (VI) concentration: 0.80 mg/L; pH: 0.9; adsorbent dosage: 50 g/L).

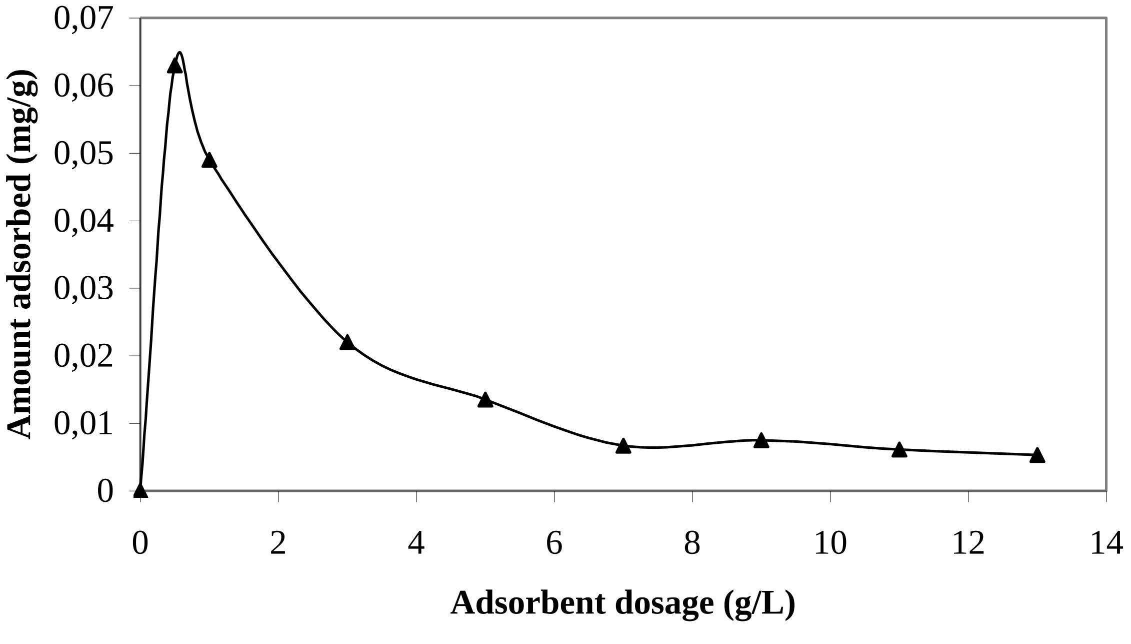
Fig. 3. Plot of q vs. $t^{1/2}$ for initial diffusion rate parameter (Initial Cr (VI) concentration: 0.80 mg/L; pH: 0.9; adsorbent dosage: 50 g/L).

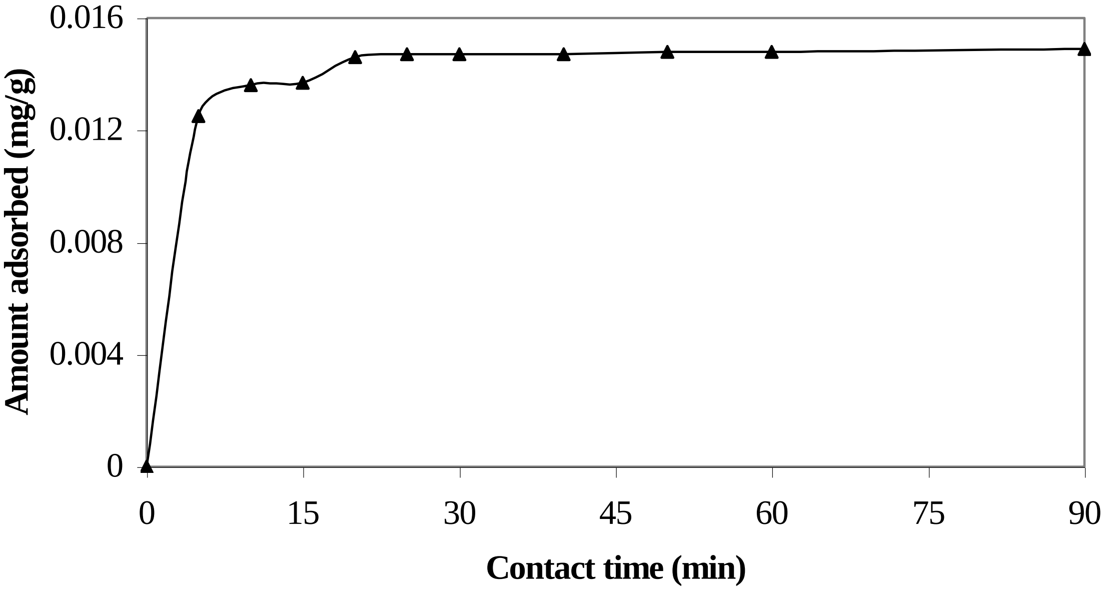
Fig. 4. Plot of Bt versus t (Boyd plot) (Initial Cr (VI) concentration: 0.80 mg/L; pH: 0.9; adsorbent dosage: 50 g/L).

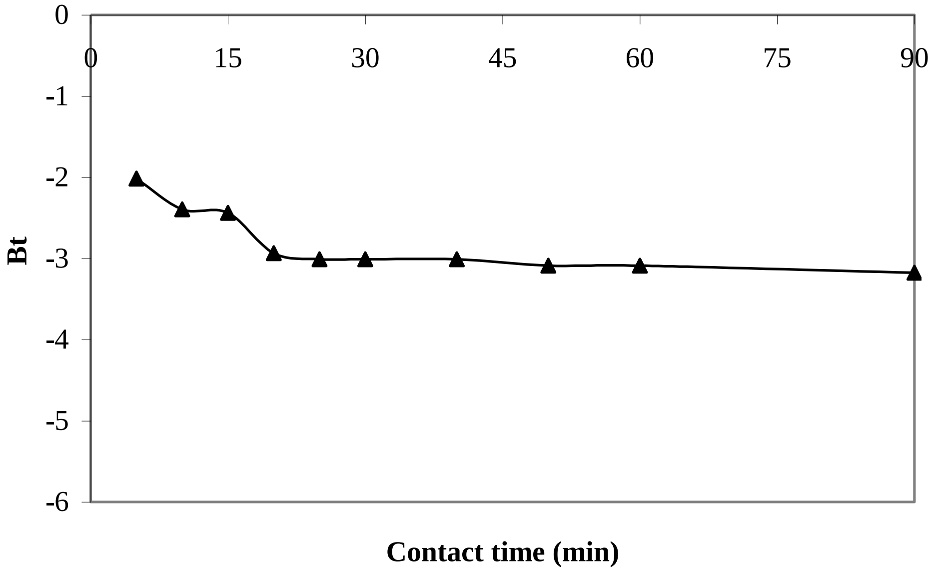
Fig. 5. Effect of initial pH on Cr (VI) removal (Initial Cr (VI) concentration: 0.80 mg/L; adsorbent dosage: 50 g/L; contact time: 20 min).

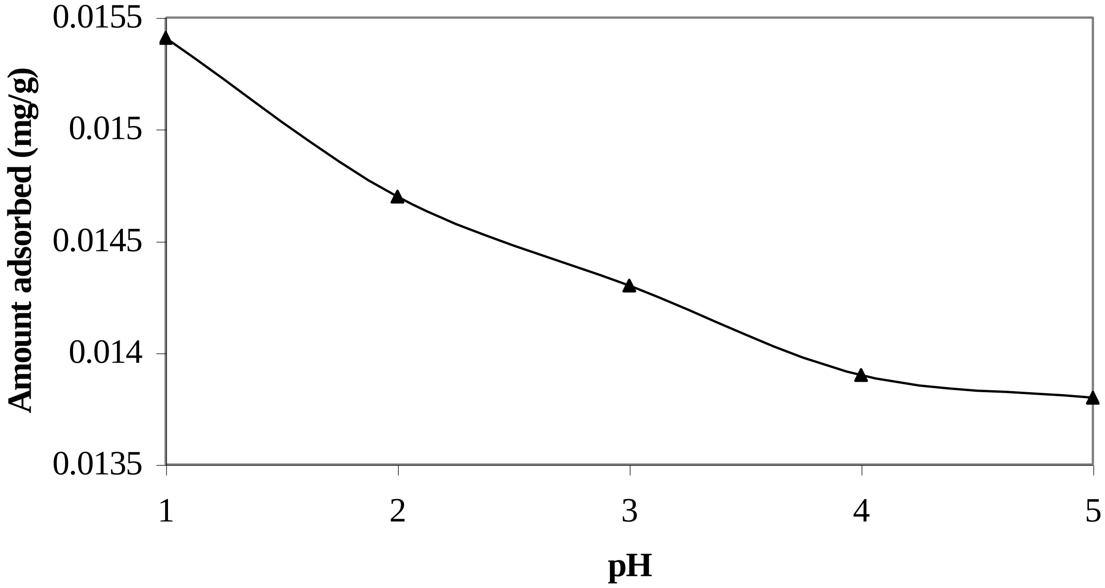
Fig. 6. Effect of initial Cr (VI) concentrations on Cr (VI) removal (Adsorbent dosage: 50 g/L; initial pH: 2.0; contact time: 20 min).

Fig. 7. The variation of Cr(VI) removal for different samples of wool, respectively wool 1 from sheep, wool 2 from sheep, wool from lamb and wool from goat (Initial Cr(VI) concentration: 0,90 mg/L; adsorbent dosage: 50 g/L; initial pH: 2.0 (Symbols; ●: wool from goat, O: wool from lamb, □: wool 1 from sheep, ■: wool 2 from sheep). P.S. wool 1 from sheep used in all of the experimental studies that revealed in this paper.




0.016
0.012
0.008
0.004
0
Amount adsorbed (mg/g)
0
15
30
45
60
75
90
Contact time (min)


0
-1
-2
-3
-4
-5
-6
Bt
0
15
30
45
60
75
90
Contact time (min)


Amount adsorbed (mg/g)
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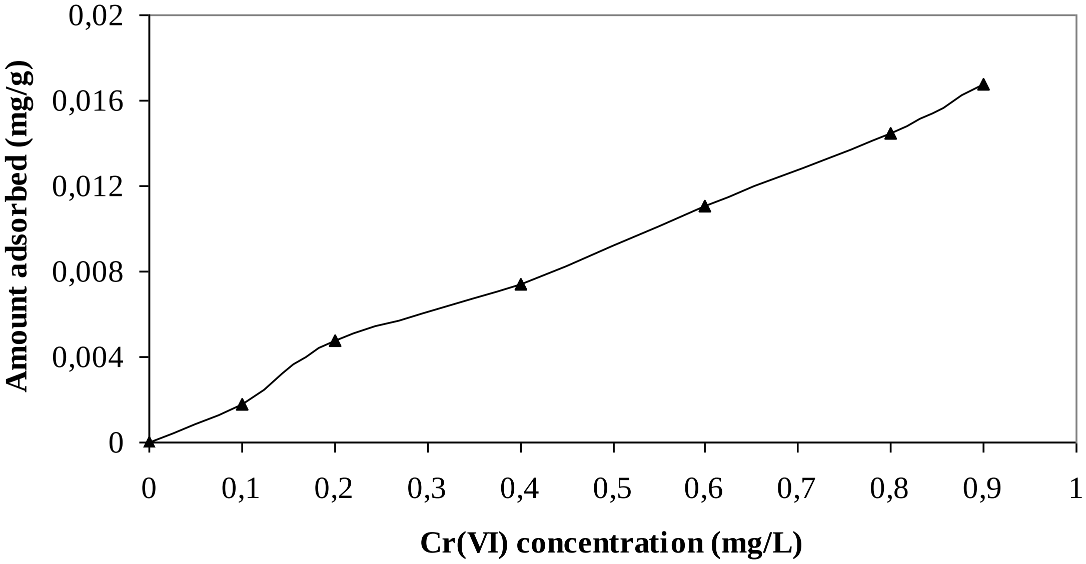
0.015
0.0145
0.014
0.0135
1
2
3
4
5
pH


Amount adsorbed (mg/g)
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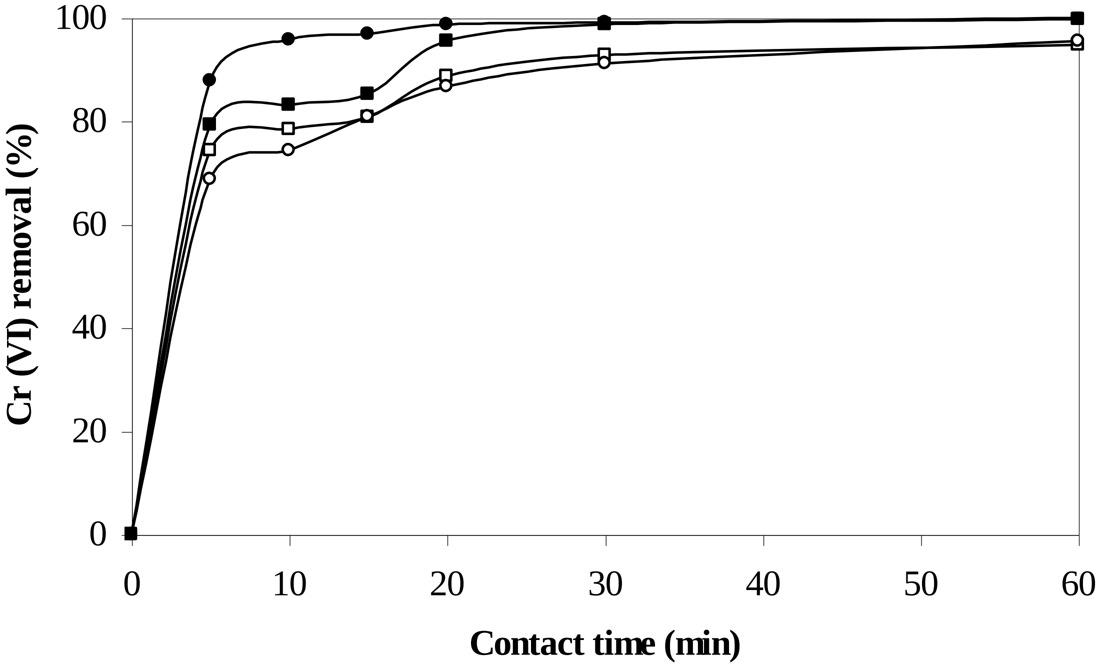
0,016
0,012
0,008
0,004
0
0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1
Cr(VI) concentration (mg/L)


100
80
60
40
20
0
0
10
20
30
40
50
60
Cr (VI) removal (%)
Contact time (min)

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REMOVAL OF LEAD FROM AQUEOUS SOLUTIONS BY PHOSPHOGYPSUM TREATED WITH LIME

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In this paper, the removal of lead ions from aqueous solutions by phosphogypsum, which is both a waste material and by-product of phosphoric acid production by wet process in a fertiliser plant, was investigated. The influence of phosphogypsum treatment with lime on lead ion adsorption was studied in a batch process. The removal capacity of lime-pretreated phosphogypsum was compared to that of untreated phosphogypsum. It was concluded that the treatment of phosphogypsum with lime not only slightly increased its adsorption capacity but also helped to remove the water-soluble impurities in phosphogypsum by converting them to water-insoluble compounds.

Keywords: *Adsorption; aqueous solution; lead; isotherm; phosphogypsum*

1. Introduction

Heavy metals are one of the most wide-spread pollutants in the environment. That they can be accumulated in the environment, is their greatest concern.

It is known that lead is a highly toxic poison. It affects many organs, especially has special affinity for bone and brain tissue. Lead exposure can also affect the nerves that arise from the brain and spinal cord (the peripheral nervous system). It also damages the kidneys. Lead has a profound effect on reproduction, in laboratory animals and humans alike [1]. As a result of its toxic effect to other life forms as well as being damaging to aquatic life, the discharge of lead wastes into streams and rivers poses a severe problem. Therefore, this toxic metal must be removed from water and wastewater.

The methods used to remove heavy metal ions such as lead, cadmium, and zinc are: chemical precipitation, adsorption, ion-exchange, reverse osmosis, electrodialysis, electrochemical reduction. Although adsorption process is one of the most frequently applied method in the industries, the activated carbon, which is a widely used adsorbent in this process, is expensive. Thus, as an alternative adsorbent for activated carbon, the usage of agricultural residues or industrial by-product has received considerable attention.

Up to now, several authors carried out studies on lead (Pb) adsorption from aqueous solutions by using various agricultural residues, industrial by-products and waste. Industrial wastes and by-products such as Fe(III)/Cr(III) hydroxide [2], red mud [3,4], fly ash [5], waste processed solid residue of oil mill products [6], spent grain [7], electric furnace slag [8001], phosphogypsum [9,10], sawdust of Pinus sylvestris [11], bagasse fly ash [12], black gram husk [13], rice bran [14] and olive stone waste [15] have been successfully used to remove Pb(II) ions from aqueous solutions.

This study aims to evaluate the use of lime-pretreated phosphogypsum as an adsorbent for the removal of Pb(II) ions. Phosphogypsum is a waste material and by-product of the phosphate fertilizer industry produced in large quantities worldwide by the dehydrate wet phosphoric acid process. It is accumulated at industrial sites and has no apparent commercial value. Therefore, its use as adsorbent seems appropriate. In this study, the removal of Pb(II) ion from aqueous solution was carried out by using lime-treated phosphogypsum, as adsorbent in batch. The effects of adsorbent dosage, pH, contact time and initial concentration on Pb(II) adsorption have been studied.

Some studies for the removal of Pb(II) ion [9,10] and Zn(II) ion [16] using this adsorbent have been reported. This present work is different from the previous study relating to Pb(II) removal by phosphogypsum by the present authors as it is an attempt to remove Pb(II) ions from aqueous solution by phosphogypsum pre-treated with lime.

2. Materials and Methods

Phosphogypsum was obtained from TÜGSAŞ Fertiliser Plant in Samsun, Turkey. It was sieved through 45 and 65 mesh respectively. The phosphogypsum fraction retained on the 65 mesh was collected and this fraction was used as the adsorbent in our study.

Some physical and chemical characteristics of the phosphogypsum have already been reported by Ölmez and Yılmaz [17] and Balkaya and Cesur [10].

All the chemicals used in the experimental studies were of analytical reagent grade. All the solutions were made with double distilled water.

Before use in the experimental studies, the phosphogypsum was washed with milk of lime as described by Ölmez and Yılmaz [17].

Lime-pretreated phosphogypsum was added to 100 ml of Pb(II) solution taken in 250 mL Erlenmeyer flasks sealed with caps. The Erlenmeyer flasks were then placed on a horizontal bench shaker (Nüve SL-350) and agitated at 100 rpm at room temperature. At the end of the experiment the samples were centrifuged at 1000 rpm for 5 min and the supernatant was analyzed for Pb(II) ions using an atomic adsorption spectrophotometer (ATI UNICAM 929 Model Flame AAS).

The pH in solution was adjusted with HNO_3 and NaOH to cover a pH range from 1-6. Each experiment was repeated two times and the results are given as averages.

3. RESULTS AND DISCUSSION

3.1. Effect of adsorbent dosage

Effect of phosphogypsum dosages on adsorption of Pb(II) ion is shown in Figure 1. The dosage was varied from 1.0 to 30.0. It is apparent that Pb(II) uptake per unit weight of the adsorbent (mg/g) decreases with increasing phosphogypsum dosages for a given initial Pb(II) concentration. Such an effect of adsorbent dosage on adsorption of heavy metals had also been observed for fungal mycelial by-product [18], rice bran [14], solid adsorbents such as sand, silika, coal and alumina [19], scoria [20], and intact and pretreated spirluna maxima biomass [21]. The low adsorption observed for increasing phosphogypsum dosages may arise for three reasons; (i) electrostatic interactions, (ii) interference between binding sites, or (iii) reduced mixing at higher adsorbent densities [14,18,22].

3.2. Effect of contact time

The Figure 2 shows the effect of contact time on the adsorption of Pb(II) by phosphogypsum. Rapid Pb(II) uptake (mg/g) was observed within the first 15 min of contact. The rapid increase is probably due to the abundant availability of active sites on the material. Slower increase in adsorption above contact time of 15 min is due to gradual occupancy of these sites [15]. Beyond 30 min, the adsorption trends remain constant and then decreased slightly as shown in Figure 2.

3.3. Effect of pH

Since the study of pH on the adsorption of Pb(II) by adsorbent is important in establishing the optimum adsorption of Pb(II) ions at the solid/liquid interface, we examined the effect on Pb(II) uptake of different pH values in the range of 1-5. At higher pH values than 6, Pb(II) ions precipitates in the form of $Pb(OH)_2$ because of the high concentration of OH^- ions in the adsorption medium [10,23], so adsorption studies at these pH values could not be performed. It can be clearly seen from Figure 3 that although Pb(II) adsorption increases with increasing solution initial pH, it did not show a very significant increase with a rise in the pH.

Pb(II) uptake was low at pH 1-3 comparing to pH 3-5. Low Pb(II) uptake low at pH 1-3 can be explained on the basis of proton-competitive sorption reactions and the decrease in positive surface charge. At this acidic pH, the proton concentration is high and protons can compete with Pb(II) ions, which are present in solution as free cation for surface sites. Various researchers have described the above metal adsorption by connecting to solution pH [5,7,15,24,25].

Due to the high adsorption capacity of adsorbent at acidic medium, phosphogypsum can be an attractive agent for the treatment of acidic industrial wastewaters.

3.4. Effect of initial Pb(II) concentration

The adsorption experiments were carried out in the concentration range of 5.0-50.0 mg/L. The results are graphed in Figure 4. It is observed that the amount adsorbed of Pb(II) ion tended to increase with increasing initial Pb(II) concentration. This increase may be due to an increase in electrostatic interactions involving sites of progressively lower affinity for Pb(II) ions [20,27].

It can also be said that this method is suitable for the removal of relatively high concentrations of Pb(II).

3.5. Adsorption isotherms

The Langmuir and Freundlich models were used to describe the adsorption equilibrium. The Langmuir model has the form [28,29]:

$$q = \frac{bq_m C_e}{1 + bC_e} \qquad (2)$$

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (3)$$

where C_e is the equilibrium metal concentration (mg/L), q is the mass of contaminant adsorbed per unit weight of the adsorbent (mg/g), q_m indicates the adsorption capacity of the adsorbent (mg/g) and b is the Langmuir isotherm constant (L/mg).

and the Freundlich model has the form:

$$q = KC_e^{1/n} \qquad (4)$$

$$\log q = \log K + \frac{1}{n}\log C_e \qquad (5)$$

where C_e is the equilibrium metal concentration (mg/L), q is the mass of contaminant adsorbed per unit weight of the adsorbent (mg/g), and K and n are constants, indicating the adsorption capacity and adsorption intensity, respectively.

The Freundlich and Langmuir constants and their values along with the correlation coefficients (r) relating to raw (untretaed) phosphogypsum and lime-pretreated phosphogypsum are given in Table 1. As can be seen from correlation values presented in the Table 1, the Freundlich isotherm was found to be more suitable than the Langmuir isotherm for raw phosphogypsum and lime-pretreated phosphogypsum.

The Freundlich equation predicts that the Pb(II) concentrations on the adsorbent will increase so long as there is an increase in the Pb(II) concentration in the liquid [30].

The adsorption isotherms of Pb(II) onto raw phosphogypsum and lime-pretreated phosphogypsum are illustrated in Fig. 5. The shape of the isotherms seems to be of type II or III in the BET classificaiton.

Table 1. Freundlich and Langmuir adsorption constants for Pb(II) ion onto phosphogypsum.

Experimental Conditions/Adsorbents	**Langmuir model**			**Freundlich model**		
Initial Pb(II) concentrations: 10-50 mg/L; pH: 4; contact time: 15min	q_m (mg/g)	b (L/mg)	r	K (mg/g)	n	r
Raw (untreated phosphogypsum)	5,6818	0,4730	0,9507	1,7860	1,6399	0,9698
Lime pre-treated phosphogypsum	-2.8011	-13.0223	0.7721	22.6568	0.5800	0.9226

r: Correlation coefficient

As known, 1/n is related with the heterogeneity of surface and the distribution of bonds [31]. It can be said that as 1/n value of raw phosphogypsum is less than 1, chemical rather than physical adsorption seems to be dominant. 1/n value of lime-pretreated phosphogypsum is not less than 1. Therefore, physical rather than chemical adsorption seems to be dominant in Pb(II) adsorption by pre-treated phosphogypsum [32].

3.6. Comparative study

In this work, the adsorption experiments were performed by raw phosphogypsum and lime-pretreated phosphogypsum in order to compare the effect of pre-treatment on Pb(II) removal. The results of kinetics studies were presented comparatively for the lime-pretreated phosphogypsum and the raw phosphogypsum in Figure 6. As can be seen from Figure 6, adsorbed amount of Pb(II) by lime-pretreated phosphogypsum was almost equal to that of Pb(II) by using raw phosphogypsum.

The isotherm data obtained from the experiments were presented comparatively in Table 1. As can be seen from Table 1, the adsorption of Pb(II) ions in the lime-pretreated phosphogypsum resulted in a decrease in the Langmuir constant b value comparing with that of raw phosphogypsum. As known, b is an indicator of the stability of the combination between adsorbate and adsorbent surface. If the value of b is small, the adsorbate has a high binding affinity for the adsorbent [33]. It can be said that the lime-pretreated phosphogypsum seems to be more efficient compared to raw phosphogypsum. Also, adsorption capacity K relating with the lime-pretreated phosphogypsum is higher than that of the raw phosphogypsum under the same conditions.

It can be said that the pretreatment of phosphogypsum by lime leads to the formation of an adsorbent with synergistic effects for Pb(II) removal compared to raw phosphogypsum. In addition, the pretreatment of phosphogypsum by lime milk neutralises the water-soluble impurities, P_2O_5 and F, in phosphogypsum. Since the Pb(II) may be retained in the form of insoluble hydroxide salts within lime-preconditioned phosphogypsum, Pb(II)-loaded phosphogypsum after adsorption can be disposed, e.g. landfilling or utilised as building or road making materials, without the suspicion of leachability of Pb(II) [10,16].

3.7. Adsorption capacities of phosphogypsum and various low-cost adsorbents.

Comparision of the adsorption capacity of the phosphogypsum with those of some other adsorbents reported in literature is presented in Table 2. It can be said that direct comparison of phosphogypsum used with other reported adsorbents is difficult. For adsorbents given Table 2, differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area, and experimental conditions employed in those studies (initial metal concentration, initial pH etc).

The Pb(II) adsorption determined here was higher than that observed for the following adsorbents in Table 2, except for palygorskite clay [40], steam-activated pecan shell carbon (PSS) and phosphoric acid-activated pecan shell carbon (PSA) [41].

Table 2. Adsorption capacities for Pb(II) adsorption to different adsorbents.

Adsorbents	**Adsorption capacity, K (mg/g)**	**References**
<u>*Low cost adsorben ts:*</u>		
Fungus Aspergillus niger (pre-treated)	8.27	[34]
Fungus Aspergillus niger (live)	0.63	[34]
Natural sepiolite	3.36-9.66	[35]
Natural clinoptilolite	5.27-21.32	[36]
Black gram husk	7.33	[37]
Fly ash	1.66-47.67	[38]
Rice brain	2.62	[14]
Intact spirulina maxima biomass	4.97	[21]
Pretreated spirulina maxima biomass	8.11	[21]
Fungus Mucor rouxii biomass (live)	14.31	[39]
Fungus Mucor rouxii biomass (pre-treated)	10.73-10.88	[39]
Palygorskite clay	23.89	[40]

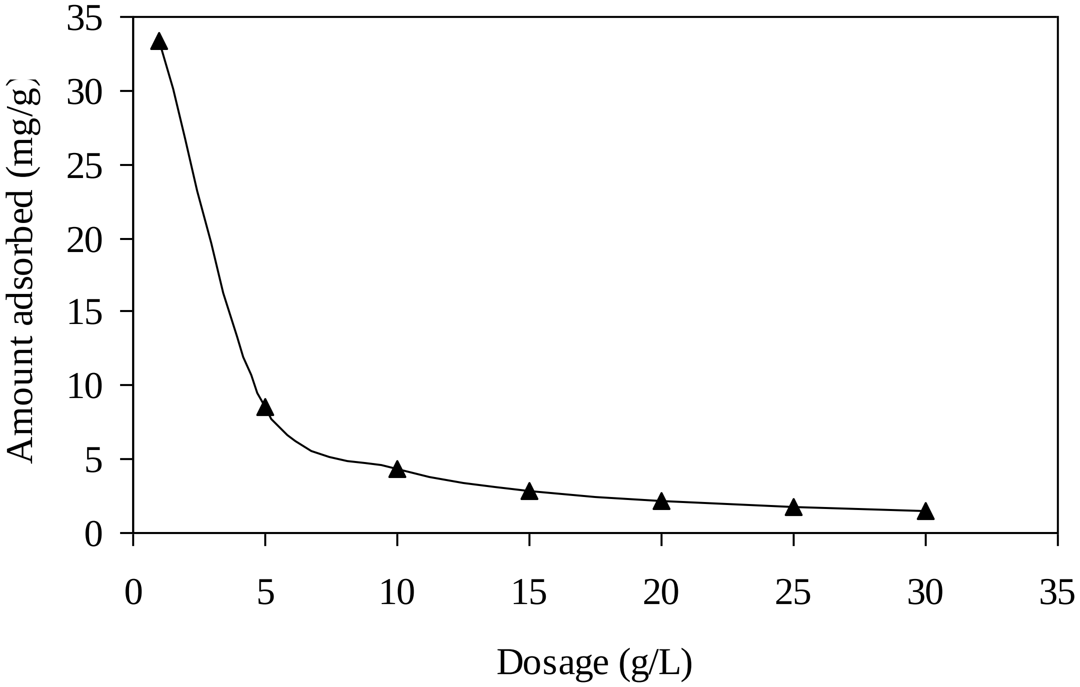
Table 2. Cont.

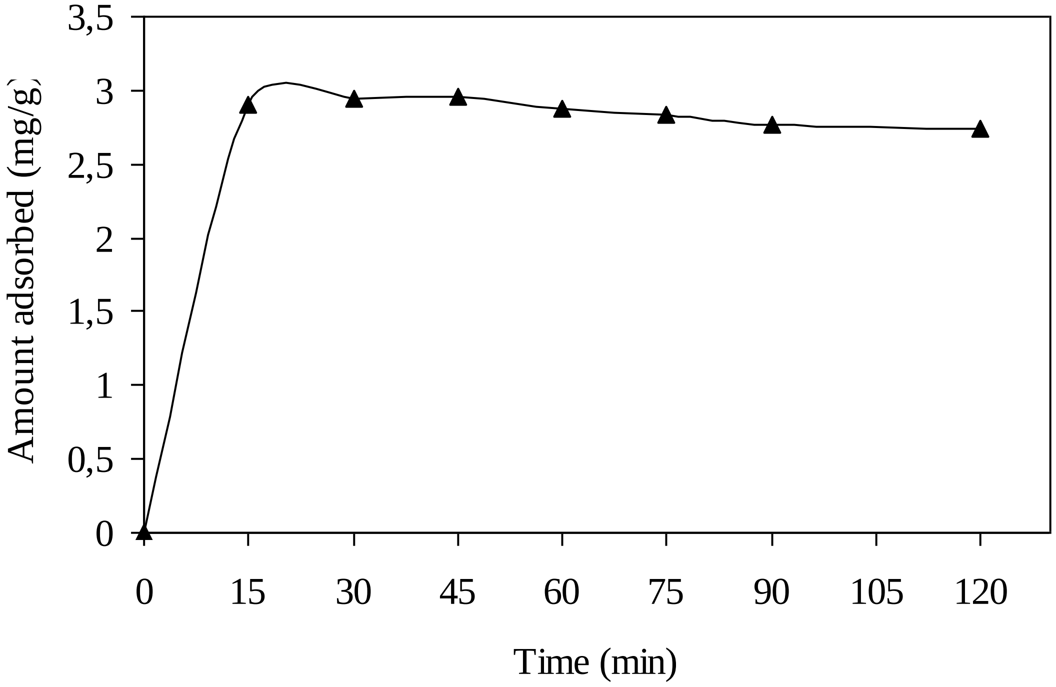
Activated carbon:		
Commercial carbon, Granular activated carbon Filtrasorb 400	7.12	[34]
Commercial carbon, Filtrasorb-200 (from Calgon Carbon Co)	14.6	[41]
Phosphoric acid-activated pecan shell carbon (PSA)	64.2	[41]
Carbon dioxide-activated pecan shell carbon (PSC)	1.94	[41]
Steam-activated pecan shell carbon (PSS)	34.7	[41]
Carbon aerogel	1.04	[25]
Lime-pretreated phosphogypsum	22.66	This study
Raw phosphogypsum	1.79	This study

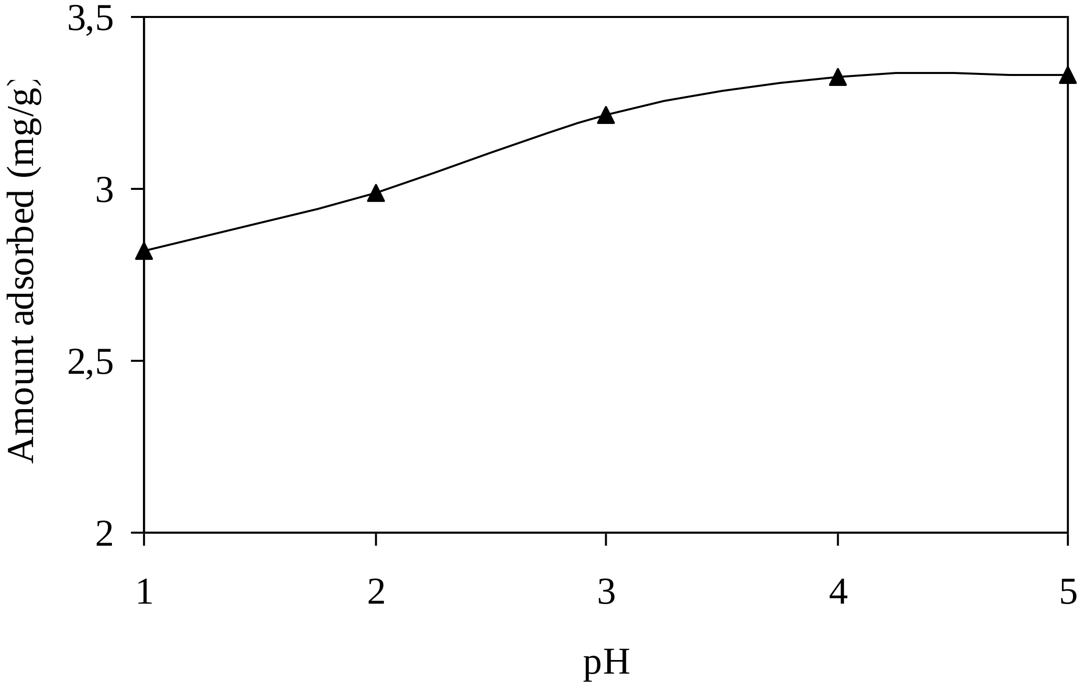
4. CONCLUSION

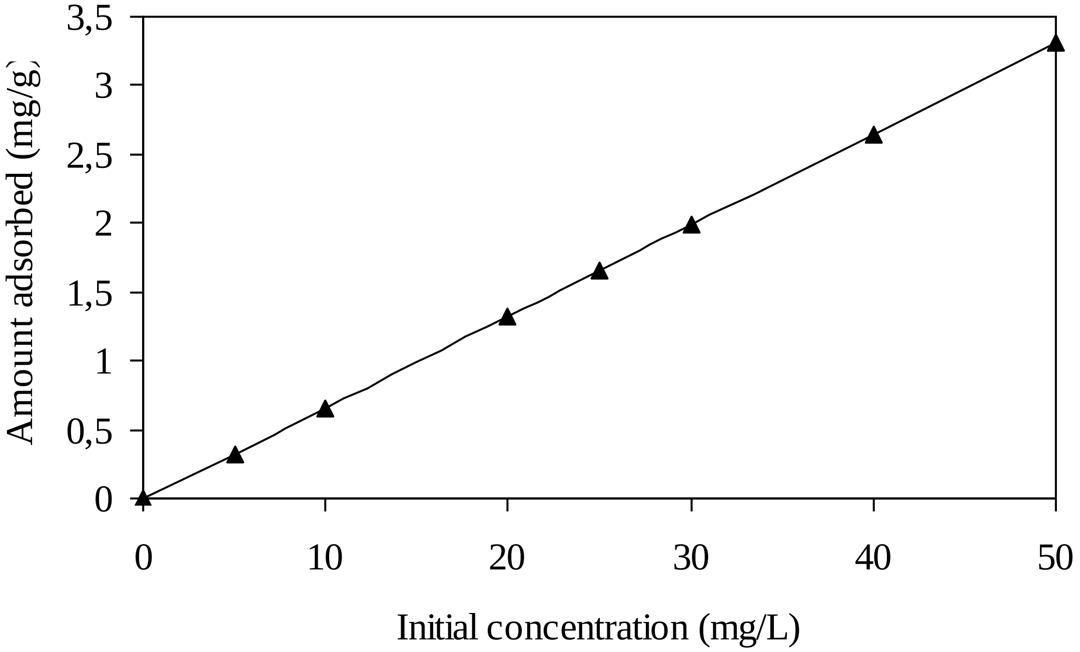
The present study showed that lime-pretreated phoshogypsum can be used as an inexpensive and efficient adsorbent material for the removal of Pb(II) ions from aqueous solutions. Lime-pretreated phoshogypsum was found to have higher Pb(II) removal compared to raw phoshogypsum.

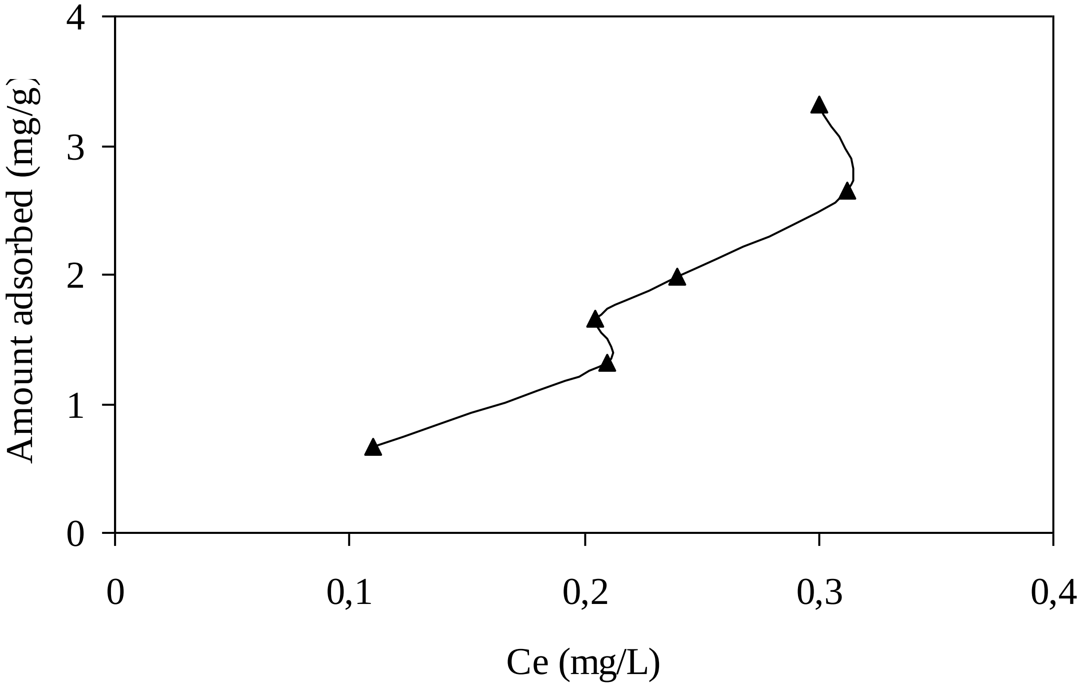
By comparing the cost of activated carcoal and carbonaceous adsorbent, which are 5.0 and 0.2 U.S. $/kg, respectively [42], the Pb(II) removal by the phosphogypsum from industrial wastewaters is expected to be economic, since the adsorbent is disposed as waste by industries. Consequently, adsorption of Pb(II) on lime-pretreated phoshogypsum can be considered as a simple, efficient and economic method for Pb(II) removal from wastewater.


Amount adsorbed (mg/g)
35
30
25
20
15
10
5
0
0
5
10
15
20
25
30
35
Dosage (g/L)


Amount adsorbed (mg/g)
3,5
3
2,5
2
1,5
1
0,5
0
0
15
30
45
60
75
90
105
120
Time (min)


Amount adsorbed (mg/g)
3,5
3
2,5
2
1
2
3
4
5
pH


3,5
3
2,5
2
1,5
1
0,5
0
Amount adsorbed (mg/g)
0
10
20
30
40
50
Initial concentration (mg/L)


4
3
2
1
0
Amount adsorbed (mg/g)
0
0,1
0,2
0,3
0,4
Ce (mg/L)

(a)

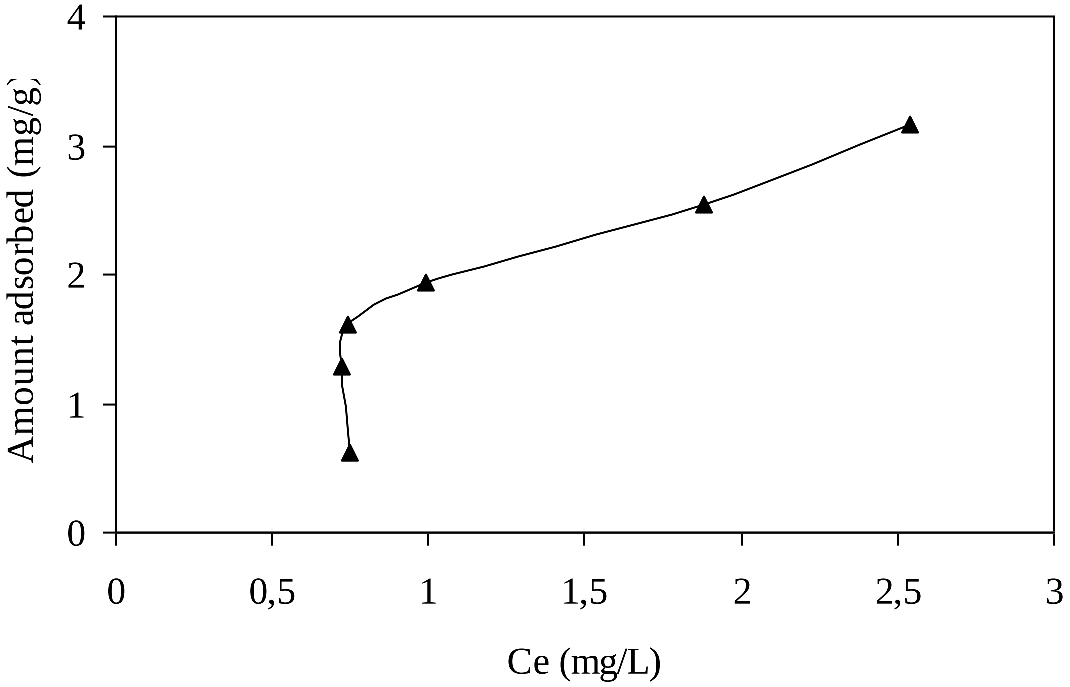

Amount adsorbed (mg/g)
4
3
2
1
0
0
0,5
1
1,5
2
2,5
3
Ce (mg/L)

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Fig. 1. Effect of phosphogypsum dosage (Initial concentration of Pb: 50 mg/L; contact time: 1 h; pH 1.6)

Fig. 2. Effect of initial contact time (Initial concentration of Pb: 50 mg/L; phosphogypsum dosage: 15 g/L: pH: 1.55)

Fig. 3. Effect of initial pH (Initial concentration of Pb: 50 mg/L; phosphogypsum dosage: 15 g/L: contact time: 15 min)

Fig. 4. Effect of Pb(II) concentration (Phosphogypsum dosage: 15 g/L; contact time: 15 min; pH: 4).

Fig. 5. Adsorption isotherm of Pb(II) on a) lime-pretreated phosphogypsum b) raw phosphogypsum (Phosphogypsum dosage: 15 g/L; contact time: 15 min; pH: 4).

DECOLORIZATION OF DRIMARENE BLUE K2-RL BY *FUNALIA TROGII* ATCC 200800 CULTURE FILTRATE IMMOBILIZED IN ALGINATE BEADS

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Synthetic dyes containing various substituents such as nitro and sulfonic groups are not uniformly susceptible to biodecolorization in conventional aerobic processes. Many fungal strains and fungal enzymes have been studied for their abilities to degrade a wide variety of structurally diverse pollutants. In this study, decolorization of Drimarene Blue K2-RL by ***Funalia trogii*** ATCC 200800 culture filtrate immobilized in alginate beads was investigated. Four different cations (Ca^{2+}, Cu^{2+}, Ba^{2+}, Zn^{2+}) were used for preparation of alginate beads to immobilize ***F. trogii*** 200800 culture filtrate. To obtain effective cations, alginate concentration, pH, temperature and dye concentration were adjusted as 3%; 4,0; 50 ^{o}C and 50 mg/L respectively. Alginate beads were re-used in dye containing media when 95 % decolorization occured. Ca, Cu, Ba, Zn-alginate beads containing culture filtrate were decolorized dye and each alginate beads re-used 4, 6, 5, 3 times respectively. Maximum decolorization was obtained by Cu-alginate beads. In order to determine the suitable Cu concantration in alginate beads for decolorization, 1, 3, 5 % Cu were used. The best result was obtained by 3% Cu-alginate beads that were re-used six times. When dye concentration was increased from 50 mg/L to 200 mg/L, higher decolorization efficiency was determined.

Key words: *Decolorization, **Funalia trogii**, Alginate Bead, Drimarene Blue K2-RL*

Introduction

Dyes are eliminated by a wide variety of aerobic or anaerobic organisms which are preferably employed as mixed cultures because of their relative robustness and versatility against xenobiotic compounds (Binkley and Kandelbauer, 2003; McMullan et al., 2001). Only recently, a combination of an anaerobic/aerobic pilot plant for the treatment of colored textile effluents was described (Sarsour et al., 2001). One major advantage of such systems is the complete mineralization often achieved due to synergistic action of different organisms (Stolz, 2001). In recent years, a number of studies have focused onsome microorganisms which are able to biodegrade and biosorb dyes in wastewaters. A wide variety of microorganisims capable of decolorizing a wide range of include some bacteria, fungi and algae.

White rot fungi such as *Phanerochaete chrysosporium* (Kirby et al., 1995), *Trametes versicolor* (Swamy and Ramsay, 1999), *Trametes hispida* (Rodriguez et al., 1999), *Pleurotus ostreatus* (Rodriguez et al., 1999), *Bjerkandera adusta* (Heinfling et al., 1998), *Pycnoporus cinnabarinus* (Schliephake and Lonergan, 1993), *Coriolus versicolor* (Mazmanci et al., 2002) and *Funalia trogii* (Özsoy et al., 2005; Mazmanci, et al, 2005) have been shown to decolorize textile dyes or colored effluent. In fungal decolorization of dye or dye wastewater, these fungi can be classified into three kinds: living cells to biosorb, dead cells (fungal biomass) to adsorb and enzymes (extracellular enzymes produced by fungi) to biodegrade or decolorize dye.

Living cells have a wide variety of decolorization mechanisms, but they have serious disadvantages. Their performance has a close relationship with the operating conditions (the concentration of influent, pH and temperature). They require a nutrient, supply, if the influent lacks nutrients, as well as cultural maintenance. Compare with living cells the daed cells may be stored, or used, for extended periods. Their biosorptive capacities may be greater than, equal to, or less than, those of living cells. Their operation is easy and their regeneration is simple but chemicals used for regenaration created a new waste. The other hand, ligninolytic enzymes produced by fungi is capable of decolorize the dye effluents and these enzymes not only decolorize but they also degrede the dye structure.

For this aim, we studied that decolorization of Drimarene Blue by the crude extract of *F. trogii* grown in SSF medium. Also, the best cation and cation concentration for immobilization of crude extract were demonstrated.

Materials and Methods

Dye and chemicals

Commercial dyes Drimaren Blue K2-RL (Figure 1) were provided by Berdan Textile Co., Tarsus, Turkey. All other chemicals were obtained from Merck.

Preparation of *Funalia trogii* Culture Filtrate

F. trogii ATCC 200800 was inoculated in SSF medium (containing 90% wheat bran 10% soybean hull) humidified with SBM (Deveci et al. 2004). Inoculated SSF medium was incubated (Sanyo) at 30°C 10 days. At the end of these incubation periods cultures were taken out of the flasks. The harvested cultures were dehumidified at 40 ˚C (Electromag 6040BP incubator) for 24 h.
After dehumidification cultures were dissolved at pH 6.0 potassium–phosphate buffer (0.1 g culture/ml) and centrifuged (Hettich micro 22R) at 5000 rpm for 15 min. Then, supernatant was filtered (Whatman No. 1). The filtrate (crude enzyme solution) was used for decolourisation studies.

Immobilization of Crude Extract

Crude extract was entrapped in Cu-, Ba-, Zn- and Ca-alginate polymer beads at a concentration of alginate of 3 % (w/v). The alginate solution was mixed with crude extract, the mixture was extruded through a needle (2 mm i.d.) into each 3 % cation containing solution ($CaCl_2$, $CuCl_2$, $BaCl_2$, $ZnCl_2$) and the beads formed (approximately 50 beats) were maintained at same cation solution at room temperature for 15 min.

Decolorization assay

Decolorization of Drimaren Blue K2-RL was determined spectrophotometrically (Shimadzu UV-160A) by measuring the decrease in 616 nm. Percentage of decolorization was calculated according to the following formulation:

Percentage of decolourisation = $(A_b – A_a) / A_b / 100$

A_b is the absorbance at the maximum absorption wavelength of dye before decolourisation and A_a the absorbance at the maximum absorption wavelength of dye after decolourisation. Same amount of dye was re-added in flask containing alginate beats after discharged liquid media when 90 % decolorization was determined. Magnetic stirred was used for agitation (150 rpm). Three different experiments were done. Four different cations, cations concentrations and dye concentrations were examined for decolorization of Drimaren Blue K2-RL by crude extract of *F. trogii* ATCC 200800. Experimental results are obtained by means of three replicates.

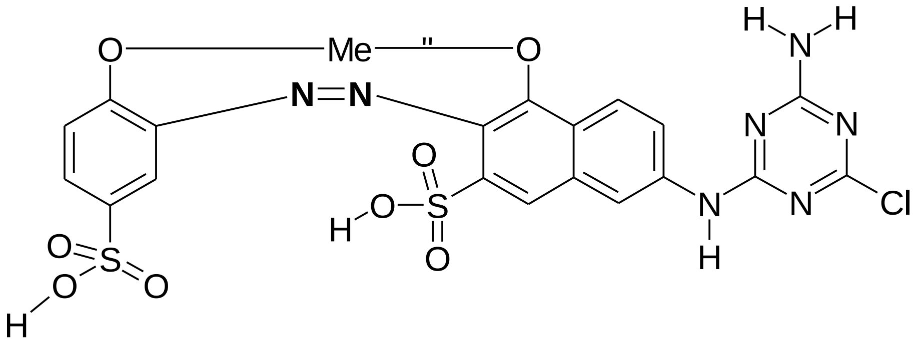

Figure 1. Structure of Drimaren Dyes (MDL ISIS^{TM}/ Draw 2.5)

Results and Discussion

Effect of Cations

Four different cations were tested. To obtain effective cations, alginate concentration, pH, temperature and dye concentration were adjusted as 3%; 4,0; 50 ^{o}C and 50 mg/L respectively. Dye was re-added to medium at same concentration when up to 90 % decolorization occurred. Dye was decolorized in the first cycle approximately 40 min. After third cycle, deformation was observed in alginate beats containing Zn^{++}. Same deformation was observed in Ca- and Ba-alginate beats on the fourth and fifth cycle respectively (Figure 2). This effect resulted in decrease of decolorization.

Ca, Cu, Ba, Zn-alginate beads containing culture filtrate were re-used 4, 6, 5, 3 times respectively. Maximum decolorization was obtained by Cu-alginate beads. At the end of the incubation period, approximately 300 mg/L dye was decolorized by Cu-alginate beats containing crude extract. Adsorption of dye on alginate beats was also monitored, but no adsorption was detected (Kandelbauer et al., 2004). Lower cation concentrations resulted in fewer cross-links at the guluronic acid binding sites leading to deformation in the alginate matrix.

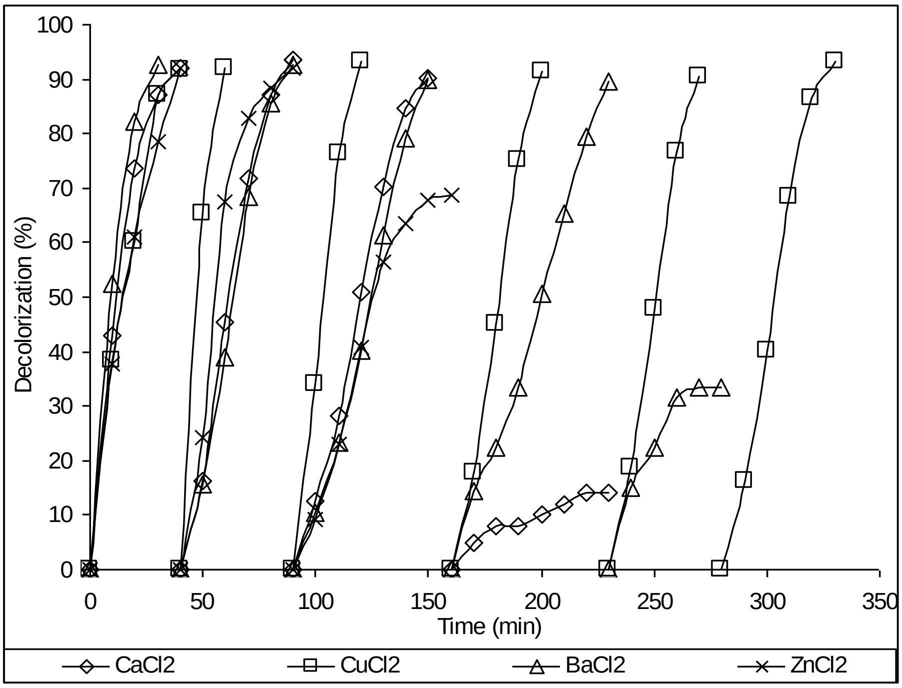

Figure 2. Effect of Cations Containing Crude Extract on Decolorization of Drimaren Blue

(50 mg/L dye, 50C, 150 rpm)

Effect of Copper and Calcium Concentration

In order to determine, suitable Cu concentration in alginate beads for decolorization, 1, 3, 5 % Cu concentration were used and the same Ca concentration was chosen for comparization. Dye concentration, temperature and agitation speed was fixed 50 mg/L, 50C and 150 rpm respectively. 5 % copper containing beats and all calcium containing beats damaged in 50 °C at the end of the first cycle. The same effect was obtained in 1 % Cu containing beats at end of the fifth cycle (Figure 3).

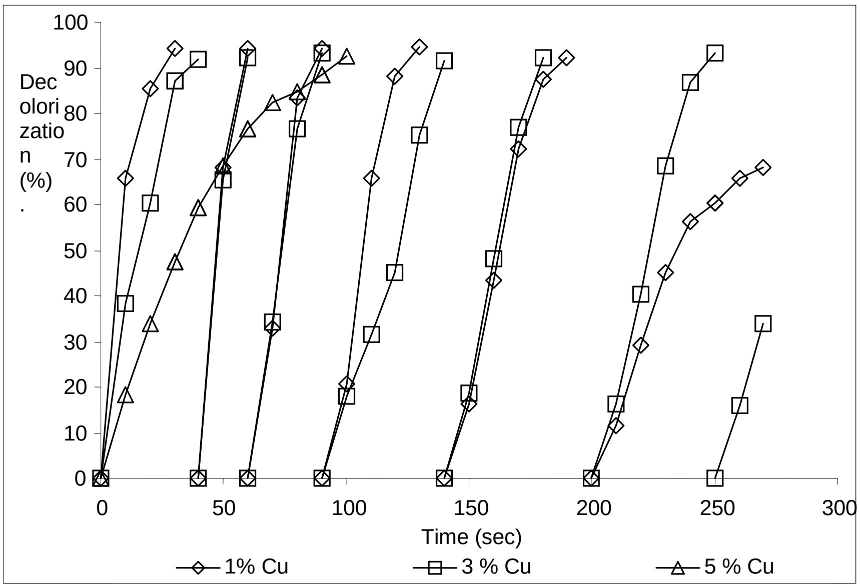

Figure 3. Effect of Cu Concentration on Decolorization (50 mg/L dye, 50C, 150 rpm)

Ca containing beats were re-used for 2 times and total decolorization (%) was reached approximately 100 mg/L. However, 3 % Cu containing beats were re-used 6 times and up to 300 mg/L dye was decolorized effectively (Figure 4).

Effect of Dye Concentration

Four different concentration of dye were used for determine maximum decolorization capacity and effect of dye concentration on decolorization (50-200 mg/L). Results show that decolorization efficiency decreased with increasing dye concentrations. This effect suggested that dye or product formed during decolorization inhibited the enzyme/enzymes activity responsible for decolorization (Figure 5).

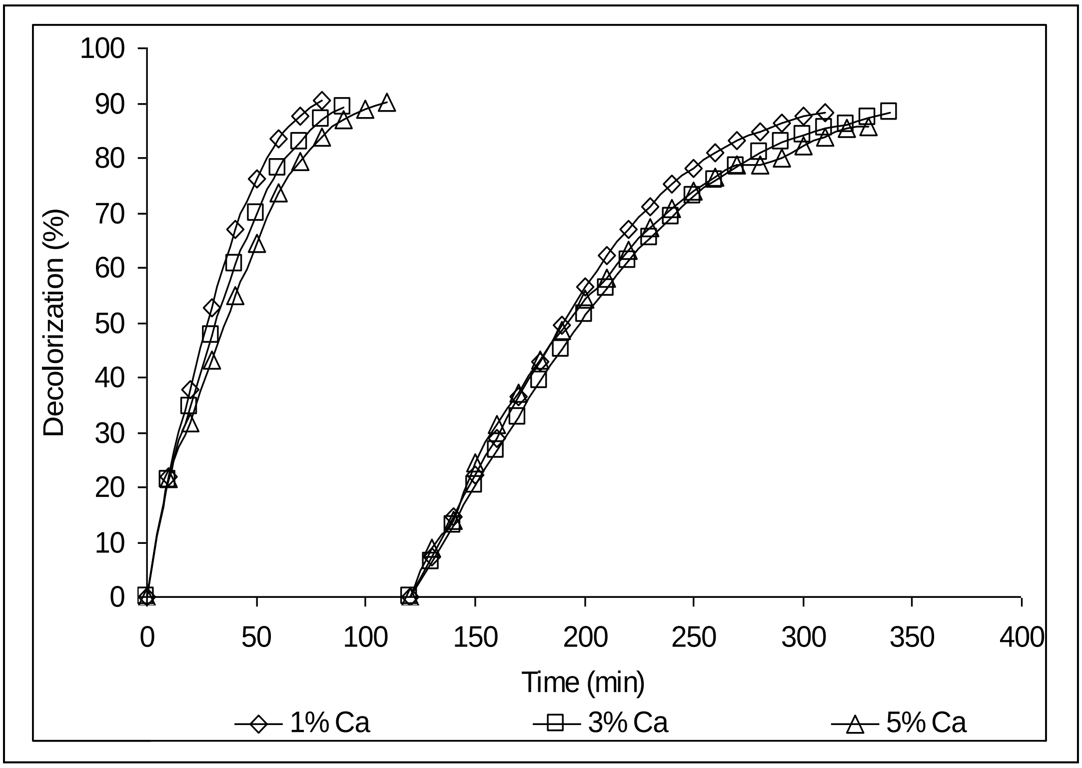

Figure 4. Effect of Calcium Concentration on Decolorization (50 mg/L dye, 50C, 150 rpm)

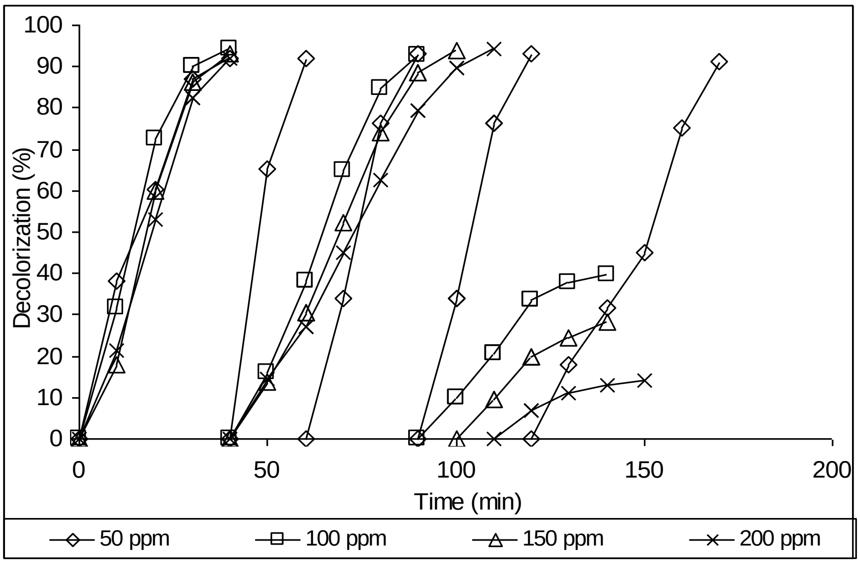

Figure 5. Effects of Dye Concentration on Decolorization

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ZETA POTENTIAL – A NEW WATER TREATMENT AND THE ALUMINUM INDUSTRY

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Electrochemical dispersion of colloidal organic and inorganic particles as well as microorganisms has been practiced for many years to treat the water in small commercial and industrial water systems. The interactions of the capacitor and dielectric particles within a framework of electrochemical principles lead to a rational explanation of the enhanced cleanliness of wetted surfaces obtainable in aqueous heat exchange systems. Biofouling in all applications is extremely well controlled. Bacterial slime accumulation is non-existent, algae do not accumulate, and foul water odor disappeared within hours.

This discussion is illustrated by citing applications of a field generation electrode (trade name Zeta Rod), in different industries and the possibility of your use in the specific aluminum industry.

Keywords: *Zeta Potential, Biofouling, Ecoeficiency, Aluminum*

1. INTRODUCTION

Composite fouling, a combination of inorganic and biological fouling, represents the greatest challenge for effective operation of a greater number of systems, that use water like mass dissolutive or energy transfer medium.

Numerous studies have focused on biological fouling or inorganic fouling separately; however, there are few studies that consider composite fouling like describe by Sheikholeslami (1999).

Common feed water pre-treatment techniques involving filtration, softening and chemical additions are costly and complex. These techniques often have limited and/or undesirable side effects.

An anti-fouling system based upon a unique high voltage capacitance-based (HVCB) design has been used since 1994 to prevent mineral and organic fouling of heat transfer surfaces in industrial water systems and in other aqueous processes (Pitts, 1992). Since 1997, this anti-fouling system has been successfully applied to reduce the problems associated with composite fouling in heat transfer surfaces, industrial water system and other industrial process where water is used like basic fluid.

Electrostatic colloid dispersion obtained by the use of HVCB technology as viewed in conjunction with accepted membrane colloid fouling theories, reveal high levels of theoretical and practical correlation. The application of such technology produces repeatable results in systems operating under many circumstances. Some of those results and observations are presented in this paper and connected with the aluminum industry.

Fouling Models and Theories

There are several models used to describe the different types of fouling in water systems, Epstein (1983) classifies fouling in terms of a 5 x 5 matrix, where five major types of fouling are described. The fouling types described are crystallization, particulate, biological, corrosion, and chemical reaction.

Industrial systems are affected mainly by crystallization (or precipitation), particulate and biological fouling. Precipitation is due to the presence of a concentration gradient of inorganic salts as a result of concentration polarization. Particulate fouling is caused by deposition of organic and inorganic colloidal matter over the surface in contact with the solutions. Biological fouling occurs due to the existence of microorganisms in the water.

A model presented in the beginning of 90’s decade (Flemming et al., 1991) identifies four fouling types in industrial systems: Crystalline fouling caused by mineral scaling; Organic fouling, caused by deposition of dissolved humic acids, grease, oil, lipids, etc.; Particle/colloidal fouling; and Microbiological fouling. Crystalline, Organic and Particle/colloidal fouling may be controlled with appropriate pretreatment techniques by removing the fouling elements from the water stream or by modifying some characteristics of the stream to prevent precipitation of the salts from the bulk solution. However, there seems to be no practical solution to the problem of Microbiological fouling (biofouling).

Costerton (1999) recently described the mechanism and sequential events present in the development of most bacterial biofilms. The architecture and dynamics of the groups of microorganisms is complex, but more easily understood when studied using the confocal scanning laser microscope.

One of the most important studies in the biofouling area (Flemming et al., 1991)) describes the formation of biofilm as a three-phase development. Induction is the phase when primary colonization takes place. This is an important stage in the prevention of biofilm development. Adhesion of bacteria to membranes occurs due to weak physiochemical interactions and electrostatic interactions.

Exponential growth describes the phase where bacterial cell growth becomes the main source of biofilm growth, and eventually contributes more to that growth than does the adherence of additional cells.

The plateau phase describes the period when biofilm growth (adhesion + multiplication) and cell detachment reach equilibrium. The thickness of the biofilm at the plateau phase will depend upon several factors, including nutrient availability, shear forces and mechanical stability of the biofilm. The mechanical stability of the biofilm is influenced by the presence or absence of oxidizing agents, biodispersants, mechanical stress, temperature, and the microorganism's properties and behavior.

In Epstein's model (1983), fouling follows five stages: Induction, transport, attachment, removal, and aging. The mechanism of deposition for crystallization and particulate fouling follows those five stages. The attachment stage is controlled by the precipitation rate for crystallization fouling and by Van der Waals and electric double layer interaction for particulate fouling.

The DLVO (Derjaguin-Landau and Verwey-Overbeek) theory has been applied to describe the initial stage of biofilm formation by Romo (Romo et al., 1999). Gibbs energy is used by the DLVO theory to describe the interaction between colloids and surfaces as a function of distance. The total or resulting force is the sum of the Van der Waals (attractive) forces and electrostatic repulsion forces (caused by the colloid's double layer).

Bacteria are similar in behavior and characteristic to colloidal particles in that their sizes are in the same range and that they typically bear negative surface charges – that is possible to see in different authors like Pitts (1995), Marshall (Marshall et al., 1991) and Costerton (1991). Therefore, interactions between bacteria and bacterial surface charge may be considered in terms of colloidal behavior. The electrostatic repulsion forces that tend to keep colloids (and for this purpose bacteria) apart, decrease as the ionic strength of a solution increases causing the collapse of the double layer.

Following this assumption, studies performed recent (Zhu et al., 1997) noted a decrease in fouling rate in cellulose acetate and composite membranes produced by the addition of a chemical surfactant. The reduction in the fouling rate under those conditions was attributed to increased electrostatic repulsion between colloids and the membrane surface by the respective attachment of surfactant molecules. Nevertheless, fouling was still present under these conditions. The dispersion caused by the increase in surface charge from the surfactant seemed to be negated as the ionic strength of the solution increased, in line with known principles of electro-kinetic dispersion/flocculation reactions. The particles became less negative due to double layer compression, which lead to a collapse of the double layer.

Electrochemical dispersion of colloidal particles has been practiced at an experimental level for many years to treat water in small commercial and industrial systems. In a recent study, Pitts (1995) describes the principles of induced electrostatic dispersion in aqueous systems. The underlying principles involve capacitance, double layer, Gaussian surface charge, dielectric properties of colloids and ionic strength of solutions.

To produce electrostatic dispersion, a cylindrical capacitor is created by inserting an insulated and sealed electrode into a metal pipe or vessel.

The system functions by inducing a time transient, positive alteration of the particle surface charge over the natural state. The effect is expressed on dielectric colloidal particles, as well as on the wetted surfaces of the pipe or vessel.

The ceramic electrode serves as one plate of the capacitor. The dielectric constant of the ceramic prevents current flow to the other plate of the capacitor. The grounded plane of the capacitor is established by the metal of the pipe or vessel. A direct current power supply charges the capacitor system with a very high potential (nominally 30 to 35 kV DC). The field strength between the plates of the cylindrical capacitor is a function of charge voltage, system dimensions, and the dielectric constant of the ceramic. Pitts (1995) established that at a sufficiently elevated voltage, the field strength across the liquid between the plates of the capacitor influences the capacitive charge of the particle. The result is a sharp increase in the surface charge of all nearby wetted surfaces. High Voltage Capacitance Based Technology has been successfully applied to numerous industrial and commercial applications in which control of mineral scaling, biofouling or composite fouling is desired. The capability of this technology to prevent the formation of biofilms on wetted surfaces, and to eliminate existing biofilms is one of the most significant benefits.
Applications in which HVCB technology has been applied have been compiling and presented by Romo (Romo et al., 2002) and a resume are outlined in Table A:

Figure 1 Table A: Industrial Applications of HVCB

Technology Application or Process	**Main Fouling**	**Type Benefit**
Cooling	Composite	Elimination of dispersants, biocides & corrosion inhibitors; elimination of biofilm, and, in some cases, scale.
Metalworking Fluids	Biofouling	Elimination of biofouling & biocide tank side additions; reduce health and safety risks of biocide use.
Sea Water Refrigeration Systems	Composite	Prevention of micro & macro biofoulants on marine vessel HVAC system
Pasteurizers	Biofouling	Elimination of biofouling and foaming.
Parts Washers	Biofouling	Elimination of biofouling, minimize use of biocides.
Can Warmers	Biofouling	Elimination of biofouling, prevention of scaling.
Pulp & Paper	Biofouling	Elimination of biofouling, cleaning of spray nozzles.
Membrane Separations	Composite	Reduction of scaling and biofouling rate at high recovery rates

From the examples show above, we could extend the use and applications of the HVCB theory to the aluminum industry, make a relation among different applications, we have the possibility of great and consistency gains in the following process:

Rolling. Control and treatment of rolling oil (synthetic) and fouling mitigation of hydraulics oil and to increase in the heat transfer spray system quality (heat transfer) and operation control.

Machining. Control and treatment of heat and cutting fluids (remember aluminum has a problem with the usual biocides).

Can manufacturing – See the examples above (Table A).

Surface treatment and finishing process. Increase the treatment bath life, decrease of the Treatment Effluent Station cost, and increase the velocity of neutralization and setting time.

Heat transfer and control temperature systems. Basically in the continuous casting furnaces process with reduction of scaling and biofouling rate at high recovery rates, elimination of dispersants and biocides.

Conclusion

In every system where HVCB technology has been applied, the results have been both remarkable and reproducible. The fouling as a result of diverse causes (crystalline, particle and biological) may be significantly reduced by manipulating the surface charge of organic particles, inorganic particles, and membranes.

Although the technology described in this study was not able to completely the fouling, it did invariably succeed in significantly reducing the fouling rate. In addition, HVCB technology also changed the nature of the fouling deposits, allowing for easier cleaning of the surfaces with less chance of (corrosion and friction) damage, and provided an excellent cleaning effect. These results have a significantly impact to reduce operating costs and maintenance cost by reducing or eliminating pre-treatment and other cleaning chemicals.

The use of a High Voltage Capacitance Based System has proven to be an extremely safe and effective method for achieving what had been only partially achieved with chemical dispersants. The use of the technology continues to be developed in membrane fouling applications and other fields of research where biological control, biodispersion, and fouling mitigation are a matter of concern.

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SIMULATION OF AN ACTIVATED SLUDGE TREATMENT SYSTEM USING ASM AND ANFIS MODELS

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International Water Association (IWA) modeling task group proposed different mathematical approaches to predict the behavior of activated sludge processes in biological wastewater treatment operations. These mechanistic approaches are defined as activated sludge models (ASM) that require a large number of complex kinetic and stoichiometric parameters which should be previously adjusted. Although the ASM models are internationally accepted they have important limitations in on-line plant simulations. On the other hand, artificial intelligence systems have been developing as a promising approach in solving the complex problems in wastewater treatment process control. This work evaluated ASM (ASM1 and ASM3) and hybrid neuro-fuzzy (ANFIS) modeling methods to estimate target effluent variables in a full-scale aerobic biological wastewater treatment plant (WWTP) in the City of Pelham, South Carolina, USA. While target effluent variables to be estimated were chemical oxygen demand (COD), NH_3-N and NO_3-N in ANFIS models, fractions of such variables (S_S, S_{NH} and S_{NO}) were estimated in ASM models. The correlation coefficients (R) obtained for the validation data set of output variables were over 0.90 and below 0.30 for ANFIS and ASM models, respectively. ASM3 model provided more reliable results than ASM1 based on correlation coefficients and error values (RMSE). Overall, ANFIS model was found to be more successful in the prediction of effluent parameters and in describing the relationship between wastewater quality parameters. ANFIS algorithms may potentially be applied in full-scale treatment plants for on-line process control.

Keywords: activated sludge modeling; aerobic wastewater treatment; ANFIS; artificial intelligence

1. Introduction

The regular operation and control of wastewater treatment plants (WWTP) is receiving increasing attention in terms of rising concerns about environmental issues. In addition, more stringent regulations and operational difficulties experienced in WWTPs have resulted in increased need for tools to evaluate the organic matter and nutrient removal performances (Çinar, 2005). In this context, some deterministic approaches such as activated sludge models (ASM1, ASM2, ASM3) were developed to describe the mass balance of microbiological (biomass) activities in treatment processes (Henze *et al.*, 1987; 1995; 1999; Gujer *et al.*, 1999). In this study ASM1 and ASM3 models proposed by the IWA (International Water Association) Task Group were used. ASM1 and ASM3 are both capable of describing the dynamic behavior in common municipal WWTPs (Koch *et al.*, 2000). However, the assumptions in these mathematical models are mainly based on engineering principles; thus, such models may not offer satisfactory description of the cause-effect relationships within processes and a large number of kinetic and stoichiometric parameters should be determined for different conditions by specific lab data and process operation (Yoo *et al.*, 2003; Çinar, 2005).

In recent years, artificial intelligence (AI) methods were examined as a decision tool in the environmental engineering practice (Rizzoli and Young, 1997; Olsson and Newell, 1999; Cortès *et al.*, 2000; Gernaey *et al.*, 2004). AI methods involve the use of artificial neural networks (ANN), genetic algorithms (GA), fuzzy logic, rule-based systems, knowledge-based systems and their associated applications called ‘hybrid architectures’ such as adaptive neuro-fuzzy inference system (ANFIS). ANFIS, first proposed by Jang (1993), is based on the first-order Sugeno fuzzy model (Takagi and Sugeno, 1983, 1985; Sugeno and Kang, 1986). ANN paradigm used is a multilayer feed-forward back-propagation network.

The main objective of this work was to evaluate the ASM and ANFIS modeling for plant quality control and predicting the performance of an existing full-scale aerobic biological WWTP. For this purpose, effluent chemical oxygen demand (COD) (S_S), NH_3-N (S_{NH}) and NO_3-N (S_{NO}) were chosen as the output parameters in both ASM and ANFIS model algorithms to represent the organic carbon and nitrogen removal in the plant (output ASM parameters are defined in parentheses).

2. Background

2.1. Activated Sludge Models (ASM1 and ASM3)

ASM1 and ASM3 models were primarily developed to identify the prediction of carbonaceous and nitrogenous substrate removal in WWTPs. In these models, COD was adopted as the measure of the concentration of organic matter. In ASM1, the wide variety of organic carbon compounds and nitrogenous compounds are subdivided into a limited number of fractions based on biodegradability and solubility considerations compared with ASM3 (Gernaey *et al.,* 2004). The ASM3 model was designated in the intend of correcting for a number of defects that have appeared during the usage of the ASM1 model (Gujer *et al.*, 1999) The major difference between the ASM1 and ASM3 models is that the latter recognizes the importance of storage polymers in the heterotrophic activated sludge conversions. In the ASM3 model, it is assumed that all readily biodegradable substrate (S_S) is first taken up and stored into an internal cell component (X_{STO}) prior to growth.

A second difference between ASM1 and ASM3 is that the ASM3 model should be easier to calibrate than the ASM1 model. This is mainly achieved by converting the circular growth-decay-growth model, often called death-regeneration concept, into a growth-endogenous respiration model (Koch *et al.,* 2000). All these variations result in different model matrix structures in ASM1 and ASM3 models. Both ASM models have a total of 13 components. ASM1 and ASM3 models contain 8 processes, 19 parameters and 12 processes, 36 parameters, respectively.

2.2. Adaptive Neuro-Fuzzy Inference System (ANFIS)

ANFIS is a technique for automatically tuning Sugeno type inference systems based on training data (Jang, 1993). It consists of five key components; inputs and outputs, database and preprocessor, a fuzzy system generator, a fuzzy inference system, and an adaptive neural network representing the fuzzy system. The integration of fuzzy systems and neural networks can combine the merits of both systems, and offer a more powerful tool for modeling (Melin and Castillo, 2005). A neural fuzzy system is such an integrated system. It uses neural networks as tools in fuzzy systems.

3. Methodology

3.1. Wastewater Treatment Plant

Pelham is one of WWTPs of the Western Carolina Regional Sewage Authority (WCRSA) in South Carolina. The plant does not include primary clarifier; so, influent wastewater passes through screens and directly enters three carousel-type aeration basins. After secondary treatment in aeration basins, the water passes through four final clarifiers and finally enters a chlorination chamber before discharging to receiving water. Operational data of 900 days (in the years of 1998-2002) from the plant were used in ASM and ANFIS models. The statistical values of the measured process variables are presented in Table 1.

Table 1. Descriptive statistics of the treatment plant data used for developing ASM and ANFIS models

Wastewater Parameters	Minimum	Mean	Maximum
$Q_{influent}$ (m^3/d)	12532	21440	28650
$COD_{influent}$(mg/L)	350	440	570
$TSS_{influent}$ (mg/L)	106	189	300
NH_3-$N_{influent}$ (mg/L)	15	23	75
$pH_{aeration\ tank}$	6.06	6.70	7.20
$Temperature_{aeration\ tank}$ (^oC)	13.60	19.50	25.60
$DO_{aeration\ tank}$ (mg/L)	1.02	2.80	5.50
$COD_{effluent}$ (mg/L)	8	15	26
NH_3-$N_{effluent}$ (mg/L)	0.07	1.12	4.40
NO_3-$N_{effluent}$ (mg/L)	1.25	6.22	10.55

3.2. Model Structure and Model Implementation

AQUASIM^{TM} 2.0 was chosen for ASM1 and ASM3 simulations, which is designed to identify and simulate aquatic systems. Furthermore, this software is capable of performing sensitivity analyses and parameter estimations (Reichert, 1998). All parameters in Table 1 were defined as the real list variables (collected data) in the AQUASIM, except pH and temperature. For the simulation, neutral pH and constant temperature (20 ^{o}C) were set up. In the ASM approach, all differential equations belonging to activated sludge process were solved with time depended numerical equations. Therefore, first of all, these equations were inserted into the software for both ASM1 and ASM3. For many kinetic and stoichiometric process parameters, default values from the literature were used. Sensitivity analysis and parameter estimation were then applied. In the sensitivity analysis of S_S, S_{NO} ve S_{NH}, relative-relative function was used and the parameters with a value of zero were removed for the clarity. Furthermore, the model parameters (stoichiometric and kinetic constants) were estimated by minimizing the sum of squares of weighted derivates between default values and calculated model outputs.
The ANFIS algorithm was employed in Fuzzy Logic Toolbox of MATLAB^{TM} (MathWorks, Inc., USA) to obtain modeling results. Due to different units of parameter variables, boundary values were set up with “xbounds” function that specifies how to map the data in inputs and outputs into a unit hyperbox. This function contains the minimum and maximum axis range values for scaling the data in each dimension. A subtractive clustering (genfis2) algorithm was used to estimate the number of clusters in optimal data obtained from the optimization step to build an initial Fuzzy Inference System (FIS). This initial FIS was then optimized using the ANFIS model. For the whole data set, cluster radius was set at 0.5.

For both of the ASM and ANFIS modeling studies, the data pairs of 630 consecutive days (70%) were used for training (calibration of ASM models) and the remaining pairs of 270 days (30%) were used to validate the models. Training and validation data pairs were selected randomly. The resulting model was verified by using a validation database provided from the original database. The performance of the model was assessed by correlation coefficient (R) and root mean square error (RMSE). Correlation coefficients were calculated based on linear regression analysis; RMSEs were calculated by the below equation:

$$RMSE=\sqrt{\frac{\sum_{1}^{N}(x_i-y_i)^2}{N}} \qquad (1)$$

where, x_i and y_i are the measured and predicted data, respectively, and N is the number of observations.

4. Results and Discussions

After setting the initial values of stoichiometric and kinetic parameters in ASM1 and ASM3 models, the sensitivity analysis was performed for S_S, S_{NH} and S_{NO} effluent concentrations. In this analysis, the most sensitive parameters describing the activated sludge process were determined and arranged based on their importance (Table 2).

Table 2. Sensitivity analysis results performed for ASM1 and ASM3 (importance of parameters are shown in decreasing order)

ASM1			ASM3		
S_s	S_{NH}	S_{NO}	S_s	S_{NH}	S_{NO}
μ_H	μ_A	Y_H	Y_H	μ_A	Y_H
b_H	K_{NH}	μ_A	Y_{STO}	b_A	b_A
Y_H	b_A	Y_A	b_H	K_{NH}	b_H
K_S	μ_H	b_A	μ_H	μ_H	Y_A

After the sensitivity analysis, the determined parameters were used for parameter estimation procedure. Typical ranges and estimated values of the selected parameters are shown in Table 3. As noted in Table 3, the last two columns contain estimated values for ASM models and only one value was reported for each parameter since similar results were obtained for the parameter estimation of the selected target effluent concentrations (S_S, S_{NH} and S_{NO}).

Table 3. Parameter estimation results for ASM1 and ASM3 modeling approaches

Parameters	Value ranges (Typical value)*	ASM1	ASM3
μ_H (d^{-1})	0.6-13.2 (2.0)	7.26	6.67
b_H (d^{-1})	0.1-1.5 (0.2)	0.62	0.89
Y_H (g COD.g^{-1} COD)	0.38-0.75 (0.63)	0.41	0.40
K_S (g COD.m^{-3})	5-225 (20)	20	9.39
μ_A (d^{-1})	0.2-1.0 (1.0)	0.99	0.20
K_{NH} (g NH_3-N.m^{-3})	1.0	0.85	1.00
b_A (d^{-1})	0.05-0.2 (0.15)	0.05	0.05
Y_A (g COD.g^{-1} N)	0.07-0.28 (0.24)	0.25	0.25
Y_{STO} (g X_{STO}.g^{-1} S_s)	0.80	-	0.87

* Typical values were defined at 20 ^{o}C for both ASM1 and ASM3 models (Gujer *et al.*, 1999).

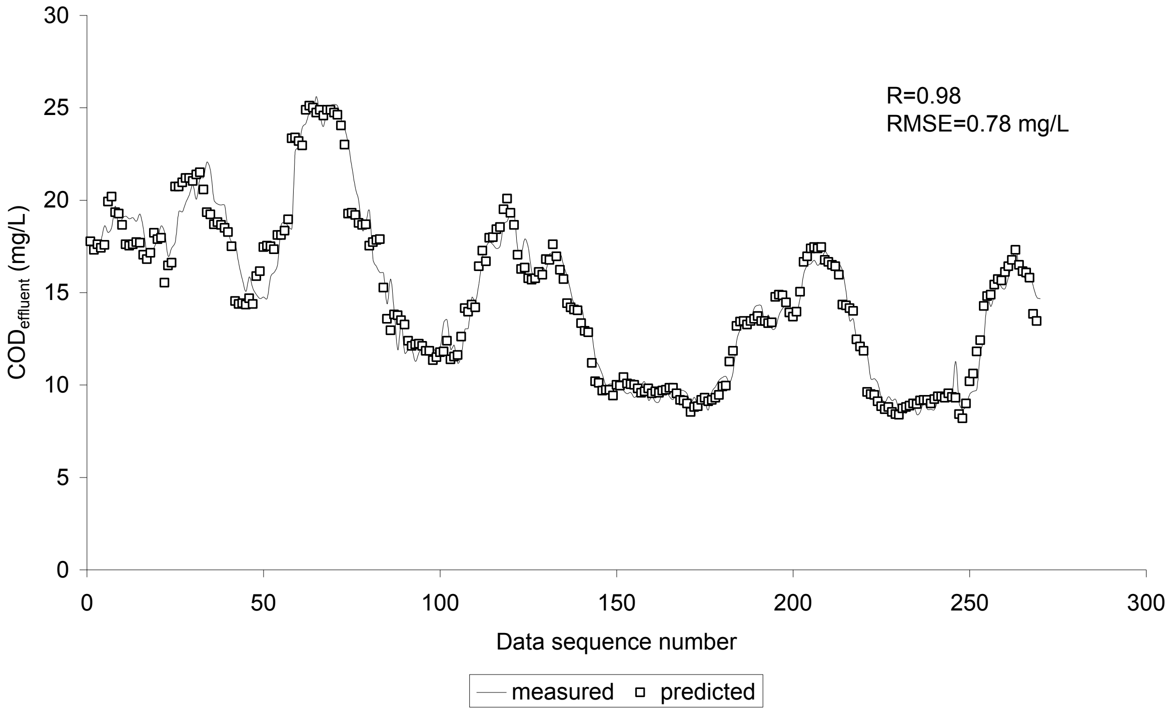
The last stages in the ASM models consist of calibration and validation. For calibration, a total of 630 consecutive values (real list values) of the components were used. Reactor configuration, dissolved oxygen concentration in the process tank and some other variables were adjusted for the best result. The validation stage was performed with 270 values, the same number as for the simulation days. After the validation simulations, the best R values calculated were 0.15 and 0.22 for ASM1 and ASM3, respectively. These results were obtained from the NO_3-N (S_{NO}) simulation. Validation results overall indicated that both ASM models were incapable in estimations for the given conditions. The major reason for this finding is most probably due to the absence of the specific lab data resulting in inadequate calibration. Similarly, the need for the determination of kinetic and stoichiometric parameters for a specific process through lab studies is indicated in the literature (Koch *et al.*, 2000; Petersen, 2000; Roeleveld and van Loosdrecht, 2002; Sin, 2004).

After obtaining unsatisfactory results from the ASM models, ANFIS modeling approach was performed to estimate target effluent variables ($COD_{effluent}$, NH_3-$N_{effluent}$ and NO_3-$N_{effluent}$). For each ANFIS modeling structure, a total of 500 iteration step was adequate to achieve minimum error criterion between iteration steps. Resulting network was successful in predicting both training and testing of the effluent COD, NH_3-N and NO_3-N. All results are presented in Table 4.

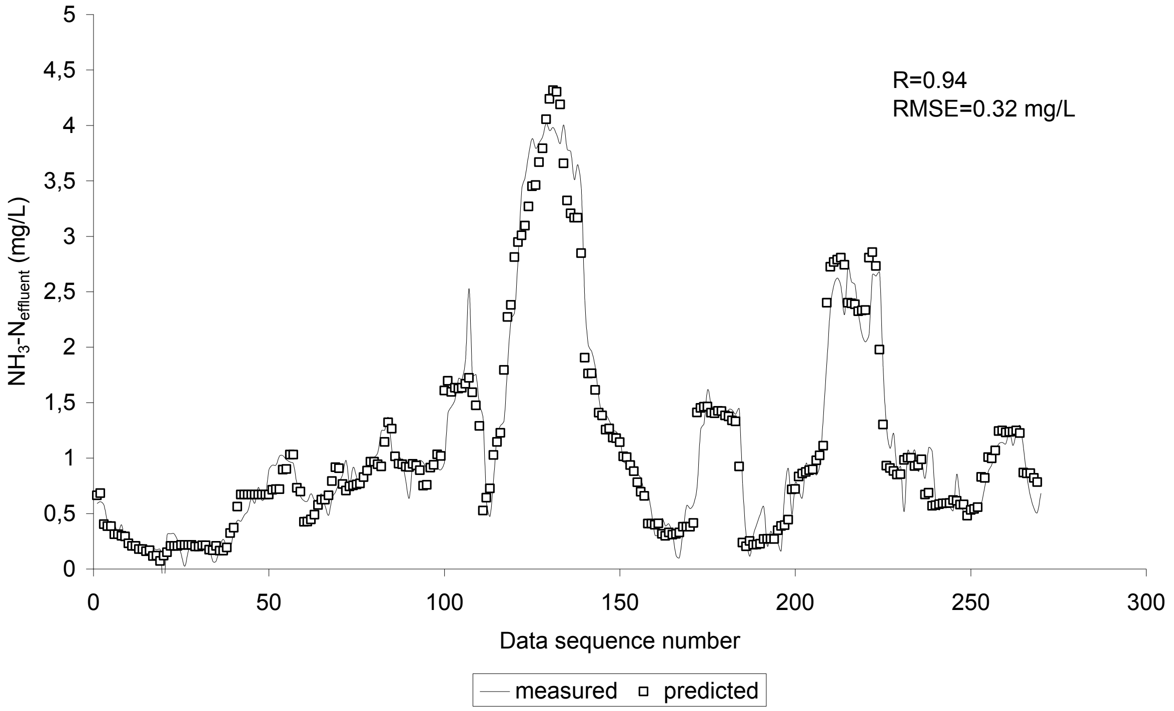
Table 4. Performance of ANFIS models

Model Inputs	Model Outputs	Training Performance		Validation Performance	
		RMSE	R	RMSE	R
$Q_{influent}$ (m^3/d) $COD_{influent}$(mg/L) $TSS_{influent}$ (mg/L) NH_3-$N_{influent}$ (mg/L) $pH_{aeration\ tank}$ $Temperature_{aeration\ tank}$ (^oC) $DO_{aeration\ tank}$ (mg/L)	$COD_{effluent}$ (mg/L)	0.66 mg/L	0.98	0.78 mg/L	0.98
	NH_3-$N_{effluent}$ (mg/L)	0.33 mg/L	0.93	0.32 mg/L	0.94
	NO_3-$N_{effluent}$ (mg/L)	0.25 mg/L	0.99	0.31 mg/L	0.99

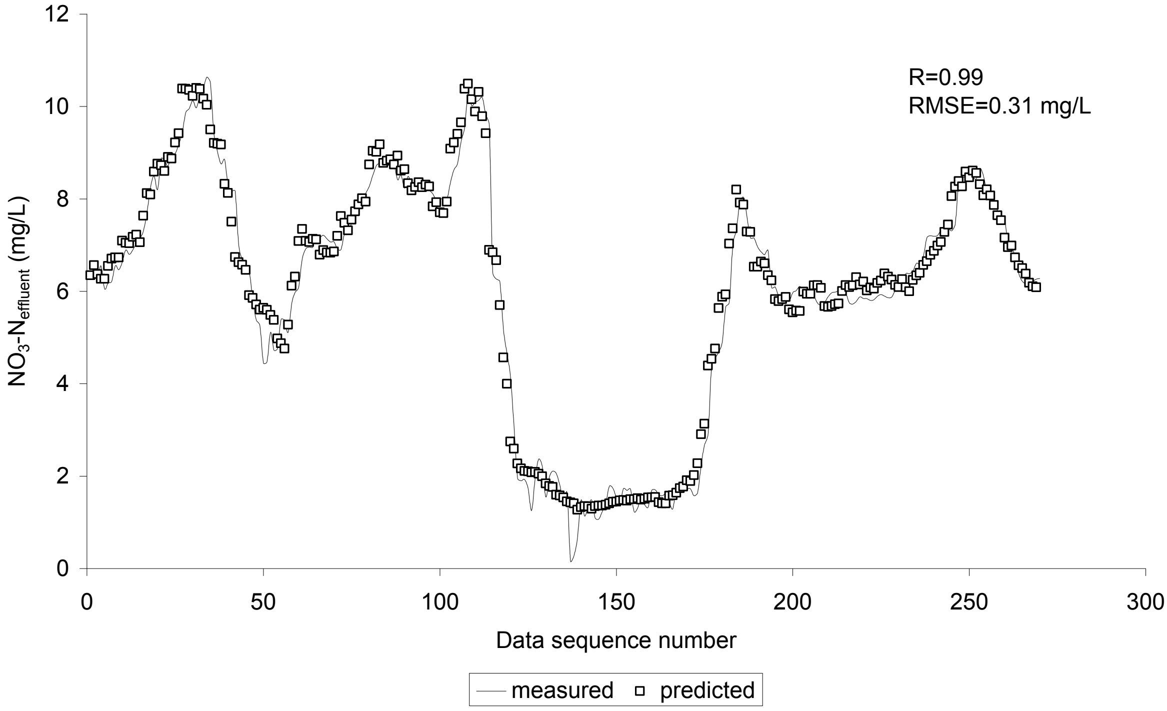
Estimated and measured values from the validation data set of $COD_{effluent}$, NH_3-$N_{effluent}$ and NO_3-$N_{effluent}$ are shown in Figures 1 (a), (b) and (c), respectively. It is clear from the simulation results that within the same given data set the ANFIS modeling is much more successful than ASM models in the prediction of effluent parameters.


30
25
20
15
10
5
0
$COD_{effluent}$ (mg/L)
0
50
100
150
200
250
300
Data sequence number
R=0.98
RMSE=0.78 mg/L
measured
predicted

(A)


5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
NH_3-$N_{effluent}$ (mg/L)
0
50
100
150
200
250
300
Data sequence number
R=0.94
RMSE=0.32 mg/L
measured
predicted

(B)



(C)

Figure 1. Simulation results of $COD_{effluent}$ (a), NH_3-$N_{effluent}$ (b) and NO_3-$N_{effluent}$ (c) with ANFIS modeling

5. Conclusions

This work evaluated activated sludge models (ASM1 and ASM3) and hybrid neuro-fuzzy (ANFIS) modeling method to estimate organic carbon (as COD) and nitrogen (as NH_3-N and NO_3-N) removal using the correlation among the past information of input and output variables in a full-scale aerobic biological wastewater treatment plant. Model development focused on providing an adaptive, useful and alternative methodology for modeling of carbon and nitrogen removal. The hybrid neuro-fuzzy method appears to be an alternative framework for carbon and nitrogen removal estimation capability; RMSE and R values of the model were found to be much well-reasonable compared to the poor estimation capacity found in ASM models. Overall, the results indicated that the ANFIS model is suitable to describe the relationship between wastewater quality parameters and suggested that the modeling algorithm has an application potential for on-line plant control.

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TOXICITY ASSESSMENT OF METHYL *TERT*-BUTYL ETHER, *TERT*-BUTYL ALCOHOL AND FORMALDEHYDE USING REDUCED INHIBITION CONSTANTS

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A new method for quantitatively estimating the toxicity of methyl *tert*-butyl ether (MTBE) and its metabolites such as *tert*-butyl alcohol (TBA) and formaldehyde (FA) is proposed. The inhibition effects of MTBE, TBA, and FA on the growth of *Escherichia coli* were evaluated using specific growth rate and reduced inhibition constants in the nutrient media supplemented with MTBE (0~ 250 mM), TBA (0~ 500 mM), or FA (0~1.4mM). The inhibition effects of binary or ternary mixtures of MTBE, TBA, and FA were also examined by similar manners. Each compound inhibited the growth of *E.coli* noncompetitively, and the toxic effect sorted FA > MTBE > TBA. The inhibition constants (K_I) of MTBE, TBA and FA were 170, 368 and 0.94 mM, respectively. Based on K_I of MTBE, the reduced inhibition constants (α_i) for MTBE, TBA and FA were 1.000, 2.160 and 0.005, respectively. No synergic inhibition effect on the growth rate of *E. coli* was observed in the mixtures of MTBE, TBA and FA.

Keywords: *Toxicity, Methyl tert-butyl ether, tert-butyl alcohol, Formaldehyde , Inhibition Constants, Reduced Inhibition Constants*

Introduction

The commercial use of methyl *tert*-butyl ether(MTBE) as fuel oxygenate, replacing alkyl lead additive, can be traced back to the late 1970s in the United States [1]. The annual production of MTBE increased from 1.38 billion lb in 1984 to 24.1 billion lb in 1993, making it the second on the list of organic chemicals being manufactured in U.S. MTBE constitutes up to 15%(v/v) of the gasoline mixture. Releases of oxygenated fuels to the surface from underground storage tanks, pipelines, and refueling facilities provides point sources for entry of oxygenated compounds as well as gasoline hydrocarbons into the hydrological cycle [2]. Due to its a small molecular, high solubility in water and low sorption tendency in soils, MTBE can rapidly penetrate the soil layer and enter the groundwater shortly after the spill. It has become one of the most problematic pollutants in urban soils and groundwater worldwide. A draft lifetime health advisory limit of 20–35 μgL^{-1} has been issued in the U.S. Organic compounds are largely dependent upon octanol-water partition coefficient (log K_{ow}), a measurement of a chemical’s affinity for water versus lipid or fats. Since the log K_{ow} for MTBE is 1.24, which is within the range that is readily effective by human, animals, and plants. The toxicity of MTBE to animals and humans is well documented. It has been established that MTBE is carcinogenic to animals [3]. Inhalation of MTBE vapors may cause headaches and nausea at higher concentrations (ppmv) for people [4].

Respiratory, neurological, cardiac, and allergic symptoms associated with chronic and low level exposure of MTBE were also reported. Toxicity of MTBE to algae, invertebrates, and fish has been intensively studied. Ecotoxicologic study of MTBE was mainly performed in freshwater ecosystem and reported the concentration of acute toxicity according to organism species. Gupta and Lin (1995) reported that *Photobacterium phosphoreum* displayed EC_{50} of 15 minutes in 42 mg/L, and 5 minutes in 54 mg/L and *Daphnia magnas* was not influenced by 1±1000 mg/L MTBE for 48 hours [5]. Kado (1997) reported *Salmpnella typhimurium* had been shown reduction of cell number within 48 hours in the MTBE concentration of around 7.4 mg/L and *Photobacterium phosphoreum* in 42 mg/L [6]. In addition, Kado (1997) reported mutagenic reaction was not particular at more than 7.4 mg/L, but there was inhibition in growth through genetoxic effect study on *Salmonella typhimurium* for 48 hours [7]. Rousch (1998) offered a toxicity estimation research about unicellular algal (*Selenastrum capricornutum, Navicula pelliculosa, Synechoccus leocornutum*) that are three kinds of phytoplankton and his results showed that the growth inhibition occurred at 2400 mg/L for 3±5 day in the case of *Navicula pelliculosa* and *Synechoccus leocornutum,* and *Selenastrum capricornutum* had tolerance to MTBE [8]. Also, *tert*-butyl alcohol (TBA) and formaldehyde (FA) that MTBE intermediates have been known as a possible human carcinogen. The effect of additive oxygenated as MTBE and its intermediates such as TBA and FA on microbial activity in complex mixture is more difficult to evaluate than in single system. The contribution of each component in mixtures to toxicity value is not proportional to weight faction (mole concentration: M) or relative numbers of materials. To evaluate the toxicity in mixtures, the development of a novel model is required. In this study, we investigated the inhibition effects of single and mixed compounds (MTBE, TBA, and FA) on the growth rate of *E.coli*. On the basis of experimental results, we also proposed a reduced inhibition model, which can allow conversion of different toxicity of each component.

Materials and Methods

2.1 Strain and Medium

Escherichia coli was used as a test strain. The strain was cultivated in Luria-Bertani (LB) broth for 12hrs at 37℃ and 220 rpm and used as an inoculum. LB broth contained the following (per liter): 10 g/L tryptone, 10 g/L NaCl, and 5 g/L yeast extract.

2.2 Experiment condition

All the experiments were carried out in 500 mL serum bottles. The bottles sealed with a butyl rubber were charged with 50 mL of LB broth and one milliliter of the inoculum, and desired concentrations of toxicants were injected to the bottle through the rubber stopper using a gas-tight micro-syringe. MTBE, TBA, and FA were used as test toxicants. The cultures were incubated at 37℃ and 220 rpm. The culture broth from each bottle was sampled every 30 minutes, and optical density was measured to determine growth rate by using an UV/visible spectrophotometer (Agilent, USA) at 600nm. All the experiments were performed in duplicate.

Table 1: Experiment Condition

Condition	Add Material	Concentration (mM)
Single	MTBE	0, 25, 50, 100, 150, 200, 250
	TBA	0, 50, 100, 150, 200, 300, 400, 500
	FA	0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4
Mixture	MTBE/TBA/FA	0/0/0, 40/50/0, 80/100/0, 100/150/0, 20/50/0.1, 20/150/0.1, 60/50/0.1, 60/150/0.1, 0/50/0.2, 40/50/0.2, 40/150/0.2, 40/50/0.2, 40/100/0.2, 80/50/0.2, 120/50/0.2, 120/150/0.2, 20/50/0.3, 20/150/0.3, 60/50/0.3, 60/150/0.3, 0/150/0.4, 0/100/0.4, 40/50/0.4, 80/100/0.4, 80/0/0.4, 80/200/0.4, 100/150/0.4, 100/0/0.4, 100/300/0.4, 160/100/0.4, 200/150/0.4, 40/50/0.6, 40/150/0.6, 120/50/0.6, 120/150/0.6, 80/100/0.8, 100/150/0.8

Detailed descriptions of the mixed toxic materials used are listed in Table 1. Response surface methodology (RSM) enabled assessment in effects of multiple parameters, either alone or in combination, on response. Based on the culture condition of single, the mixture conditions in Table 1 were designed to assess the effect of toxicity of *E. coli* in multiple system.

2.3 Reduced inhibition model

This model is used to evaluate the effect of toxicants on the growth of *E. coli*. Various inhibition models such as competitive, non-competitive, and uncompetitive models can be used to explain the effect of an inhibitor on microbial growth. These models cannot be applied to mixed inhibitors, however, and only provide comparative information on the inhibition intensity of microbial growth resulting from each individual inhibitor.

Monod equation is employed to perform a kinetic analysis of *E. coli*.

The non-competitive inhibition model is expressed as follows:

$$\mu = \frac{\mu_m}{\left(1+\frac{[I]}{K_I}\right)\left(1+\frac{K_m}{[S]}\right)} = \frac{\mu_{m,app}}{1+\frac{K_m}{[S]}} \qquad (1)$$

where K_I is an inhibition constant, and [S] and [I] are the concentrations of substrate and inhibitor, respectively. Since the inhibitor exist generally as a mixture in growth media, an advanced inhibition model, which can be applied to mixed as well as single inhibitors, is needed. Therefore, we now propose a new model (the reduced inhibition model) that allows the conversion of the effects of various inhibitors on microbial growth to that of the reference inhibitor.

Central to the proposed model is the reduced inhibition constant, defined as the ratio of the inhibition constant (or inhibitor concentration) of each metal species to that of a reference inhibitor metal species:

$$\alpha_i = \frac{(K_I)_i}{(K_I)_{ref}} = \frac{[I]_i}{[I]_{ref}} \tag{2}$$

If MTBE is the reference compound, the reduced inhibition constant is as follows:

$$\alpha_i = \frac{(K_I)_i}{(K_I)_{MTBE}} = \frac{[I]_i}{[I]_{MTBE}} \tag{3}$$

This means that the reduced inhibition constant represents the tolerance of any other inhibitor relative to that of the reference inhibitor. The reduced inhibitor concentration is the conversion of an inhibitor concentration to a reference inhibitor concentration via the reduced inhibition constant, and is expressed mathematically as:

$$[I]_{reduced} = \frac{[I]_i}{\alpha_i} \tag{4}$$

The basic idea behind the reduced inhibition constant is that all the inhibitors behave alike at the same reduced concentration.

The new model enables universal and simple evaluation of inhibition effects in complex mixed systems. The reduced inhibition model is obtained with modification of Equation (1) by the reduced inhibition constant that is derived from the inhibition constant (K_I) and inhibitor concentration [I]:

$$\mu = \frac{\mu_m}{\left(1 + \frac{[I]_{ref}}{(K_I)_{ref}}\right)\left(1 + \frac{K_m}{[S]}\right)} = \frac{\mu_m}{\left(1 + \frac{[I]_i}{\alpha_i (K_I)_{ref}}\right)\left(1 + \frac{K_m}{[S]}\right)} = \frac{\mu_m}{1 + \frac{[I]_{reduced}}{(K_I)_{ref}}}$$

(5)

In this experiment, initial concentration of substrated fixed, and then Equation (5) is expressed as follows:

For a single inhibitor:

$$\mu = \frac{\beta}{1 + \frac{[I]}{\alpha_i (K_I)_{ref}}} = \frac{\beta}{1 + \frac{[I]_{redused}}{(K_I)_{ref}}} \tag{6}$$

Where, $\beta = \frac{\mu_m}{1 + \frac{K_m}{S}}$

For multiple inhibitors:

$$\mu = \frac{\beta}{1+\sum_{i=1}^{n}\frac{[I]_i}{\alpha_i (K_I)_{ref}}} = \frac{\beta}{1+\sum_{i=1}^{n}\frac{[I]_i}{(K_I)_{ref}}} \qquad (7)$$

where α_i is the reduced inhibition constant of inhibitor *i*, $(K_I)_{ref}$ is the inhibition constant of the reference inhibitor, and $(K_I)_i$ is the inhibition constant of inhibitor *i*.
Rearrangement of Equation (5) yields:

$$\beta\left(\frac{1}{\mu}\right) = 1 + \frac{[I]}{K_I} \qquad (8)$$

A plot of $1/\mu$ versus [I] results is a line of slope $1/K_I$.

3. Results and Discussions

3.1 Toxicity of Single compound

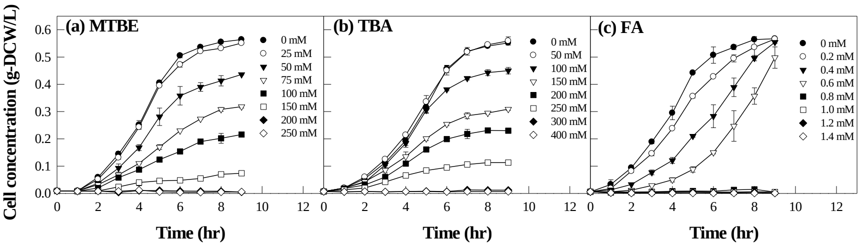

Figure 1: Time profile of OD in LB medium containing a toxic material
(a) MTBE (b) TBA and (c) FA

Fig. 1 presents the cell concentrations of *E. coil* with time at each concentration of MTBE (0 ~ 250 mM), TBA (0 ~ 500 mM) and FA (0 ~ 1.4 mM). No addition toxicant, the specific growth rate of *E. coli* is 0.98 h^{-1}, and biomass constant is about 0.55 g/L. In the addition of MTBE, the growth of *E. coli* completely inhibited at more than 200 mM MTBE. In the addition of TBA, the growth of *E. coli* showed completely inhibited at more than 300 mM TBA. MTBE and TBA affected the maximum growth of this bacterium, while FA influenced lag time which become longer as the concentration increased, its growth was completely inhibited at more than 0.8 mM FA. The effective concentration (EC 50) of the microbial growth rate for each compound was 75 and 150 mM for MTBE and TBA, respectively. The toxic effect order in three compounds was FA>MTBA>TBA. The relationship between $1/\mu$ obtained from the kinetic analysis and concentration of MTBE, TBA, or FA is shown in Fig. 2. The data from the experiment is applied to reduced inhibition model, and K_I was calculated using the equations as described above.

Priority, the growth of *E. coli* followed Monod equation and the inhibition models assume non-competitive inhibition. In the single toxicity system, *E. coli* growth rate clearly decrease with increasing each MTBE/TBA/FA concentration. The K_I and α values for each metal species were calculated from the data in Fig. 2. The K_I and α values for MTBE, TBA and FA are summarized in Table 2.

The inhibition constants (K_I) of MTBE, TBA and FA were 170, 368 and 0.94 mM, respectively. Based on K_I of MTBE, the reduced inhibition constants (α_i) for MTBE, TBA and FA were 1.000, 2.160 and 0.005, respectively. Using reduced inhibition constant, we converted the concentration of each MTBE, TBA, and FA to the reduced concentration: the relationships of the each concentration to apparent illustrated in Fig. 3 (a)~(d). The results in Fig. 3 clearly demonstrate that the microbial growth decreases by increasing reduced compound concentration. This result indicates that inhibition effects of diversity compounds can be generalized using the reduced inhibition model.

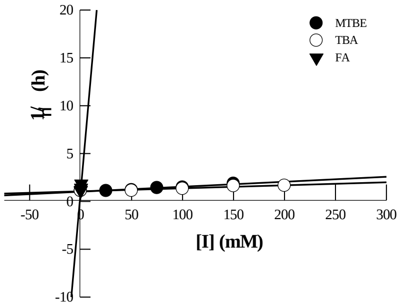

Figure 2: Relationship between 1/μ and [I]

Table 2: K_I and a_i values from MTBE, TBA, FA

Component	*MTBE	TBA	FA
K_I (mM)	170	368	0.94
a_i	1	2.16	0.005

*: Reference compound

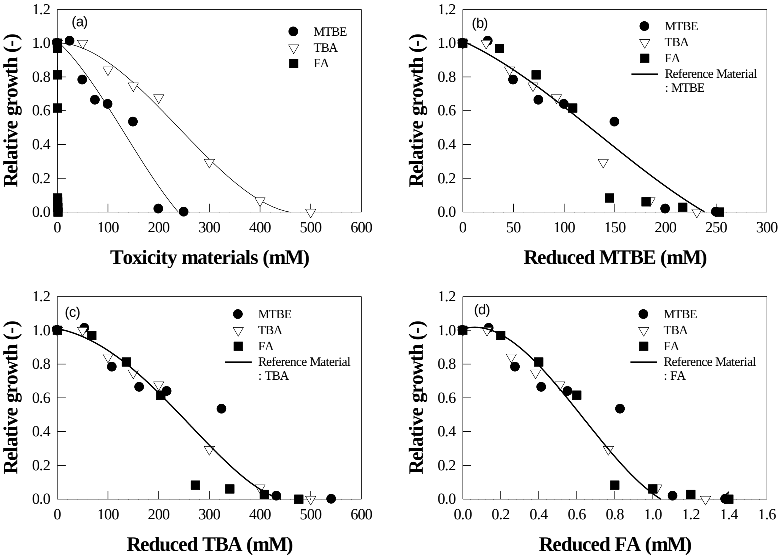

Figure 3: Relative growth rate with the reduced inhibitor concentration.

3.2 Toxicity of mixed compounds

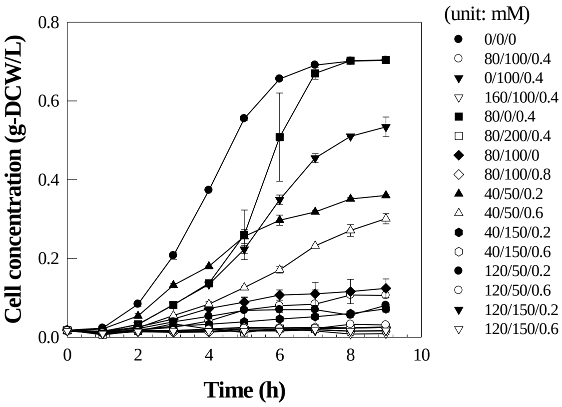

Figure 4: Time profile of the growth of *E. coli* in LB medium containing MTBE, TBA and FA

The growth of *E. coli* in LB media amended with binary and ternary mixtures of MTBE, TBA or FA is shown in Fig. 4. As the total concentration of MTBE, TBA or FA increased, the growth inhibition of *E. coli* significantly increased.

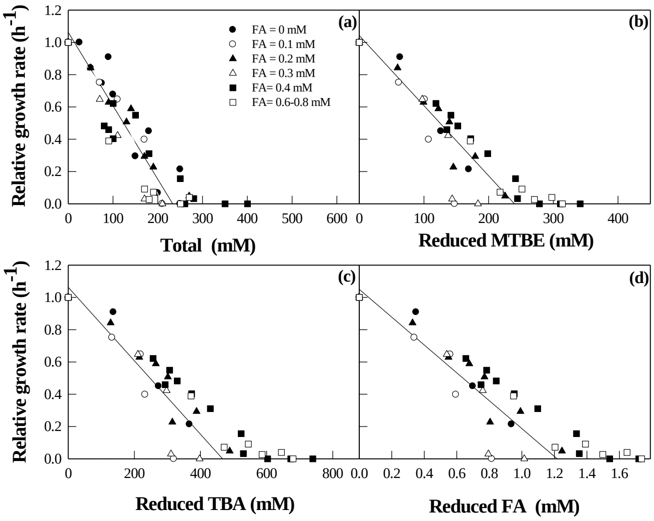

Figure 5: Relative growth rate with reduced inhibitor concentration in mixture component system (solid line: reference line)

To confirm applicability of the reduced inhibition model, the concentration of MTBE, TBA and FA in mixtures are converted to the reduced concentration, and then the results are plotted against the relative growth rates as shown as Fig. 5. After this conversion, the relative growth rates for all mixed conditions lie close to the reference line. No synergic inhibition effect on the growth rate of *E. coli* was observed in the mixtures of MTBE, TBA and FA. The results suggest that the effects of the mixed inhibitors on call growth can be normalized to the effect of the reduced inhibition concentrations derived from the reduced inhibition constants.

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A GRAPHICAL APPLICATION IN TREATMENT OF RESIDENTAL WASTEWATER BY THE ACTIVATED SLUDGE PROCESS

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Parametrical value variations of pollution characteristics have an important role in wastewater treatment plants designing studies and researching of receiver environment pollution. Difference of using processs in terms of theoretical and experimental have also important effect on designing in forming of quality-quantity profile of receiver environment and wastewaters. In this study, it is aimed to calculate reactor volumes with a graphical process in treatment of KTU central campus wastewaters by activated sludge process for discharge and respirometric biochemical oxygen demand (BOD) measurements, different sludge ages, biomass concentrations, pollution loads and effluent souble BOD concentration.

This study shows that daily average pollution load of KTU central campus wastewaters (Q.So) is 350 kg/day (average discharge is 20L/s and influent souble BOD concentration is 200 mg/L), activated sludge pond's volume is 200-250 m^3 for different effluent souble BOD concentration and biomass concentrations.

***Key words**: Respirometer, Biochemical Oxygen Demand, The Moment Method, The Least Squares Method, Activated Sludge Process.*

Introduction

Biochemical Oxygen Demand (BOD) is defined as oxygen amount used by microorganisms during the stabilization (transformation into inorganic materials) of organic materials under specific conditions. Economic calculations of wastewater treatment facilities, control of operations of these facilities and research made on river pollutions are mostly based on BOD measurements. BOD evaluation is affected by the number and adaptation of microorganisms, concentration of natural and fragmented organic materials, amount of nutrients and incubation time, temperature and light effect, and biological or biochemical operations of materials that have poisonous effects (Berkün, 1982).

According to Gibbon (1974), Muslu (1994), Milenko (1996), Gebara (1999) and Papkov (2000), the fundamental of purification with active sludge process are defined as experiencing structural change (assimilation) and material change (dissimilation), turning into precipitating biological bobble (active sludge) and transforming into stable and harmless material and heat energy, as a result of metabolism functions of aerobic microorganisms, which consists of organic materials, mostly bacteria, not removed by physical and chemical processs in the wastewater.

Material and Method

It is possible to determine BOD values with respirometers and standard dilution technique. For the last few years, they can also be determined with UV spectrophotometers and their cuvettes. In standard dilution technique, samples are used with diluting during BOD measurements. BOD value of the diluted sample stored inside a glass bottle is calculated from its oxygen content difference between the starting date and end of incubation (5 days) period. During respirometric measurements, samples are used without being diluted. CO_2 gas, which is emitted from the samples stored in colored experiment bottles with magnetic mixer as a result of biochemical reaction, is absorbed with KOH solution and the used O_2 amount is read from the manometers with the drop-off of total pressure due to dissolving of the oxygen in the gas phase above the wastewater to dissect the organic material, this value is multiplied by the adaptation factor and daily BOD values are obtained (Berkün, 1982; Rump and Krist, 1988).

Wastewater treatment plants are a big part of water economy. Therefore, various parameters such as benefiting from surface water, pollution capacities, applicable purification processs, degree of purification, location of the plant, benefiting opportunities from purification side products, and terrain conditions should be considered. Accordingly, it greatly facilitates the preparation of different pollution loads (Q.So) - volume (V) charts in the case of knowing some coefficients that belong to wastewaters similar to active sludge process during resizing studies. In other words, sludge age required with different pollution loads, reactor volumes corresponding to outlet water and biomass concentration can be estimated with the help of these charts easily.

Equation (1) is used for resizing of active sludge plants, where numerous factors such as toxic and inhibitive wastes, lack of nutrients, discharge, suspended solids amount, temperature, biomass concentration, sludge age, sludge volume index, recirculation ratio, sludge detention time, loading speed, hydraulic detention time, aerator types (diffuser, mechanical surface, radial current low cycle, axial current high cycle, horizontal spindle brush shaped, sunk turbine aerators), pond design (completely mixed, plug flow) are effective in resizing (Benefield and Randoll, 1988; Escritt and Haworth, 1984; Fair et al. 1968; Tchobanaglous and Burton, 1991; Qasım, 1985).

$$V = \frac{Y.\theta_c.Q.(S_o - S)}{X.(1 + Kd.\theta_c)} \tag{1}$$

Where

V : Reactor volume, m^3
Y : Yield coefficient (Typical value for municipal wastewaters 0,5 - 0,73)
θc : Mean cell residence time,day (sludge age)
Q : Avarage municipal water consumption, m^3/day
So : BOD concentration at the reactor inlet, mg/L (influent souble BOD concentration)
S : BOD concentration at the reactor outlet, mg/L (effluent souble BOD concentration)

X : Biomass concentration, g/L (Microorganism concencration in activated sludge pond), (concentration of MLVSS)
Kd : Endogenaus decay coefficent, day^{-1} (Typical value for municipal wastewaters 0.045- 0.125)

Results and Discussion

Samples taken from 1st septic tank outlet and 2nd septic tank inlet (Fig. 1) in whole and composite form are mixed and precipitating suspension materials in the wastewater are homogenized. Preheating in the water bath were applied to the samples different from 20°C. Wastewater samples at required volume (164 mL) are filled in plastic corked experiment bottles with magnetic mixer and KOH tablet inside to enable CO_2 absorption, and then placed in Warburg type respirometer. Manometer measures the pressure drop of air above the samples. The oxygen content in the water decreases as bacteria use oxygen to dissect the organic material. In this case, water takes the oxygen in gas phase above itself and dissolves it. This causes the drop of total pressure of gas phase above the water. Consequently, mercury level on the manometer arm starts to rise. At the end of the fifth day, the measurement ended and the values read from the scale are filled and “Five days biochemical oxygen demand (BOD_5)” values are obtained with multiplying sample amount by compatibility factor (C.F.=10).

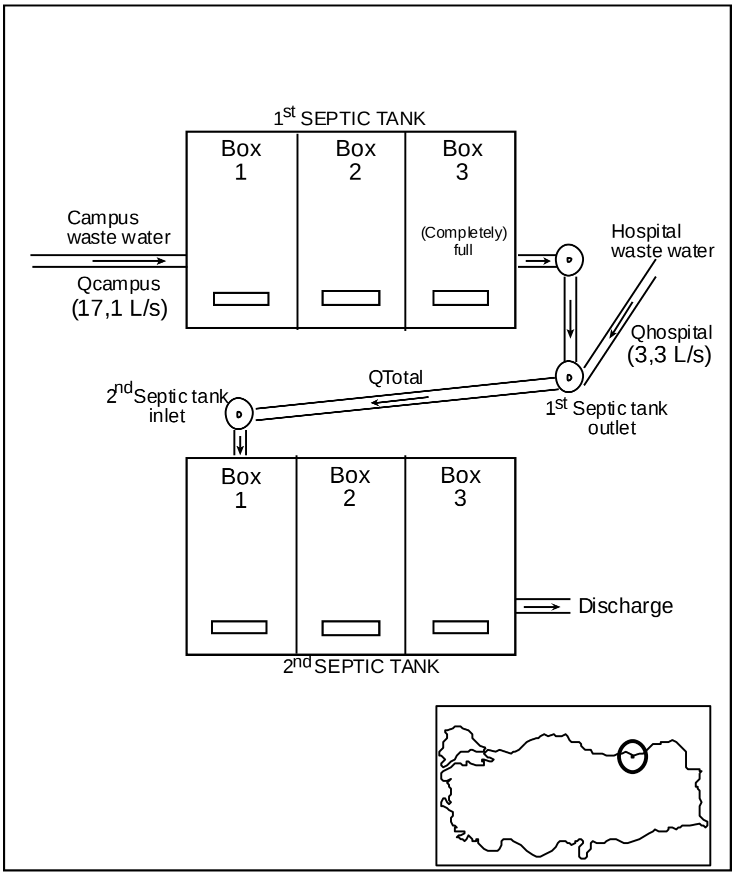
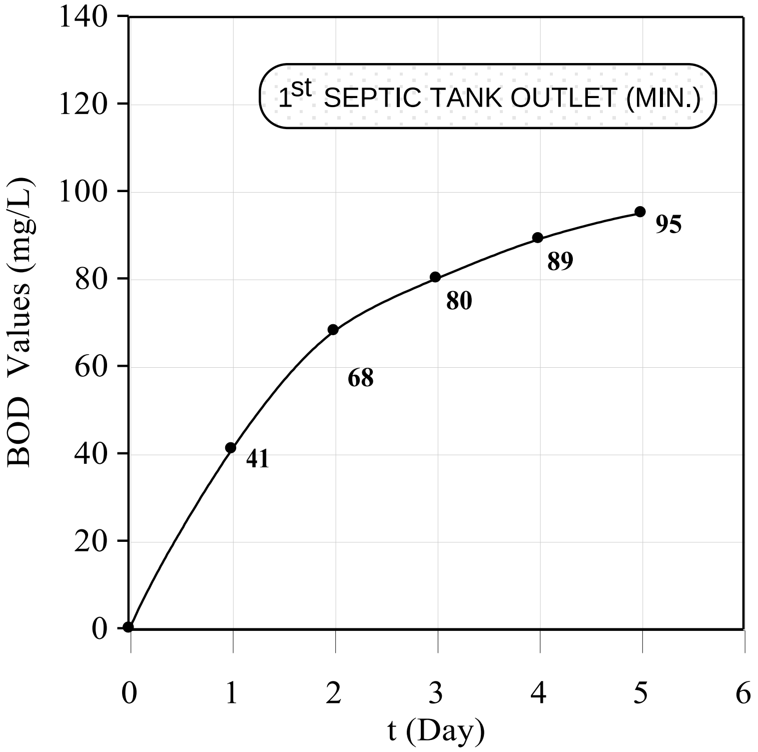


Figure 1 Location of the sample plots.

It is observed from the results of flow measurements at the location of KTU central campus wastewater that average waste water coming from academic and administrative units is 17.1 L/s, wastewater from Farabi Hospital is 3.3 L/s, and the total flow is 20.4 L/s. 5 days (BOD_5) values obtained from 1st septic tank outlet and 2nd septic tank inlet are presented in Fig. 2-3.



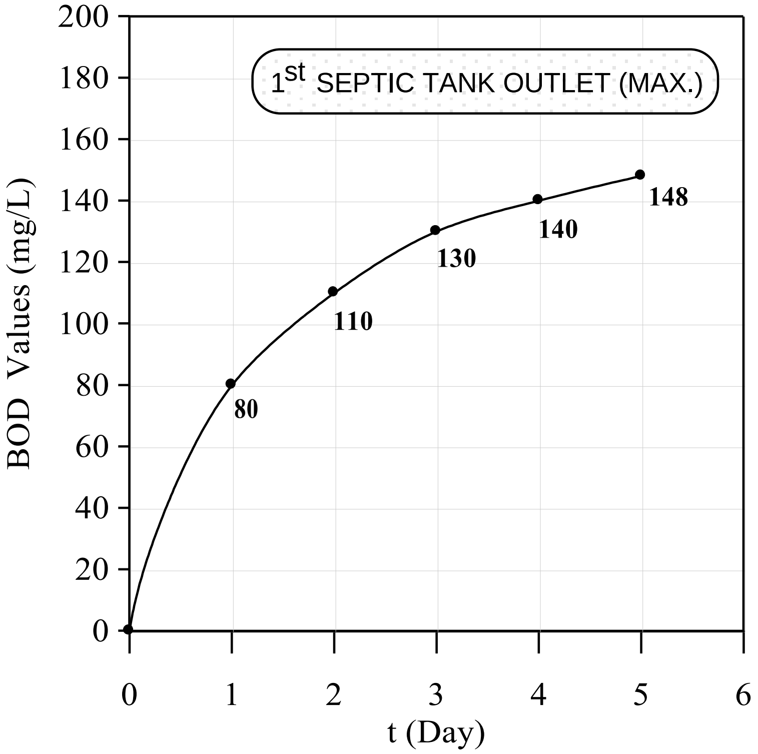


Figure 2 1st Septic tank outlet BOD (5 days) values.

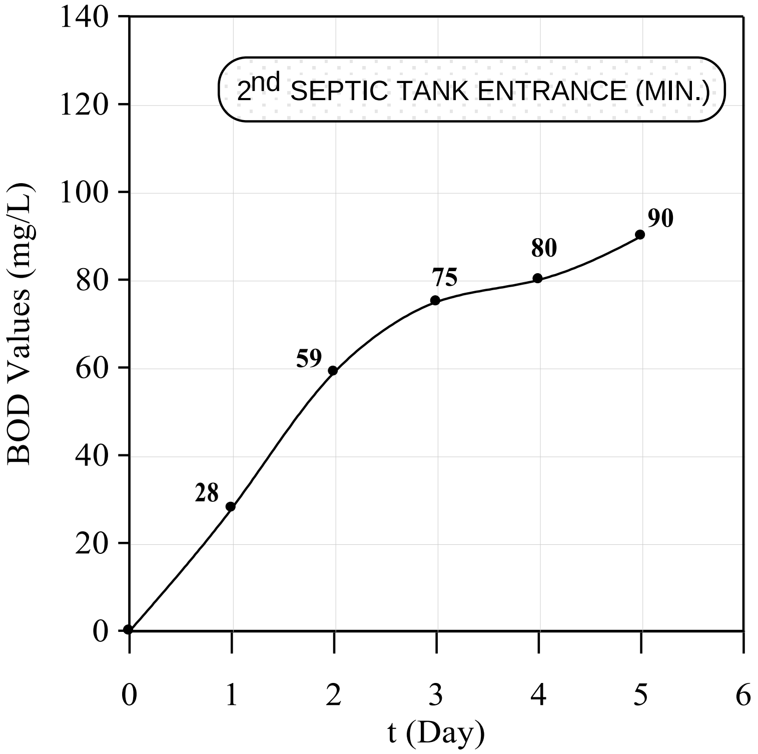
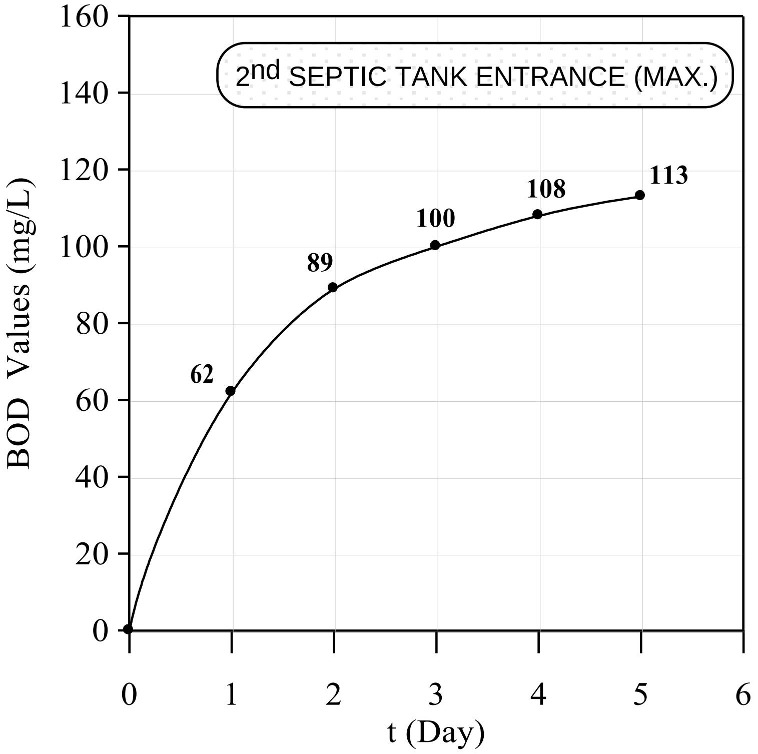


Figure 3 2nd Septic tank inlet BOD (5 days) values.



Total biochemical oxygen demands (L) based on The Least Squares method (Mancy, 1971), The Moment method (Moore, Thomas and Snow 1950) and bio-oxidation velocity constants (k_1) of minimum and maximum 5 days (BOD_5) values obtained from 1st septic tank outlet and 2nd septic tank inlet are given in Table 1-2.

Table 1 k and L values of respirometric BOD values according to The Least Squares Method.

Y_1	Y_2	Y_3	Y_4	Y_5	**Equation**	**k** (day^{-1})	**L** (mg/L)
41	68	80	89	95	4*a+ 278*b- 71.5 =0 278*a+ 20626*b-4227.5=0	0.568	101
80	110	130	140	148	4*a+ 460*b- 104 =0 460*a+ 55000*b- 10360=0	0.762	149
28	59	75	80	90	4*a+ 242*b- 71 =0 242*a+ 16290*b-3600=0	0.422	103
62	89	100	108	113	4*a+ 359*b- 79.5 =0 359*a+ 33429*b- 6102=0	0.855	113

Table 2 k and L values of respirometric BOD values according to The Moment Method.

Y_1	Y_2	Y_3	Y_4	Y_5	**ΣY**	**ΣY*t**	**ΣY/ΣY*t**	**k** (day^{-1})	**L** (mg/L)
41	68	80	89	95	373	1248	0.298878	0.526	102
80	110	130	140	148	608	1990	0.305528	0.711	150
28	59	75	80	90	332	1141	0.290973	0.343	111
62	89	100	108	113	472	1537	0.307092	0.758	114

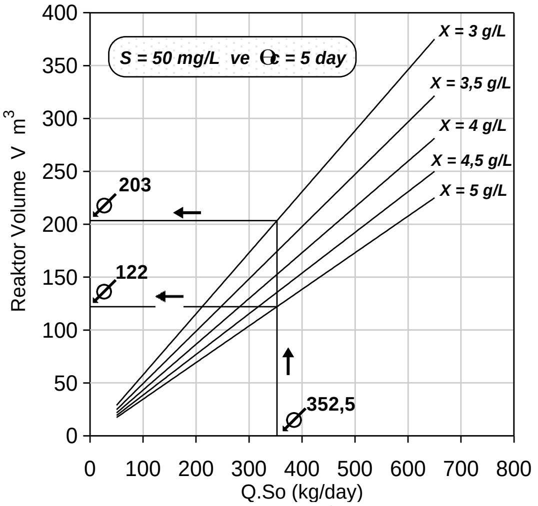
During the arrangement of equations that give out active sludge reactor volumes, influent souble BOD concentration is taken (So) 200 mg/L at the pond inlet (it is presumed that BOD pollution reduction of wastewater that passes mechanical purification varies between 20 – 45 %). Mixtures of the industrial wastewater and residential wastewater at different ratios affect the efficiency of the activated sludge process as measured by BOD and COD reduction. BOD reduction of the conventional activated sludge system was approximately 75 - 95 % (Murathan and Yıldırım, 2001). If sludge ages and outlet water concentrations are taken as (θc) 5–10-15 days and (S) 50-40-30-20-10 mg/L respectively, values acquired from computations are presented in Table 3.

Table 3 Reactor volumes for different effluent souble BOD concentrations and sludge ages.

	Sludge Ages (θc)		
Effluent souble BOD Concentration (S)	θc = 5 day	θc = 10 day	θc = 15 day
S= 50 mg/L	$\frac{0,3461.Q}{X}$	$\frac{0,5625.Q}{X}$	$\frac{0,7105.Q}{X}$
S= 40 mg/L	$\frac{0,3692.Q}{X}$	$\frac{0,6.Q}{X}$	$\frac{0,7579.Q}{X}$
S= 30 mg/L	$\frac{0,3923.Q}{X}$	$\frac{0,6375.Q}{X}$	$\frac{0,8053.Q}{X}$
S= 20 mg/L	$\frac{0,4154.Q}{X}$	$\frac{0,675.Q}{X}$	$\frac{0,8526.Q}{X}$
S= 10 mg/L	$\frac{0,4385.Q}{X}$	$\frac{0,7125.Q}{X}$	$\frac{0,9.Q}{X}$

Domestic water usage values that correspond to prospective populations (5000-100000-150000-200000-250000-30000) are used as (500-1000-1500-2000-2500-3000) m^3/day with using the specific flow value as 100 L/day/person. These flow values, reactor volume charts for different effluent souble BOD concentrations (S = 40-30-20-10 mg/L) and X=3-3,5-4-4,5-5 g/L biomass concentrations are plugged into the equations in Table 3 (using sludge age as 5 days) to obtain Fig 4-5.

Figure 4 (Q.So-V) volume charts for S=50mg/L and θc=5 days



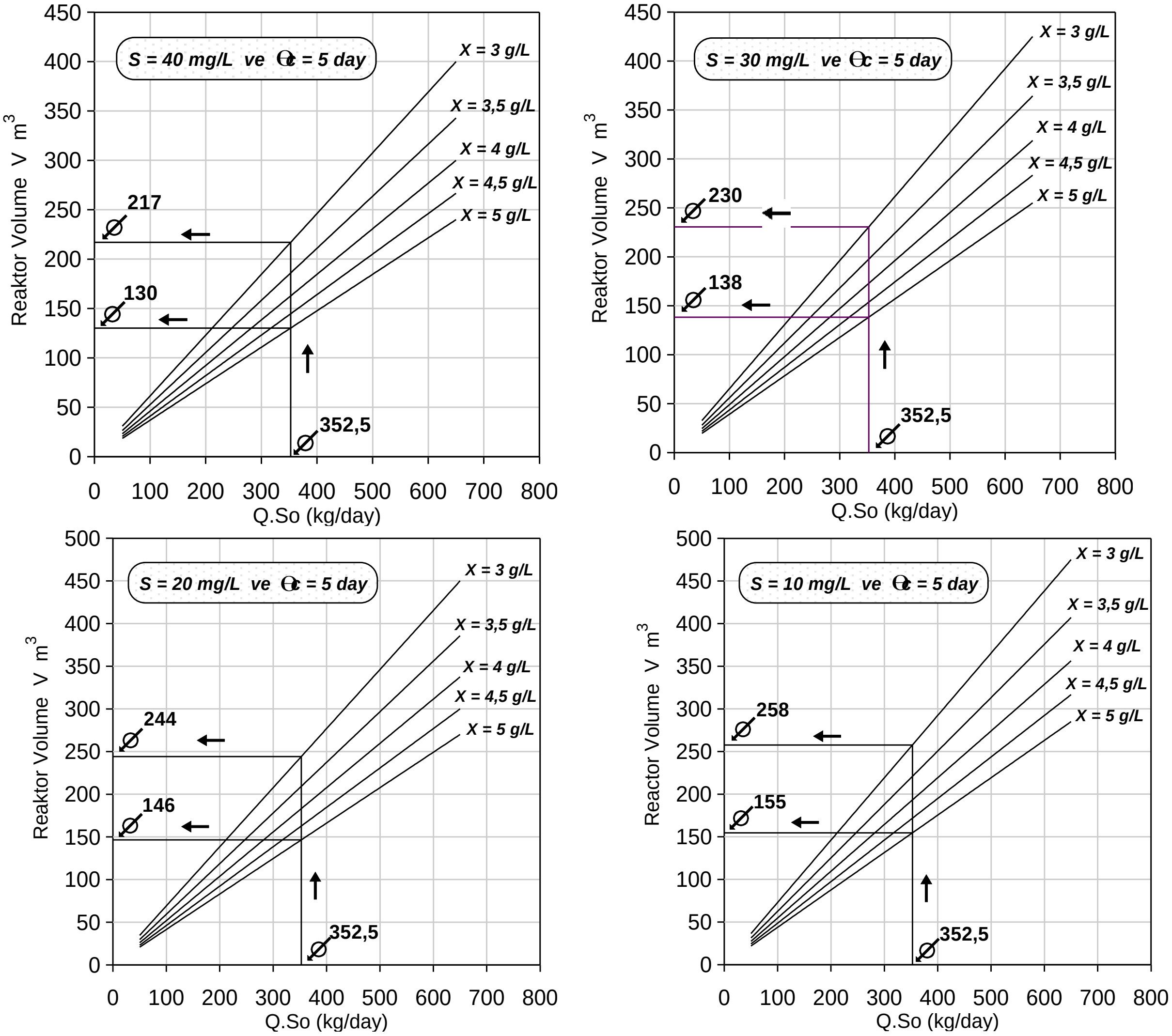


Figure 5 (Q.So-V) volume charts for S=40-30-20-10 mg/L and θc=5 days.

Conclusions

Total BOD values of domestic wastewaters vary between 100 - 600 mg/L (Nemerow, 1971). According to The Least Squares Method, total BOD values (L) of minimum and maximum five days KTU central campus wastewater are between 101 - 149 mg/L at 1st septic tank outlet and 103 - 113 mg/L at 2nd septic tank inlet. According to The Moment Method, total BOD values (L) are between 102 - 150 mg/L at 1st septic tank outlet and 111 - 114 mg/L at 2nd septic tank inlet. Since BOD pollution reduction in the wastewater that passed mechanical purification vary between 20 - 45 %, it is assumed that total BOD values will stay around 100 - 600 mg/L at the 1st septic tank inlet. Besides the graphs are prepared using the influent souble BOD concentration as 200 mg/L with assuming the mechanical purification production is 25 % during computations. The daily average pollution load (Q.So) of KTU central campus wastewaters is 350 kg/day (average flow 20 L/s and influent souble BOD concentrations 200 mg/L), no matter what the source (domestic, industrial, agricultural) and pollution loads of wastewater are, active sludge volume to be estimated for different effluent souble BOD concentration and biomass concentrations becomes 200 - 250m^3 with the graphical method that facilitates timing during computations and creates an algorithm for optimization.

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INVESTIGATION OF RADON RISK IN WELL WATER

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The Radon is not chemically active so it migrates through porous materials like the ground and it has a small chance of decay as anybody breath it in and out. Radon in water arises from the decay of the small amounts of radium present, and also from diffusion through the surrounding soil and rock formations. In this work the radon concentration measured in total of 10 different types of well waters of about 100 meter depth in the Afyonkarahisar area (Turkey), will be represented.

Radon is a radioactive gas and its half-life about 4 days. It is colorless, odorless, tasteless, and chemically inert. Although there is no way of telling how much radon is present, it can be measured by different types of devices. It is formed by the natural radioactive decay of uranium in rock, soil, and water. Some remains below the surface and dissolves in water that collects and flows under the ground's surface. Radon is a radioactive gas originating from ^{226}Ra decay, a member of the natural ^{238}U decay series. Radon risk may exist when the radioactive gas accumulates in the atmosphere of enclosed environments like dwellings and underground cavities. Radon in water arises from the decay of the small amounts of radium present, and also from diffusion through the surrounding soil and rock formations. The radon solubility in water is 510 $cm^3\ kg^{-1}$ at 0 °C and decreases at higher temperatures [1]. Thus, the domestic use of showers, cooking, washing up, laundering, etc., may lead to additional increases in indoor radon concentrations. The ingestion of radon in water can give rise to an additional exposure dose to the whole body. Inhalation of radon along with its daughter nuclides attached to microscopic particulate matter delivers highly ionizing radiation to lung cells, causing biological damage and ultimately leading to lung cancer. From epidemiological and experimental studies, the carcinogen effects of radon, such as the increased risk of lung cancer for exposed miners compared to the non-exposed population, have demonstrated potential negative impact on human health. This has prompted worldwide efforts to measure radon levels in man's environment to assess the such radiological risk [2]. As in many countries (including Turkey), some homes obtain drinking water from groundwater sources which moves through rock containing natural uranium and radium that produce radon, it is important to monitor radon in water.

Thus in this paper, the measured data of radon levels in drinking water from Afyonkarahisar province, Turkey, and annual effective dose due to the radon will be presented.

The measurements were performed using the commercially available WG-1001 Vacuum Water Degassing System and AB-5R Radiation Monitor produced by Pylon Electronics.

Following the operating instructions of the experimental system used for radon and radium determination described in detail by the manufacturer [3] the was determined using the following relationship:

$$A = \frac{(C-B)}{F \times 6.66 \times D \times S \times V} \times 0.037$$

where A is the radon concentration in Bq.L^{-1}, C is the gross count rate (cpm), B is the background rate (cpm), F is the cell counting efficiency which normally is 0.745 in the present case, D is the degassing efficiency of 300A Lucas cell and its value is 0.9, S is the correction for decay of radon from sample time T_s to the count time T_c, V is the sample volume in litres (0.19 L) and 0.037 is the conversion factor between pCi and Bq. As detailed in [4] the water samples were collected every week, from 10 different wells. A 500 ml plastic bottle was used to collect water sample.

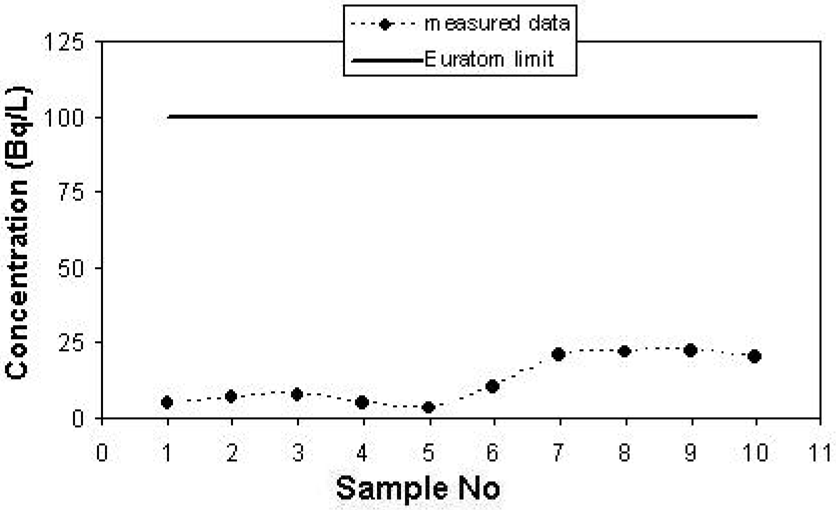

Figure 1 The radon concentration of 10 different sample and comparison with the European Commission Recommendations limit.

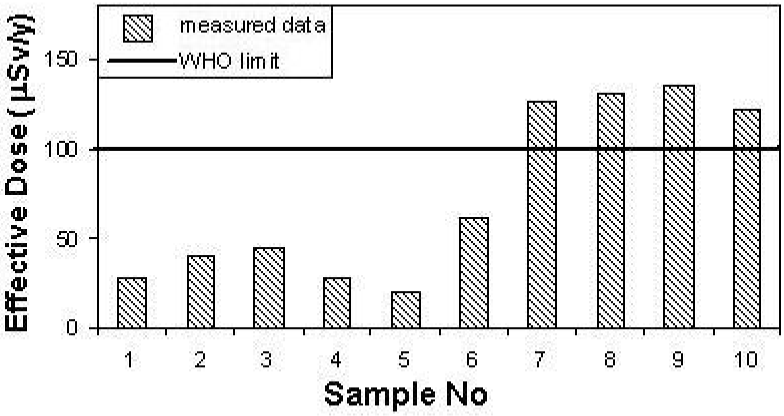

Figure 2 The annual effective dose as a function of sample no and comparison with the WHO limit.

The radon concentrations from 10 different wells in the Afyonkarahisar region have been measured. The average values of all results for each well are displayed in Fig.1. It can be seen from this figure that the highest radon concentration was observed in the samples from well #8 while the lowest radon concentration was in the samples from well #3. The reason for this difference could be a function of the geological structure of the area, the depth of the water well. When the radon concentrations measured are compared with the allowed maximum contamination level for radon concentration in water, proposed by the European Commission Recommendations on the protection of the public against exposure to radon in drinking water supplies (2001/928/Euratom) [5] which recommends action levels of 100 Bq.L^{-1} for public water supplies and 1000 Bq.L^{-1} for private water supplies, it can be seen that the levels we measured were below these limits. The annual effective doses have been calculated using the dose conversion factors of 6 □ Sv ӯ^{1}.(Bq L^{-1})$^{-1}$ [6] and the results are displayed in Fig. 2. It can also be seen from this table that the annual effective dose obtained for same samples exceed the limit recommended by WHO which is 0.1 mSv.y^{-1} for the general public [7].

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THE EFFECT OF SOLAR - COSMIC RAYS ON THE BACKGROUND RADIATION

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The source of natural radiation in the earth and its level is generated by the sun and cosmic rays from outside the solar system strikes our planet all the time. The cosmic rays consist of energetic nuclei of all naturally occurring elements, interacting with atmospheric constituents, through atomic and nuclear collisions. Background radiation levels in the atmosphere vary in intensity with latitude, altitude, throughout the year and through the solar cycle. The variation of background radiation with solar cycle has been investigated in Isparta region of Turkey.

Radiation is energy that comes from a source and travels through any kind of material and through space. There is a background of natural radiation everywhere in our environment. It comes from space (i.e., cosmic rays) and from naturally occurring radioactive materials contained in the earth and in living things. In general about 13% of the background radiation at the surface of the Earth is due to cosmic radiation. This is the result of particles from the Sun but also of very energetic protons and heavier nuclei from outside our Solar system. Although the Sun's contribution is probably quite small at the surface of the Earth it is important for astronauts and satellites not protected by the Earth's magnetic field. The particles comes from Sun are mostly proton, electron or helium are charged and so they interact with the Earth's magnetic field. They spiral along the field lines and are directed towards the magnetic poles. If they reach the top of the atmosphere they excite the atoms there and an auroral display occurs. Otherwise they are trapped in the radiation belts that encircle the Earth out to about ten Earth radii.
The effect of this cosmis rays on the background radiation is important and tis will be monitored. In this paper the radiation dose has been measured to investigate such effect in Isparta region of Turkey.

The absorbed radiation dose were measured using a portable scintillator detector of NaI(Tl) which has 2x2 inch dimensions size and was connected to ASP/2e counter developed by Eberline [1]. The energy response of the detector covers the majority of significant □ -ray emission from terrestrial and cosmic sources. The all measurement has been performed at 1 meter above the ground.

The absorbed radiation dose has been measured as a function of different parameter to investigate solar effect in the background radiation in Isparta region of Turkey. In Fig.1 it was displayed as a function of local solar time. It was found that the absorbed radiation dose varied between 13.9 and 15.22 □ R/h. It can also be seen from this figure that even not much fluctuation have been observed the radiation dose have been increased during the sundown.

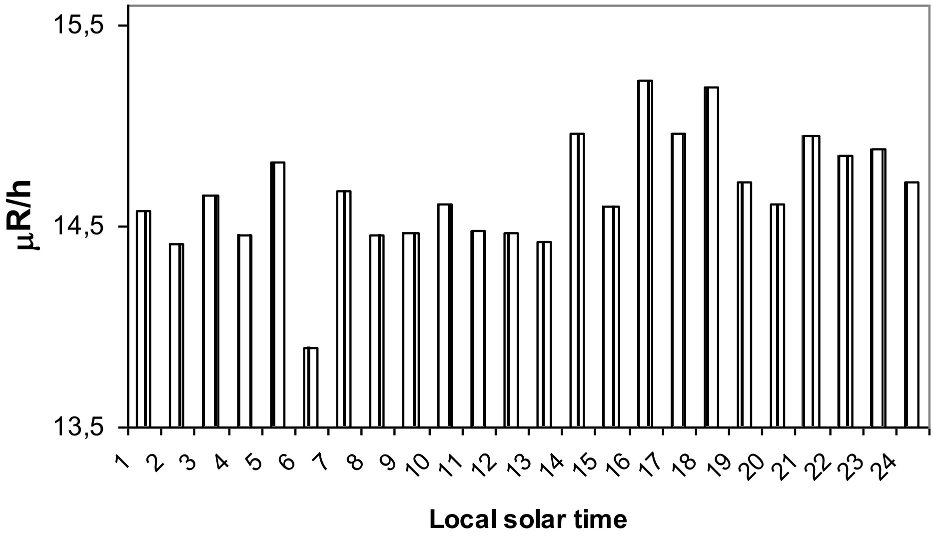

Fig1. Exposure radiation rate as a function local time over a day

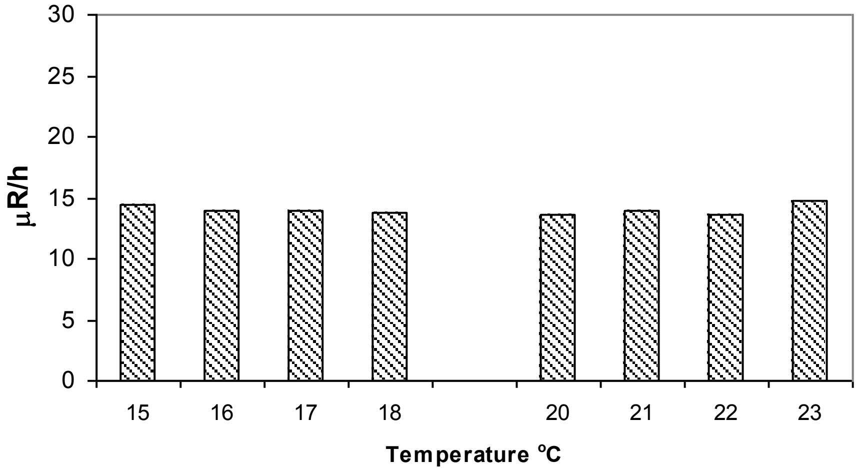

Fig2. Exposure radiation rate as a function of temperature during the day

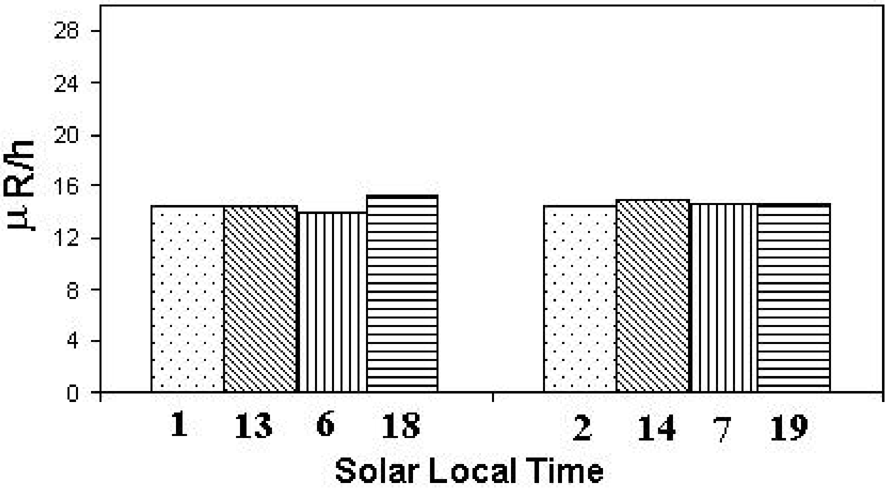

Fig3. The comparison radiation exposure rate as a function of same local time during a day

As the temperature can change with the sun effect it was thought that it will be interesting to investigate absorbed dose as a function of temperature. This is displayed in Fig.2 where it can be seen that there is not any significant derivation has been observed. When the day considered two part for local time the absorbed dose obtained at the same time of two part, was compared. As showing in Fig.3 there is no differences have been observed between this two solar time.

Although the effect of the sunlight on the background radiation can be seen from this work, further investigation will be performed all during the year covering summer season.

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SEASONAL AND SPATIAL DISTRIBUTIONS OF THE METALS IN THE WATER, SEDIMENT AND AFRICAN CATFISH, *CLARIAS GARIEPINUS*, FROM THE RIVER ASI (ORONTES) IN SOUTHERN EAST MEDITERRANEAN AREA OF TURKEY

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Seasonal and spatial variations of cadmium, iron, lead, zinc, copper, manganese, nickel, chrome, and cobalt were determined in water, bottom sediment and tissues (muscle, liver, gill and skin) of African catfish, *Clarias gariepinus*, from River Asi in northern east Mediterranean area. Concentrations of the analyzed metals in water, sediment and fish tissues were significantly affected by sampling sites and seasons. Metal levels in water, sediment and fish muscle were compared with national and international water quality criteria, background concentrations and permissible limits. Although concentrations of the metals such as Cu, Fe and Zn in water were generally found higher than background and legal concentrations, the levels in sediment and fish tissues were generally lower. Metals in the edible parts of the investigated fish were in the permissible safety levels for human uses.

Keywords**:** *Metals, Seasonal variations, River Asi, water, sediment, Clarias gariepinus*

INTRODUCTION

Metals such as iron, copper, zinc and manganese, are essential metals since they play an important role in biological systems, whereas mercury, lead and cadmium are non-essential metals, as they are toxic, even in traces. The essential metals can also produce toxic effects when the metal intake is excessively elevated. Heavy metal discharges to the aquatic environment are of great concern all over the world, and have a great ecological significance due to their toxicity and accumulative behavior. Thus, it can both damage aquatic species diversity and ecosystems (1). Heavy metals in aquatic environment can remain in solution or in suspension and precipitate on the bottom or be taken up by organisms. The analysis of metal concentrations in biota samples at the same locations can indicate the transfer of metals through food chains (2). Because of their important roles in the aquatic environments, heavy metals have been studied by many researchers all over the world (3-9).

River Asi rises near the city of Baalbek in Lebanon, and flows in a northerly direction between the Lebanon and anti-Lebanon mountains into Syria. It runs through the Syria and enters Turkey, in the province of Hatay. It flows north to the city of Antakya, bends westward, and then empties into the sea near Samandağ, in the northern east of Mediterranean Sea, through a total course of about 380 km. The damming of the River Asi in Syria provides irrigation water for the rich river valley. In ancient times the valley of the river formed a corridor between Asia Minor and Egypt. Like all other rivers in the world, this river has also an important role in the irrigation of the fields surrounding it, especially in Syria and Turkey. The river includes a number of the economically important fish species such as African catfish, *Clarias gariepinus* (most consumed species by local people), common carp, *Cyprinus carpio*, chub, *Liza aurata*, eel, *Anguilla anguilla* and *Carasobarbus luteus*. Mainly untreated agricultural, municipal and industrial wastes affect the river direct or indirectly. This study has been undertaken to determine the seasonal and spatial variations of cadmium, iron, copper, chrome, cobalt, zinc, lead, nickel and manganese in the water, sediment and the muscle, liver, gill and skin of the African catfish, *Clarias gariepinus* from the River Asi.

MATERIALS AND METHODS

Water, sediment and fish samples were collected from selected four stations along a length of 88 km in the part of Turkey of River Asi. These stations are the Border Area (BA), Güzelburç Area (GA), Sümerler Area (SA) and Samandağ Area (SAM) (Figure 1). All samples were collected in October 2003 (except fish) and January, April and July 2004. Water samples were collected from a depth of 0.5 m in 1 liter polyethylene bottles, which had previously had been washed with detergent, deionized water, 2 M concentrated nitric acid, deionized water again and finally medium water. Samples were acidified with 0.5 ml high-purity concentrated HNO_3 (Merck), brought to laboratory by placing on ice, filtered through a 0.45 μm micropore membrane filter, and after kept at -18 ^{o}C they were analyzed for metals with in two weeks. Sediment samples were collected using a sediment collector with an acid-washed plastic scoop from a depth of 10 cm from the surface. They were dried and passed through a 63 μm plastic sieve. One gram of the dried sediment sample was extracted with 1:1 HCL/HNO_3 acid mixture at 130-140 ^{o}C, brought to 25 ml in volumetric flasks with deionized water and filtered through a 0.45 μm micropore membrane filter (10).

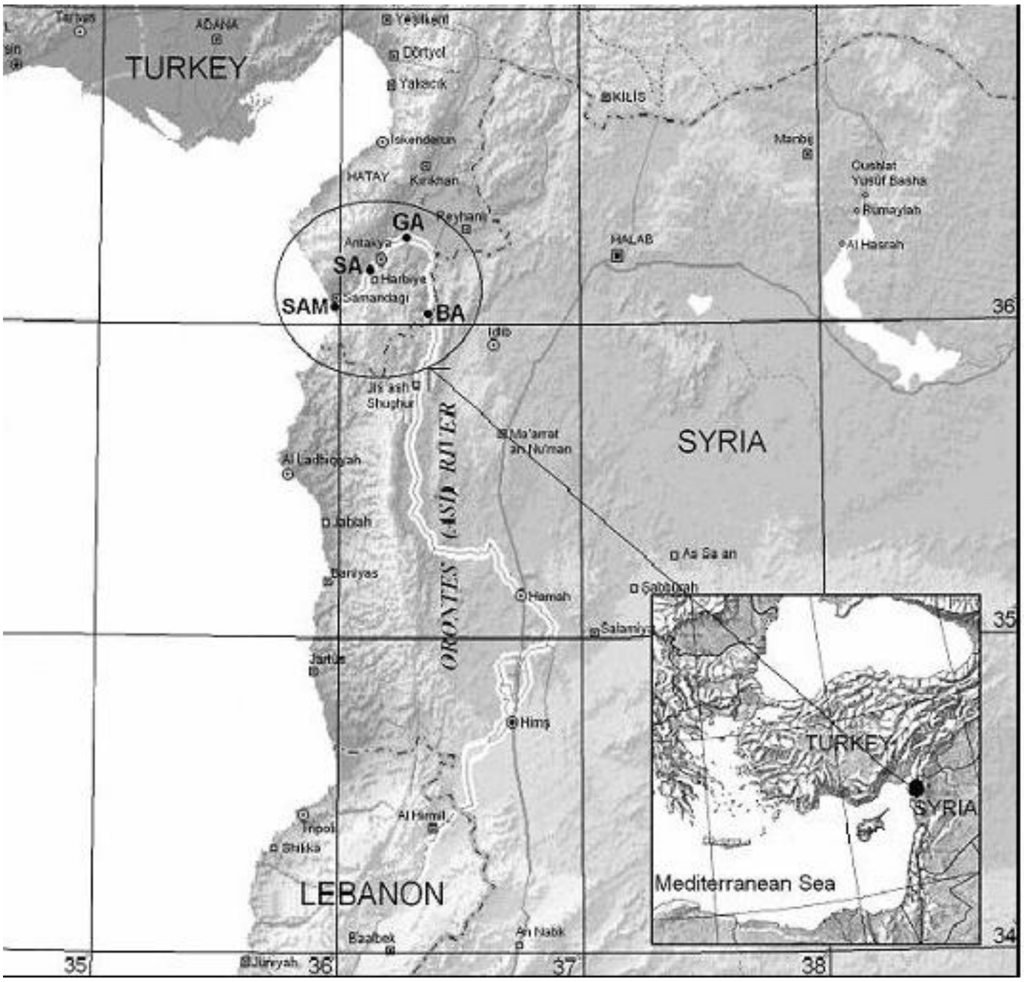

Figure 1. Location map of sampling stations in River Asi (Orontes)

At each sampling period, 10 fish samples (*C.gariepinus*) caught from the river were brought to laboratory in ice on the same day. Total length and weight of the samples were measured to the nearest millimeter and gram before dissected. Approximately 1 g sample of muscle and skin, two gill racers and entire liver from each specimen were dissected, washed with distilled water, weighed, packed in polyethylene bags and stored at -18 ^{o}C prior to analysis. All tissue samples were transferred to a 100 ml Teflon beaker. There after, 10 ml ultrapure concentrated nitric acid was added slowly to the sample. The Teflon beaker was covered with a watch glass, and the sample heated at 200 ^{o}C on a hot plate for 3 h. There after, the solution was evaporated slowly to near dryness. Two milliliters of 1 N HNO_3 was added to the residue and the solution was evaporated again on the hot plate.

By repeating the additional digestion twice, all organic material in every sample was completely digested. After cooling, a further 2.5 ml of 1 N HNO_3 was added. The solution was transferred to 25 ml volumetric flasks and diluted with deionized water. Before analysis, the samples were filtered through a 0.45 μm nitrocellulose membrane filter. Sample blanks were prepared in the laboratory in a similar manner to the field samples (11). Metal contents were expressed as $\mu g\ g^{-1}$ wet weight for fish tissues, as $\mu g\ l^{-1}$ for water and as $\mu g\ g^{-1}$ dry weight for sediment.

All samples were analyzed three times for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn by ICP-AES Varian Liberty Series-2. Standard solutions were prepared from stock solutions (Merck, multi element standard). For fish samples, the accuracy and precision of our results were checked by analyzing standard reference material (SRM, Dorm-2). The results indicated good agreement between the certified and the analytical values (Table 1), the recovery of elements being partially complete for most of them. The absorption wavelengths for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were 228.8, 238.9, 267.7, 324.8, 259.9, 257.6, 231.6, 220.4, and 213.9 in nm, respectively.

A logarithmic transformation was done on the data to improve normality. To determine the differences between months and stations for the water and sediment samples, and the differences between months and tissues for fish, one way and univariate two way ANOVA were performed. Post hoc test (Duncan) was tested to determine statistically significant differences following ANOVA. Possibilities less than 0.05 were considered statistically significant ($p<0.05$). All statistical calculations were performed with SPSS 13.0 for Windows.

Table 1. Concentrations of metals found in Standard Reference Material DORM-2 (dogfish muscle) from the National Research Council, Canada (all data as means ± standard errors, in $mg\ kg^{-1}$ dry wt)

Value	Cd	Cu	Cr	Pb	Zn	Ni	Mn	Fe	Co
Certified	0.043	2.34	34.7	0.065	26.6	19.4	3.66	142	0.182
SE	0.008	0.16	5.5	0.007	2.3	3.1	0.34	10	0.031
Observed[a]	0.046	2.38	33.9	0.069	24.5	20.6	3.45	132	0.175
SE	0.007	0.16	1.58	0.009	1.86	0.91	0.51	13	0.022
Recovery (%)	107	102	98	106	92	106	94	93	96

[a] Each value is the average of ten determinations.

RESULTS AND DISCUSSION

Metals in Water

This study examined the seasonal and spatial variations of the concentrations of Cd, Fe, Cu, Zn, Cr, Co, Mn, Ni and Pb in water, sediment and muscle, liver, gill and skin of *C. gariepinus* from River Asi in Northern East Mediterranean Area of Turkey. In water samples, iron was found in the highest concentrations ranging from 7.9 to 9734 μg l^{-1}, and its concentrations were also higher than those of other metals in all stations and months, except Co, Cu, Ni, Pb and Zn in October 2003 in station BA and Zn in October 2003 in station SA (Table 2). Following Fe; Zn showed the second highest levels in all months for all stations except Mn level in July in station SA. In October, although Cd, Co, Cr, Cu and Pb levels were generally similar in all stations, Fe, Mn and Zn in station BA, and Ni in station SAM were minimum levels. Fe and Zn in station GA, Mn in station SAM, and Ni in station BA were maximum levels. In January, Cu, Ni and Pb levels in station BA, Cr, Fe, Mn and Zn levels in station GA, and Co and Zn levels in SA were higher than those in other stations. In April, Cu and Zn levels in station GA, and Co, Cr, Fe, Mn, Ni and Pb levels in station SA were higher than those in other stations. In July, Co, Cr, Cu, Fe, Mn, Ni and Pb levels in station GA, Cd in station SA, and Zn in station SAM were higher than those other stations. In general, there are statistically differences between the metal levels in different stations ($p<0.05$). In addition, there are differences between the metal levels in different months from the same stations ($p<0.05$).

Table 2. The seasonal and spatial variations of the mean metal concentrations in the water from the River Asi (five water samples in each month for each station).

Stations/ months	Metal concentrations, in μg l^{-1*}								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
BA									
October-2003	1.5^{a}	11.7^{b}	5.4^{a}	30.4^{a}	7.9^{a}	1.1^{a}	33.2^{a}	12.0^{a}	39.2^{a}
January-2004	---nd	0.8^{a}	4.6^{a}	23.8^{b}	408^{b}	69.3^{b}	13.6^{b}	2.4^{b}	91.4^{b}
April-2004	---	0.4^{a}	5.5^{a}	23.6^{b}	683^{c}	21.1^{c}	17.4^{ab}	2.1^{b}	244^{c}
July-2004	0.1^{b}	2.3^{a}	31.1^{b}	23.7^{b}	5474^{d}	246^{d}	54.2^{c}	2.6^{b}	103^{d}
Total	0.80^{x}	3.8^{x}	11.6^{x}	25.4^{x}	1643^{x}	84.4^{x}	29.6^{x}	4.8^{x}	119^{x}
GA									
October-2003	1.0	10.2^{b}	7.8^{a}	29.0^{a}	170^{a}	6.9^{a}	22.6^{a}	9.1^{a}	137^{a}
January-2004	---	9.7^{b}	10.1^{ab}	23.3^{b}	2250^{b}	124^{b}	7.3^{b}	0.8^{b}	103^{b}
April-2004	---	0.3^{a}	11.4^{b}	23.9^{b}	641^{c}	30.5^{c}	9.3^{b}	4.0^{b}	526^{c}
July-2004	---	25.9^{c}	253^{c}	49.6^{c}	9734^{d}	760^{d}	653^{c}	17.4^{c}	155^{d}
Total	1.0^{x}	11.5^{y}	70.5^{y}	31.4^{y}	3199^{y}	230^{y}	173^{y}	7.8^{x}	230^{y}
SA									
October-2003	1.1^{a}	10.9^{b}	7.9^{a}	30.7^{a}	55^{a}	1.6^{a}	24.9^{a}	8.6^{a}	71.9^{a}
January-2004	---	10.9^{b}	5.2^{a}	23.0^{b}	901^{b}	116^{b}	5.4^{b}	---	103^{b}
April-2004	---	1.4^{a}	61.4^{b}	22.8^{b}	956^{c}	37.6^{c}	26.1^{a}	2.7^{b}	292^{c}
July-2004	0.8^{a}	1.1^{a}	34.9^{c}	24.2^{b}	3339^{d}	202^{d}	44.8^{c}	10.0^{a}	144^{d}
Total	0.95^{x}	6.1^{z}	27.4^{z}	25.1^{x}	1313^{z}	89.2^{z}	25.3^{x}	7.1^{x}	153^{z}
SAM									
October-2003	1.2	13.2^{a}	5.3^{a}	29.9^{a}	159^{a}	14.1^{a}	12.5^{a}	8.4^{a}	48.4^{a}
January-2004	---	10.6^{a}	6.4^{ab}	21.7^{b}	1050^{b}	103^{b}	4.0^{a}	0.6^{a}	7.2^{b}
April-2004	---	0.8^{b}	7.6^{ab}	23.5^{c}	272^{c}	25.1^{c}	20.1^{a}	2.3^{a}	233^{c}
July-2004	---	0.5^{b}	9.9^{b}	23.0^{bc}	1315^{d}	75.2^{d}	16.7^{a}	9.4^{a}	172^{d}
Total	1.2^{x}	6.3^{z}	7.3^{w}	24.5^{x}	699^{w}	54.2^{w}	13.3^{z}	5.2^{x}	115^{w}

[*] Vertically, letters a, b, c and d show differences among different months at same stations; x, y, z and w between stations. Within columns, means with the same letter are not statistically significant, $p>0.05$

[nd] not detected

The concentrations of metals in the water of River Asi were compared with other studies, world average and water quality criteria in Table 3. When compared with Turkish water quality criteria, the river is acceptable as polluted water for Cr, Fe and Ni, as less polluted water for Cu and Mn, and as clean water for Cd, Co, Pb and Zn (12). Although the concentrations of Cu, Fe and Zn measured in this were higher than Turkish permissible concentrations, others were lower than those (13).

Table 3. Comparison of the overall metal concentrations in the water of River Asi with other studies and water quality criteria (μg l^{-1}).

Studies and guidelines	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
This study[a]	0.83	6.90	69.0	26.6	1713	114.5	60.3	5.80	154.4
TEG (12)[b]									
Class I	3.0	10	20	20	300	100	20	10	200
Class II	5.0	20	50	50	1000	500	50	20	500
Class III	10	200	200	200	5000	3000	200	50	2000
Class IV	>10	>200	>200	>200	>5000	>3000	>200	>50	>2000
TKB (13)[c]	10	1000	100	10	700	1000	300	100	3.0
US EPA (14)[d]									
CMC*	4.3	-	16	13	-	-	470	65	120
CCC*	2.2	-	11	9.0	-	-	52	2.5	120
An & Kampbell (15)[e]	20	<2.0	4.0	24	119	7.0	5.0	15	59
Singh et al. (16)[f]	-	-	1.3-5.7	-	34-117	1.3-5.3	9-17	19-39	11-32
Turgut (17)[g]	0.81	-	0.093	13.1	-	-	2.27	0.59	249
Pekey et all. (18)[h]	8.0	21	42	37	4030	-	-	120	700
Klavins et all. (19)[i]	0.02	0.08	-	1.0	-	6.0	0.3	0.2	10

[a] Mean ± standard error, the number of analyzed samples=40 for Cd, 75 for Pb, 80 for others.

[b] Turkish Water Quality Criteria (Class I: clean water, Class II: less polluted water, Class III: polluted water, Class IV: heavily polluted water).

[c] Turkish Permissible Concentrations.

[d] US EPA Recommended Water Quality Criteria (CMC and CCC: Criteria Maximum Concentration and Criterion Continuous Concentration)

[e] Lake Texoma, border of Oklahoma and Texas.

[f] Gomti River, India

[g] Küçük Menderes River, Turkey.

[h] Dil Deresi (Stream), Turkey.

[i] Background concentrations, world average.

As seen in Table 3, when compared with US EPA recommended water quality criteria, the metal concentrations measured in this study were higher than it except Cd (for CMC and CCC), Ni and Pb for CMCs (14). On the other hand, if compared with world average back ground concentrations, the concentrations of all metals measured in this river were higher (19). When other studies are considered (Table 3), Cd, Cr, Ni and Mn concentrations in River Asi were generally higher than those in other waters. Pb concentration was only higher than that in Küçük Menderes River (17). Co, Cu and Fe concentrations measured in present study were generally lower than others except Dil Deresi waters where concentrations were higher. Finally, Zn concentrations were higher than Küçük Menderes River and Dil Deresi waters, lower than others.

Metals in Sediment

In sediment samples like water samples, iron was found in the highest concentrations ranging from 863.22 to 1473.3 μg g^{-1}, and its concentrations were also higher than those of other metals in all stations and months (Table 4). Following Fe; Mn showed the second highest levels in all months for all stations except Ni level in January in station SAM. In October, Co, Cr, Fe, Mn and Ni levels in station GA, Cd and Cu levels in station SA, and Cu and Zn levels in station SAM were higher than those in other stations.

Table 4. The seasonal and spatial variations of the mean metal concentrations in the sediment from the River Asi (five sediment samples in each month for each station).

Stations/ months	Metal concentrations, in µg g^{-1} dry wt[*]								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
BA									
Oct.2003	0.003^{a}	0.19^{a}	3.91^{a}	0.71^{a}	936^{a}	8.91^{a}	7.29^{a}	0.12^{a}	1.88^{a}
Jan.2004	0.008^{b}	0.25^{a}	3.71^{ab}	0.73^{a}	948^{a}	11.7^{b}	6.29^{a}	0.16^{a}	1.57^{a}
Apr.2004	0.008^{b}	0.19^{a}	3.93^{a}	0.68^{a}	863^{a}	10.5^{ab}	6.73^{a}	0.05^{b}	1.51^{a}
July.2004	$<0.001^{a}$	0.41^{b}	3.18^{b}	0.68^{a}	877^{a}	14.7^{c}	6.63^{a}	0.04^{b}	1.78^{a}
Total	0.005^{x}	0.26^{x}	3.68^{x}	0.70^{x}	906^{x}	11.5^{x}	6.73^{x}	0.09^{x}	1.69^{x}
GA									
Oct.2003	0.001^{a}	0.59^{a}	8.22^{a}	0.75^{a}	1371^{ab}	14.8^{a}	16.2^{a}	0.09^{a}	1.28^{a}
Jan.2004	0.006^{b}	0.90^{b}	8.91^{b}	1.03^{b}	1300^{b}	19.3^{b}	16.1^{a}	0.46^{b}	1.66^{b}
Apr.2004	0.008^{b}	0.57^{ca}	7.09^{c}	1.41^{c}	1473^{a}	16.6^{c}	9.98^{b}	0.29^{c}	2.46^{c}
July.2004	0.009^{b}	0.36^{c}	7.39^{c}	1.42^{c}	1035^{c}	14.1^{a}	8.29^{c}	0.19^{c}	2.82^{d}
Total	0.006^{x}	0.61^{y}	7.90^{y}	1.15^{y}	1295^{y}	16.2^{y}	12.6^{y}	0.25^{y}	2.06^{y}
SA									
Oct.2003	0.007^{a}	0.40^{ab}	7.22^{a}	1.17^{a}	1225^{a}	13.2^{a}	11.8^{a}	0.27^{ab}	2.36^{ab}
Jan.2004	0.009^{a}	0.59^{b}	7.77^{a}	1.41^{b}	1362^{b}	15.8^{b}	12.9^{b}	0.30^{b}	2.68^{b}
Apr.2004	0.009^{a}	0.48^{ab}	7.35^{a}	1.36^{b}	1377^{b}	13.6^{a}	12.7^{b}	0.18^{c}	2.56^{ab}
July.2004	0.014^{b}	0.28^{a}	5.22^{b}	1.11^{a}	1177^{a}	13.2^{a}	7.39^{c}	0.20^{ac}	1.91^{a}
Total	0.010^{y}	0.44^{z}	6.89^{z}	1.26^{z}	1285^{y}	13.0^{z}	11.2^{z}	0.24^{y}	2.38^{z}
SAM									
Oct.2003	0.005^{a}	0.47^{a}	6.94^{a}	1.49^{a}	1219^{a}	13.9^{a}	9.41^{a}	0.18^{ab}	2.95^{a}
Jan.2004	$<0.01^{b}$	0.62^{a}	7.96^{b}	0.78^{b}	1221^{a}	14.3^{a}	16.1^{b}	0.16^{ab}	1.08^{b}
Apr.2004	0.003^{c}	0.94^{b}	6.83^{a}	1.17^{c}	1399^{a}	16.5^{b}	14.5^{c}	0.24^{b}	1.98^{c}
July.2004	0.001^{b}	0.55^{a}	8.96^{c}	0.65^{d}	1376^{b}	15.8^{b}	12.1^{d}	0.13^{a}	0.97^{b}
Total	0.002^{z}	0.64^{y}	7.67^{y}	1.02^{w}	1304^{y}	15.1^{w}	13.0^{w}	0.18^{z}	1.74^{x}

[*] Vertically, letters a, b, c and d show differences among different months at same stations; x, y, z and w between stations. Within columns, means with the same letter are not statistically significant, $p>0.05$

In January, Co, Cr, Mn and Pb levels in station GA, Cd, Cu, Fe and Zn levels in SA, and Ni level in station SAM were higher than those in other stations. In April, Cu, Mn and Pb levels in station GA, Cd, Cr and Zn levels in station SA, and Co, Fe and Ni levels in station SAM were higher than those in other stations. In July, Cu and Zn levels in station GA, Cd and Pb levels in station SA, and Co, Cr, Fe, Mn and Ni levels in station SAM were higher than those in other stations. The differences between the metal concentrations in different stations were generally significant ($p<0.05$). In addition, there are differences between the metal levels in different months from the same stations ($p<0.05$). The concentrations of metals in the sediment of River Asi were compared with other studies, probable effect concentrations (PECs) and background concentrations in Table 5. When compared with PECs and background concentrations, our results were generally lower than them (20-21). When other studies are considered, the mean metal concentrations in River Asi were generally lower than those in the Lake Texoma, Gomti river, Büyük Menderes river, Gediz river and Hazar lake (15-16, 22-23). As can be seen, to the contrary of the water, concentrations in sediment were generally lower than other studies, probable effect concentrations (PECs) and background concentrations.

Metals in Fish

In fish samples, iron showed the highest levels in examined tissues of *C. gariepinus* in all months, and following Fe; Zn showed second highest levels except Mn levels in muscles, livers and gills in January (Table 6). In general, the metal concentrations in liver were higher than those in other tissues except Cr and Mn levels in gill, and Zn levels in skin. In January, Co, Cu, Fe, Mn and Pb levels in liver, Cr and Ni levels in gill, Cd levels in muscle, and Zn levels in skin were higher than those in other tissues. In April, Co, Cu, Fe, Ni and Pb levels in liver, Cd, Cr, Mn and Zn levels in gill were higher than those in other tissues. In July, Cd, Cu, Fe, Ni, Pb and Zn levels in liver, Co, Cr and Mn levels in gill were higher than those in other tissues. The differences between the metal concentrations in different tissues were generally significant ($p<0.05$). In addition, there are differences between the metal levels in different months from the same stations ($p<0.05$). Table 7 compares the concentrations of metals in the muscle of African catfish, *Clarias gariepinus*, from River Asi with other studies, Turkish permissible concentrations (TPCs) and Tolerable concentrations in fish. As can be seen, when compared with TPCs and Tolerable concentrations in fish, concentrations of Cd, Cr, Cu, Pb and Ni in *C. gariepinus* were lower than them (13, 24). On the other hand, if compared other studies, concentrations found in *C. gariepinus* were lower than those found in fishes in Lake Nasser (except Mn), Lake Kasumigaura, Pearl River estuary, seven different lakes in Tokat and İskenderun bay (3, 6, 11, 25-26). Similarly to the concentrations in sediment, the measured concentrations in muscles of *C. gariepinus* were lower than other studies, Turkish permissible concentrations (TPCs) and tolerable concentrations in fish.

CONCLUSION

Present study provides primary information on the distribution of metal concentrations in water, sediment and fish tissues from the River Asi. Although concentrations of the metals such as Cu, Fe and Zn in water were generally higher than background and legal concentrations, those in sediment and fish were generally lower than them. This situation can indicate that concentrations in sediment and fish are not generally effected from concentrations in water. *Clarias gariepinus*, not a pelagic fish, is omnivore and feeds on benthic organisms. Thus it is expected that the metal concentrations in *C. gariepinus* can reflect the ones in sediment. Based on the samples analyzed, metal concentrations found in the edible parts of fish are not heavily burdened with metals, and the concentrations are below the legal values for fish and fishery products proposed by Nauen (24), TKB (13) and other studies.

Table 5. Comparison of the overall metal concentrations in the sediment of River Asi with other studies and guidelines (µg g^{-1} dry wt).

Studies and guidelines	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
This study[a]	0.006	0.49	6.54	1.03	1198	14.2	10.9	0.19	1.97
An & Kampbell (15)[b]	2.0	9.0	30	38	19393	377	17	10	89
Singh et al. (16)[c]	2.42	-	8.15	5.0	2661	143.1	15.17	40.33	41.67
Akcay et all. (22)[d]	-	29	165	137	18500	388	315	54	120
Akcay et all. (22)[e]	-	38	200	140	25500	510	106	128	160
Özmen et al. (23)[f]	-	24-33	17-79	10-64	3650-30000	85-625	38-130	-	46-210
MacDonald et all. (20)[g]	4.98	-	111	149	-	-	48.6	128	459
Bervoets & Blust (21)[h]	0.38	-	17	8.0	-	-	11	14	67

[a] Means, the number of analyzed samples= 80.

[b] Texoma, border of Oklahoma and Texas.

[c] Gomti River, India.

[d] Büyük Menderes River, Turkey.

[e] Gediz River, Turkey.

[f] Hazar Lake, Turkey

[g] PEC: Probable Effect Concentrations.

[h] Background Concentrations.

There is also legislation in other countries regulating the maximum concentration of metals. For example, Spanish legislation establishes maximum levels for Cd at 1 μg g^{-1}, Cu at 20 μg g^{-1} and Pb at 2 μg g^{-1} (27). According to the UK Food Standards Committee report, Cd, Pb, Cu and Zn levels in food should not exceed 0.2, 2, 20, 50 μg g^{-1} respectively (28). These limits were not exceeded in the muscles of *C. gariepinus* from River Asi. We can, therefore, conclude that this metal presents no problem for the consumption of edible parts of this fish at this time. However, in the future, bioaccumulation of analyzed metals in this study can be a possible risk for the consumption of this species.

Table 6. The seasonal variations of the mean metal concentrations in different tissues of the African catfish, *C.gariepinus* from the River Asi (ten fish samples for each month).

Months/ tissues	Metal concentrations, in μg g^{-1} wet wt*								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Muscle									
Jan.2004	0.003^{a}	0.002^{a}	0.01^{a}	0.28^{a}	1.82^{a}	0.49^{a}	0.003^{a}	0.004^{a}	0.38^{a}
Apr.2004	$<0.001^{a}$	0.001^{a}	0.008^{a}	0.10^{b}	0.34^{b}	0.01^{b}	0.009^{b}	0.004^{a}	0.22^{b}
July.2004	$<0.001^{a}$	0.004^{b}	0.015^{a}	0.09^{b}	1.63^{a}	0.01^{b}	0.01^{b}	0.008^{a}	0.21^{b}
Total	$0. 001^{x}$	0.002^{x}	0.011^{x}	0.16^{x}	1.26^{x}	0.17^{x}	0.008^{x}	0.006^{x}	0.27^{x}
Liver									
Jan.2004	$<0.001^{a}$	0.004^{a}	0.014^{a}	1.45^{a}	15.7^{a}	1.06^{a}	0.002^{a}	0.011^{ab}	0.95^{a}
Apr.2004	0.001^{a}	0.004^{a}	0.027^{b}	0.24^{b}	17.2^{a}	0.07^{b}	0.04^{b}	0.004^{a}	0.74^{a}
July.2004	0.006^{a}	0.013^{b}	0.028^{b}	0.25^{b}	18.9^{a}	0.05^{b}	0.03^{b}	0.014^{b}	0.88^{a}
Total	0.003^{x}	0.007^{y}	0.023^{xy}	0.64^{y}	17.3^{y}	0.39^{y}	0.03^{y}	0.010^{x}	0.86^{y}
Gill									
Jan.2004	0.002^{a}	0.002^{a}	0.024^{a}	0.42^{a}	3.05^{ab}	1.03^{a}	0.01^{a}	0.01^{a}	0.85^{a}
Apr.2004	0.002^{a}	$<0.001^{a}$	0.028^{a}	0.16^{b}	2.14^{a}	0.19^{b}	0.02^{b}	$<0.001^{b}$	0.84^{a}
July.2004	0.002^{a}	0.013^{b}	0.078^{b}	0.11^{b}	4.99^{b}	0.16^{b}	0.03^{b}	0.01^{a}	0.69^{a}
Total	0.002^{x}	0.005^{z}	0.043^{y}	0.23^{x}	3.39^{x}	0.46^{y}	0.02^{z}	0.005^{x}	0.79^{y}
Skin									
Jan.2004	$<0.001^{a}$	0.002^{a}	0.006^{a}	0.15^{a}	1.23^{a}	0.38^{a}	0.003^{a}	0.004^{a}	1.28^{a}
Apr.2004	0.001^{a}	0.001^{a}	0.026^{a}	0.13^{a}	0.87^{a}	0.01^{b}	0.01^{b}	$<0.001^{b}$	0.79^{b}
July.2004	0.001^{a}	0.008^{b}	0.011^{a}	0.14^{a}	2.36^{a}	0.02^{b}	0.02^{b}	0.007^{c}	0.56^{b}
Total	0.001^{x}	0.004^{x}	0.014^{x}	0.14^{x}	1.49^{x}	0.14^{x}	0.01^{x}	0.004^{x}	0.87^{y}

[*] Vertically, letters a, b and c show differences among different months at same stations; x, y and z between different tissues. Within columns, means with the same letter are not statistically significant, p>0.05

Table 7. Comparison of the overall metal concentrations in the muscle of *C.gariepinus* from River Asi with other studies and guidelines (µg g^{-1} wet wt).

Studies and guidelines	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
This study[a]	<0.01	<0.01	0.01	0.16	1.26	0.17	0.01	0.01	0.27
Alam et all. (11)[b]	<0.01	<0.01	0.07	0.25	2.73	0.31	0.04	0.03	5.43
Rashed (3)[c]	-	0.06	0.08	0.26	2.18	0.03	0.06	-	0.63
Ip et all. (25)[d]	0.041	0.10	0.67	1.81	-	-	0.65	2.20	18.4
Mendil et all. (26)[e]	0.1-1.2	-	0.6-1.6	1.1-4.1	64.3-197	11.1-72.9	1.2-3.4	0.7-2.4	11.9-37.1
Türkmen et all. (6)[f]	0.95	1.42	1.69	1.57	10.2	1.71	2.90	2.32	4.36
Türkmen & Ciminli (9)[g]	<0.01	<0.01	0.01-0.02	0.08-0.11	1.49-3.68	0.07-0.45	0.01	0.01	0.29-0.46
TKB (13)[h]	0.1	-	-	20	-	-	-	1.0	50
Nauen (24)[i]	0.05-5.5	-	1.0	10-100	-	-	-	0.5-6.0	30-100

[a] Means, the number of analyzed samples= 30.

[b] Lake Kasumigaura, Japan (wild carp).

[c] Lake Nasser, Egypt (*Tilapia nilotica*), (µg g^{-1} dry wt).

[d] Pearl River Estuary, South China.

[e] Seven different lakes in Tokat, Turkey (seven fish species).

[f] İskenderun Bay, Mediterranean Sea (three fish species).

[g] Lake Gölbaşı, Mediterranean region of Turkey (two fish species)

[h] Turkish Permissible Concentrations.

[i] The ranges of maximum permissible concentrations for different countries.

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GEOSYNTHETIC MATERIALS USED IN WASTE CONTAINMENT SYSTEMS

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Geosynthetics have gained widespread popularity all around the world. They are used in many civil engineering applications. They have functions such as reinforcement, drainage, filtration, separation and protection. As geosynthetics used in various civil engineering applications, the most important application area is the waste containment systems. Geomembrane liners, geosynthetic clay liners and geocomposites are used at most. Their properties and their application areas are mentioned in this paper in detail. Their cost analysis is given at the end of the paper.

INTRODUCTION

Geosynthetics are synthetic polymer materials that are specifically manufactured to be used in geotechnical and geoenvironmental applications.

Geosynthetic materials such as geomembranes, geotextiles, geonets have been used in waste containment systems in civil engineering applications. There are many liner systems in waste containment systems. The most important ones are geomembrane liners, geosynthetic clay liners (GCL), and geocomposites.

GEOMEMBRANE LINERS

Geomembrane liners are made up of high density polyethylene. It is used for satisfying the maximum security of the solid waste contaminant. Some of the geomembranes are textured and some of them are smooth. A smooth geomembrane liner is used in collection ponds, because they are not covered with soil or other liners. Collection ponds also do not have steep side slopes which results in minimal slipping if additional liners are placed. A textured geomembrane is used for mining and solid waste landfills. This creates a surface for additional layers such as geocomposite or soil to adhere to and releases pressure from the seams of the liner. The primary use of the geomembrane liner is to contain the contaminants of solid waste.

Geomembrane liner is used in waste water treatment, tank linings, sewage lagoons, reservoirs, ponds, canals, lakes and landfill linings.

Landfill linings are made up of placing a liner within the landfill. Clay, bentonite, asphalt and plastic are used. Impermeable plastic membranes have been used successfully for years in preventing the seepage of water and various waste liquids. They have long service life and resistant to leachate. Tank liners are used to hold water, liquids, waste water, and sludge. PVC linings are used to contain water in transport canals.

They have many advantages such as easy to weld and deploy in the field, have long service life as a containment membrane, and very cost effective material rather than resin, sheet, fabricated panels. The soil and groundwater beneath the ponds are protected in sewage lagoons with the usage of the polypropylene because it has a long service life and physical properties. Polypropylene provides the following advantages:

- 20 year service life as a membrane
- Excellent tensile/tear strength properties provide strength required in steep ponds of 3:1 slope angle or steeper
- Easy to field seam and repair
- No specialized equipment necessary
- Not subject to environmental stress cracking
- Excellent chemical resistance

GEOSYNTHETIC CLAY LINERS (GCL)

Geosynthetic clay liners(GCL) are manufactured hydraulic barriers consisting of clay bonded to a layer or layers of geosynthetics. They consist of:

- A carrier layer, which is comprised of a woven, slit film geotextile, incorporated into a non-woven, needle punched, polypropylene or high density polyethylene geotextile, forming a woven/non-woven, composite,
- A natural sodium rich bentonite layer and,
- A cover layer, comprised of non-woven, needle punched synthetic fibers.

They are made up of a compacted layer of bentonite clay which is placed over the geocomposite to complete the lining system. GCL can be used as a protective cap to cover the landfill. They consist of clay material, usually bentonite, woven between two geotextile layers. This lining mechanism uses the properties of bentonite and the material to which it is bonded holds the clay in place. Different types of GCLs and their conditions are shown in Figure 1 and 2 below.

(a) Adhesive bound bentonite to upper and lower GTX

(b) Stitch bonded bentonite between upper and lower GTX

(c) Needle punched bentonite through upper and lower GTX

(d) Adhesive bound bentonite to a geomembrane

Figure 1. Different type of GCls.

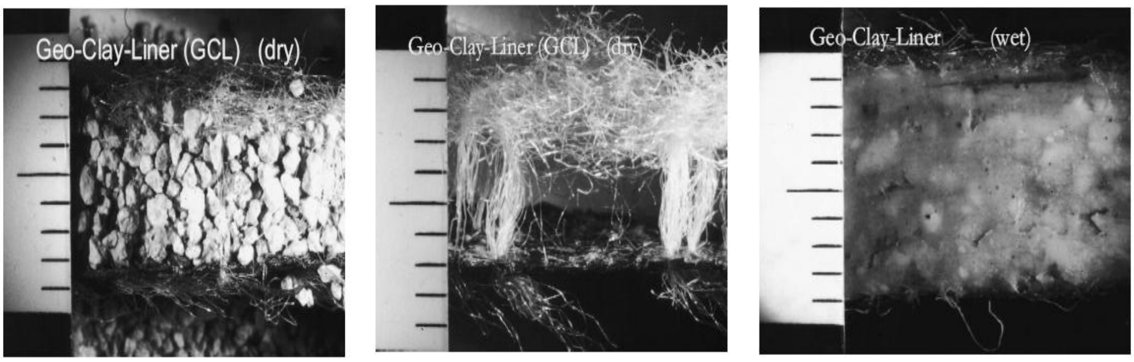

Figure 2. GCLs in different conditions.

GCL is used in waste containment cover systems, because of these features:
- Consistent hydraulic and engineering properties
- Relatively high manufacturer quality control
- Thin – maximizes landfill volume
- Variety of material choices to satisfy site-specific requirements
- Available at every project
- Simplified installation and construction quality control
- Some self-healing capabilities
- Simplified repair
- Simplified installation of penetrations in covers
- Cost competitive with CCLs and GMs

GCLs provide an engineered alternative to a compacted clay liner (CCL). GCLs provide excellent sealing properties and unique self sealing attributes, reducing risk of failure due to adverse field and operating conditions. The significant reduction in thickness of a GCL versus a CCL, provides a great deal of additional capacity for the containment facility to be lined.

Compacted clay in covers have these characteristics:
- Concerns that CCL will not retain hydraulic properties over time
- Desiccation from above and/or below
- Cracking during differential settling, freezing
- Difficult to place and compact

When GCL and CCL are compared with each other, the following propeties are gained:
- GCLs are often offered as a replacement or partial substitution for CCLs
- GCLs, like any other engineering material, have unique properties
- GCLs are not identical to CCLs, but may perform similarly
- GCLs show far less damage than CCL.

GCLs are high performance environmental liners comprised of a layer of low-permeability sodium bentonite combined with geosynthetic carriers such as woven and/or nonwoven geotextiles and in some cases polymer geomembranes. GCLs have been proven to provide better engineered performance and durability than several feet of compacted clay with a total composite thickness of less than one quarter of an inch.

Applications

Composite Lining Systems: For waste and liquids containment, the most effective liners are comprised of geomembrane/low permeability soil composites. The primary benefit of geomembrane/clay composite is derived from intimate contact of two layers.

Waterproof Layers: Adjacent to basement walls and other structures, GCLs provide a positive barrier to water which can accumulate behind the wall, allowing removal of the water through a properly designed drain behind the wall.

Spill Containment Systems: GCLs provide an effective temporary barrier for spills from aboveground tank storage of petroleum products or other potential contaminants allowing total and rapid recovery of spilled materials.

Single-component Lining Systems: GCLs can be utilized as stand alone liners for ponds containing potable or storm water (not subject to toxic containment constraints), artificial lakes, landfill cap systems, mine tailing compounds, earth dams and canal lining systems.

Geomembrane Cushion/Protective Layers: GCLs can be used as a cushion/protective layer above geomembranes, providing superior protection to thick, non-woven geotextile cushions, particularly in cases where coarse drainage, and granular drainage layers overlie the liners.

Installation of GCLs

GCLs require soil cover of at least 300mm to provide sufficient normal force to confine the expansion of the bentonite core layer. The bentonite swells and extrudes through the geotextile fabric at the overlap, forming a seal by producing a dense and uniform clay barrier with the same hydraulic qualities in all parts of the clay liner (Curtis, 1998).

Figure 3. Installing the GCL.

Figure 4. Burying the GCL.

GEOCOMPOSITE

Geocomposite is a combination of two types of liners. The first and main component is a geonet. Geonet is a high density polyethylene. It is placed either above or below the geomembrane liner. It is used as a collection system for the leachate produced by the solid waste. The second component which makes up the geocomposite liner is a nonwoven geotextile. Geotextile is bonded to the geonet either on one side or both. The purpose of the geotextile is to prevent soil from clogging the geonet. This satisfies proper collection of the contaminant. When the geotextile layed over a textured geomembrane, it prevents the geocomposite liner from slippping on the steep slopes of the landfill. The geocomposite leads to the final step of the lining system.

Applications

- Landfill leachate collection
- Landfill leak detection
- Landfill caps / closures
- Landfill methane gas collection
- Pond leak detection
- Foundation wall drainage
- Athletic field and landscape drainage
- Erosion control

SIMPLIFIED COMPARISON OF BARRIERS

Different types of barriers are compared in the table below.

Table 1. Comparison of barriers

Configuration	Est. Installed Cost ($/m2)	Benefit/Cost Ratio*	Rank in Group
CCL	5-22	49	3
GM	8	90	1
GCL	5-11	66	2
GM/CCL	13-30	41	2
GM/GCL	13-19	47	1
GM/CCL/GM	21-38	34	2
GM/GCL/GM	18-41	37	1

**Adapted from Daniel, 1993*

The costs are presented in table below. The total cost of lining the channel was $11.91/m^2 (2002) .

Table 2. Breakdown of costs for buried HDPE

Item	Cost ($)	Cost ($/m^2)[1]
Site preparation (excavator, grader, etc.)	$10,125	$2.03
Materials (inc. delivery)	$33,447	$6.69
Installation (contractor joining)	$ 7,228	$1.45
Backfilling (excavator, etc.)	$ 3,680	$0.74
WMW staff wages, on-costs, etc.	$ 3,148	$0.63
Fencing	$ 1,905	$9.52/m
	$59,532	$11.91

TOTAL

1. Cost per square metre based on 5,000m^2 of material supplied.
2. Cost per metre of fencing based on 200m section of channel.

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RADIONUCLIDE EMISSION FROM THE SEYİTÖMER COAL-FIRED POWER PLANT AND THE POPULATION EXPOSURE TO EXTERNAL RADIATION IN ITS VICINITY

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The combustion of coal in a thermal power plant results in release to environment of naturally occurring radionuclides. The reason for the research on this subject takes its importance due to the radiological impact of the plants on the surrounding and population living in the vicinity.

In this study, samples of lignite, fly and bottom ash of Seyitömer coal-fired power plant were taken approximately along a period of 1 year and 19 surface soil samples were collected from the vicinity of coal-fired power plant during the same periods. The natural terrestrial gamma radiation dose rates (1 m above ground level) were calculated for the region of Seyitömer-Kütahya, and found to be 42 nGy h^{-1}.

Keywords: *Coal, soil, natural radionuclide, dose rate.*

1. Introduction

Technologically enhanced natural radiation in the vicinity of large industrial plants resulting in an additional exposure of the local population has been a continuous subject of concern. Particularly, combustion of fossil fuel containing naturally occurring radionuclides from the uranium and thorium series as well as ^{40}K may have an impact on environmental radioactivity level in the vicinity of power plants. Fly ashes escaping from stacks contain these radionuclides concentrated a few times in comparison with their content in coal or surface soil. Therefore, apart from inhalation, the main additional radiation hazard can be fallout as dust resulting in elevated concentrations of natural radionuclides in surface soils around power plants.

Lignite is a vital source in the production of electric energy for Turkey since it has rich lignite reserves. Turkish lignite reserves are estimates to be over 8 billion tons, ranking Turkey seventh largest in the world. Almost one-forth (23 %) of Turkey's total electric production (149 882 GW h) was obtained from lignite in 2004 (Say, 2006). In Figure 1, the location of the existing coal fired power plants and lignite fired power plants planned for establishment by the Ministry of the Energy and the Natural Resources in Turkey are depicted and available plants, indicated on the map, have been numbered based on their first running dates. As seen in this Figure, while only Çatalağzı (Zonguldak) and Sugözü (Adana) power plants are hard coal fired among the existing power plants, the others utilize domestic lignite (Gür, 2006).

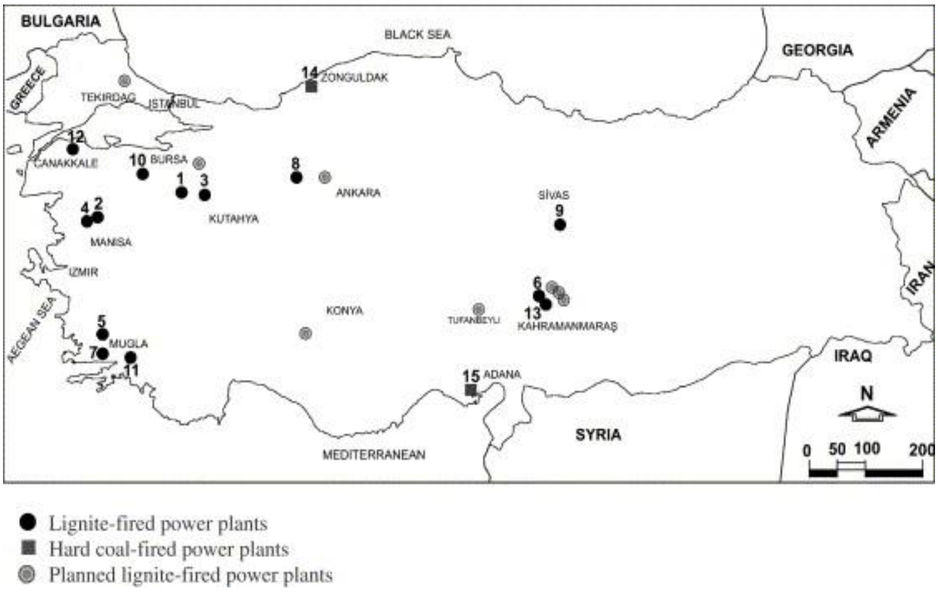

Fig.1. Location of the Turkish coal-fired power plants (Say, 2006).

In this study, the radiological impact from the airborne routine discharges of a modern coal-fired power plant at Seyitömer, Kütahya (Turkey) is evaluated. As a first step, the natural radioactivity of the coal and the fly-ash has been measured. Second step, nineteen soil samples from the vicinity of Seyitömer coal-fired power plant were collected and natural radioactivity concentrations were analyzed. Finally, natural gamma dose rate 1 m above ground level were calculated.

2. Methods

2.1 Description of the coal-fired power plant

At the northwest of Turkey, there are four power plants from west to east Çan (ÇaCPP), Orhaneli (OrCPP), Tunçbilek (TuCPP) and Seyitömer (SeCPP), respectively (Fig.2). The lignite-fired power plant of Seyitömer is located near the city of Kütahya (Fig. 2). The Seyitömer coal basin is one of the most rich lignite basins in northwest Anatolia, Turkey. Mining activities started in 1935 and total reserves were estimated during exploration at 203 million tones lignite. SeCPP burns about 6.5 million tones of lignite yearly and produces electrical energy of about 4x150 MW at full load, with a total capacity of 600 MW. The fuel for the Seyitömer lignite-fired power plant (SeCPP) is supplied from lignite beds which also lie in this region. The lignite available in this region has very low calorific value, high moisture and ash contents. The basic characteristics of the SeCCP are presented in Table 1, and Figure 3 shows its photograph.

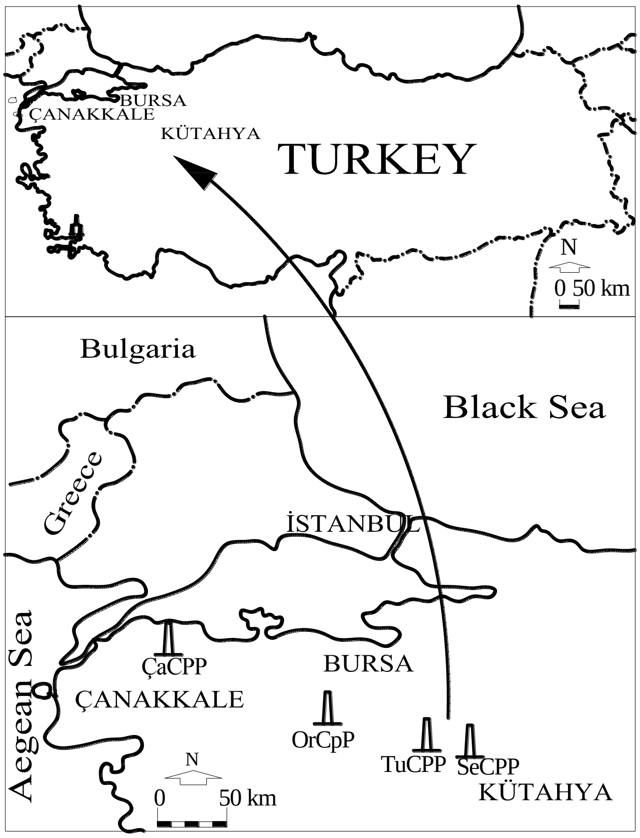

Fig.2. The map of the northwest Turkey indicating the location of coal-fired power plants.

Table 1. Basic Characteristics of SeCPP-TURKEY*

Basic Characteristics	**Seyitömer Power Plant**	**Coal-Fired**
Number of Units	#1-2-3	#4
Working capacity (MWe)	150	150
First running	1973-1974-1977	1989
Caloric value of coal (kcal kg^{-1})	1819	1692
Total coal consumption (ton h^{-1})	188	190
Ash (%)	32.2	35.0
Moisture (%)	32.7	31.7
Airborne matter (%)	29.9	29.7
Efficiency of electro filters (%)	98	98
Chimney height (m) (four chimney)	100	100

*The data in this table were taken from the SeCPP chemistry laboratory.

Fig. 3. Seyitömer Lignite-Fired Power Plant

2.2 Sampling and Analytical Procedures

Samples of coal, bottom ash and corresponding captured fly ashes were supplied from each unit on a monthly basis during 2003-2004. Surface soil samples (~ 20 cm in depth) were also collected in a grid pattern (interspaces ~ 3 km) within 6 km around SeCPP. Totally 19 soil samples were collected around coal-fired power plant allowed for the mapping of the surface soil activity of natural radionuclides.

All samples (coal, ashes and soils) were dried in oven to obtain constant weight, well homogenized and sealed in Marinelli beakers (1L capacity) to achieve radioactive equilibrium between radium and radon. The samples were analyzed for ^{226}Ra, ^{232}Th and ^{40}K by employing a gamma spectrometry which consists of a p-type 184 cm^3 HPGe coaxial detector with a 25 % relative efficiency, an 1.87 keV resolution and a peak to Compton ratio of 57:1, all referred to ^{60}Co line of 1.33 MeV. The detector was coupled with a PC based 8K multi-channel analyzer with associated software and surrounded by 10 cm- thick lead well internally lined with a 1.5 mm copper foil in order to reduce the back scattering photon reacting the detector.

The ^{226}Ra concentration was determined from gamma lines of 295 keV, 352 keV, 609 keV, and 1765 keV, originating from ^{214}Pb and ^{214}Bi as the mean value of the results of these gamma lines. The concentration of ^{232}Th was determined from gamma lines of 583 keV, 911 keV and 2614 keV from ^{208}Tl and ^{228}Ac, respectively. The ^{40}K concentration was calculated from its 1460.8 keV gamma line. The detector was calibrated with standard reference sources (^{152}Eu (Amersham)) for its energy response and the efficiency calibration was performed using the standards gamma sources, U_3O_8 pitch-blend (IAEA S-7) and thorium (IAEA S-16), made up to same geometry as the samples by mixing a standard calibration source of known strength with silica and starch.

3. Results and discussion

3.1 Radiological Characteristics of Seyitömer Coal-Fired Power Plant

The natural radionuclides (^{226}Ra, ^{232}Th and ^{40}K) levels measured in samples of coal, fly ash and bottom slag from the SeCPP are presented in Table 2. All results are represented in Bq kg^{-1} to compare them with data from other studies. Minimum detectable activity (MDA) values for ^{226}Ra, ^{232}Th and ^{40}K are 2 Bq kg^{-1}, 1 Bq kg^{-1} and 5 Bq kg^{-1} for our counting geometry and 10 000 sec. counting time, respectively.

As seen from Table 2, the natural radionuclide activity concentrations in fly ash are significantly higher than the corresponding activity concentrations in the coal. The activity concentrations of radionuclides in lignites burned showed that the average ^{226}Ra activity concentration varied between 39-48 Bq kg^{-1} in lignites, 107-115 Bq kg^{-1} in fly ash and 78-97 Bq kg^{-1} in bottom slag.

Table 2. Specific Activity Levels in Coal and Ash Samples From SeCPP

CPP	**Radionuclides**	**Natural Radioactivity Concentrations (Range) (Bq kg^{-1})**		
		Coal	**Fly Ash**	**Bottom Slag**
1.unit*	-	-	-	-
2.unit	^{226}Ra	39 ± 2 (36-42)	107 ± 4 (94-118)	78 ± 3 (73-82)
	^{232}Th	30 ± 2 (28-33)	69 ± 2 (62-74)	54 ± 2 (52-58)
	^{40}K	222 ± 6 (207-242)	488 ± 9 (450-516)	344 ± 8 (328-358)
3.unit	^{226}Ra	48 ± 2 (35-73)	115 ± 4 (99-127)	81 ± 3 (73-90)
	^{232}Th	35 ± 2 (30-43)	74 ± 2 (65-80)	56 ± 2 (48-61)
	^{40}K	261 ± 6 (200-345)	566 ± 9 (482-686)	346 ± 7 (300-398)
4.unit	^{226}Ra	43 ± 2 (40-51)	112 ± 4 (103-120)	97 ± 3 (80-111)
	^{232}Th	35 ± 2 (34-38)	70 ± 2 (64-82)	62 ± 2 (56-70)
	^{40}K	259 ± 6 (232-318)	524 ± 9 (463-571)	395 ± 7 (371-444)

* First unit was turn off.

The average of natural radioactivity concentrations obtained in this study from lignite and ashes is compared with data available on different studies at TURKEY (Table 3).

Table 3. The Average Natural Radioactivity Concentrations of Coal and Fly Ash of Different Studies at TURKEY and UNSCEAR Reports

CPP	**Material**	**Average Natural Radioactivity Concentrations (Bq kg^{-1})**			**Reference**
		^{226}Ra	**^{232}Th**	**^{40}K**	
Seyitömer	Coal	44 ± 3	34 ± 1	252 ± 9	This study
	Coal	24 ± 3	25 ± 2	174 ± 12	Eren, 2005
	Coal	11 ± 3	43 ± 14	191 ± 11	Öztürk and Özdoğan, 2004
	Coal	35 (17-60)	30 (11-64)	400 (140-850)	UNSCEAR, 2000
Seyitömer	Fly ash	112 ± 1	71 ± 1	534 ± 8	This study
	Fly ash	150 ± 8	76 ± 4	364 ± 14	Toktay and Erdoğdu, 1998
	Fly ash	240	70	265	UNSCEAR, 1982

As seen from the Table 3, results obtained from coal in the current study are in good agreement with UNSCEAR 2000 report, however, considerable high comparing to those reported by Eren (2005) and Öztürk and Özdoğan (2004) at the same region. Furthermore, activity concentrations of fly ash are similar to Toktay and Erdoğdu (1998) and UNSCEAR (1982) results.

3.2 Terrestrial Gamma Dose Rate Around Coal-Fired Power Plant

Activity concentrations of surface soil samples are given in Table 4. These results are too low compare to the UNSCEAR (2000) report values.

Table 4. Natural Radionuclide Activity Concentrations in Vicinity Soils of the SeCPP

Location	**Radionuclide Activity Concentrations (Range) (Bq kg^{-1})**		
	^{226}Ra	**^{232}Th**	**^{40}K**
SeCPP	29 ± 4 (4-65)	26 ± 3 (3-44)	298 ± 20 (142-463)
UNSCEAR (2000)	40 (8-160)	35 (4-130)	370 (100-700)

External gamma-ray dose rate of terrestrial origin due to ^{226}Ra, ^{232}Th and ^{40}K calculated from the equation suggested by UNSCEAR (2000):

$$D = 0.0417\, A_{K\text{-}40} + 0.604\, A_{Th\text{-}232} + 0.462\, A_{Ra\text{-}226}$$

where D is the absorbed dose rate in air as nGyh^{-1}, and $A_{K\text{-}40}$, $A_{Th\text{-}232}$ and $A_{Ra\text{-}226}$ are the activity concentrations of ^{40}K, ^{232}Th and ^{226}Ra in soil respectively, in Bq kg^{-1}.

In accordance with the UNSCEAR (2000) data, the average absorbed dose rate in air 1 m above the ground surface due to the ^{226}Ra, ^{232}Th and ^{40}K concentrations in soil is 57 nGy h^{-1}, ranging from between 18-93 nGyh^{-1}. In this study, terrestrial gamma-ray dose rate in around areas of SeCPP ranged from 10 nGyh^{-1} to 72 nGyh^{-1} with an average value of 42 nGyh^{-1}. These values are low compare to those reported in UNSCEAR (2000).

The distribution of terrestrial gamma dose rates around coal-fired power plant and wind rose belonging to study area are shown in Figure 4.

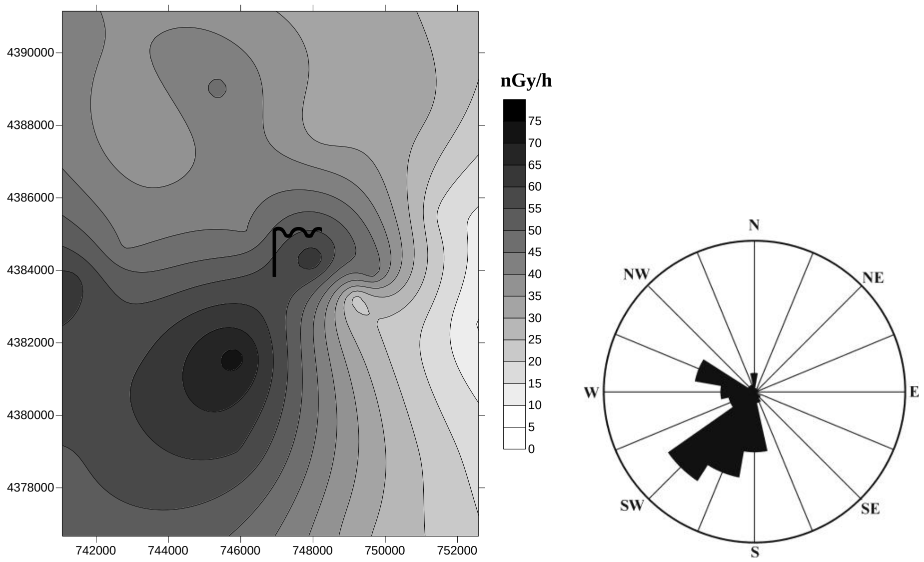

Fig. 4. Distribution of terrestrial gamma dose rates around SeCPP and wind rose.

The highest exposure dose rates were found on the flat area of southwest of SeCPP and around plant (Figure 4).

4. Conclusion

For more than 150 years, coal has been an important source of energy for both developing and industrial societies. Fossil fuels such as coal and lignite play an important role in electric power production worldwide. After coal combustion in a coal-fired power plant, the main problem of technologically enhanced natural radioactivity caused by its' is the increase of the background gamma radiation level. Therefore, the local population is exposed to higher gamma radiation doses than in their absence. Consequently, it is necessary to pay attention to environmental pollution from coal-fired power plants and to regulate ionizing radiation exposure caused by technologically enhanced natural radioactivity.

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BIOMONITORING OF TRACE ELEMENTS OF ZINK AND MANGANESE POLLUTION BY THE BARK OF TURKISH RED PINE *(PINUS BRUTIA)* IN WESTERN ANATOLIA

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Turkish red pine (*Pinus brutia* Ten.) is a widespread evergreen tree in Mediterranean and Aegenan regions of Turkey. The barks of Turkish red pine were tested as a possible biomonitor of trace element pollution studied in Western Anatolia, Turkey. Samples collected from control, industry, roadside, suburban and rural areas from thirty locations in the study area were investigated. The concentration of zink and manganese were determined in the bark of the red pine by atomic absorption spectrometry. As a result of this study, the following concentrations were determined: Zn: 8.4–14.1 μg g^{-1}, and Mn: 19.1–24.0 μg g^{-1}.
Keywords: *Biomonitor; Turkish pine bark; trace element pollution; Western Anatolia*.

Introduction

All compartments of the biosphere are polluted by a variety of inorganic and organic pollutants as a result of anthropogenic activities and alter the normal biogeochemical cycling [1]. Among the pollutants, heavy metals in the environment are of major concern because of their toxicity and threat to human life and the environment [2]. Although heavy metals are natural components of the environment, they are emitted into the environment in different ways, i.e. transportation, industry, fossil fuels, agriculture, and other anthropogenic activities [3]. Heavy metal contamination of the biosphere has increased sharply since 1900 and poses major environmental and human health problems worldwide [1]. Therefore, recently, they have been the object of many studies [4].

Botanical materials such as fungi, lichens, tree bark, tree rings and leaves of higher plants, have been used to detect the deposition, accumulation and distribution of metal pollution. Lower plants, especially mosses, algae and lichens, in view of their higher capacity for metal accumulation, are probably the organism most frequently used for monitoring metal pollution in urban environments [5].

In the related literature there are many studies focusing on using barks of different tree species as biomonitors [6, 7, 8, 9, 10, 11, 12, 13]. For example, Pacheco et al. [14], Pacheco et al. [15] and Pacheco et al. [16] studied with only barks or lichens on olive trees (*Olea europaea* L.), while Santitoro et al. [17] studied on *Quercus ilex* L. and its epiphytic foliose lichen (*Physcia biziana* (Massal.) Zhalbr. v. *leptophylla* Vezda). In some studies only pine species were investigated to decide whether pine species can be used as a biomonitor for the determination of heavy metals. Results of such studies identified that the barks of the pine trees are good adsorbents of airborne pollutants, including anthropogenic heavy metals (18, 19).

Since the barks of the pine trees are good adsorbents of airborne pollutants, the aim of this study is to determine the pollution levels of Zn and Mn by using the bark of *P. brutia* as bioindicator in Western Anatolian part of Turkey.

Materials and Methods

1. *Pinus brutia* Ten. (Turkish Red pine)

The Turkish red pine is a native pine to the eastern Mediterranean region. It is dominantly distributed in Turkey, at lower altitudes from sea level to 600 m, can also be seen upto 1200 m in the southern parts. The species is also extends to the East Aegean Islands and Greece, the Crimea, Georgia, Azerbaijan, northern Iraq, Jordan, western Syria, Lebanon, and Cyprus.

It is a medium–size tree, reaching 20–35 m tall and with a trunk diameter of up to 1 m, exceptionally 2 m. The bark is orange–red, thick and deeply fissured at the base of the trunk, and thin and flaky in the upper crown. The needles are in pairs, slender, mostly 10–16 cm long, bright green to slightly yellowish green. The cones are stout, heavy and hard, 6–11 cm long and 4–5 cm broad at the base when closed, green at first, ripening glossy red–brown when 24 months old. The seeds are 7–8 mm long, with a 15–20 mm wing, and are mainly wind–dispersed [20].

2. Study area

The study area which includes the cities of Izmir, Manisa, Aydin, Denizli, Mugla, Balikesir, Canakkale and Kutahya and their surroundings covers about 100 000 km^2 of land piece. There are many small and medium sized industries, predominantly metallurgical, textile, petroleum refinery, cement and electronic factories, in the study area. The mountains of Akdag, Bozdag, Murat Dagı and Kaz Dagı were selected as control sites, and the samples were collected from the approximate altitude of 1000 m, at a distance of 35–40 km away from the city center with a negligible traffic and pollution load. The urban roadside sampling material was collected about 2 m away from the main road.

2. Bark Sample Collection and Preparation

The barks of *P. brutia* were collected from different sites during July–August 2000. The number of sites from each category sampled was as follows: Industrial: 8, roadside: 6, suburban: 6, rural area: 6 and control: 4. The trees used for sampling were of the same age (approximately 35–40 years old). The barks were carefully removed with a stainless stell pen knife at an average height of about 2 m above the ground. About 200 g of upper part of the bark of *P. brutia* from each direction of the trees were collected.The samples were dried in oven at 80^{o}C for 24 h, milled in a micro–hammer cutter and fed through a 0.2 mm sieve. Bark samples were stored in clean self–sealing plastic bags under silica gel desiccant. Contamination from the micro–hammer cutter was negligible during the grinding because it was washed after every grinding, first with absolute alcohol then with triple distilled water. In this step, the samples were not digested. The digestion was made only before the analysis.

2. Wet Digestion Procedure

The bark digestion method used in this study was described by Perkin Elmer Corporation [21]. The digested samples were aspirated into an air–acetylene flame and the metals were determined by flame atomic absorption spectrometry (FAAS). The reproducibility of the method used in decomposing the bark samples was checked by carrying out a triplicate analysis. All samples were analyzed as soon as possible after preparation.

2. Reagents and Instrumentation

All chemicals used were of analytical reagent grade unless otherwise specified. Triple distilled water was used throughout the experiments. Working metal standard solutions were prepared just before use, by diluting the stock standard solution with water.

Determination of the metals was performed with Perkin Elmer Analyst 700 model flame atomic absorption spectrometer equipped with deuterium background correction, hollow cathode lamps (HCl) and acetylene burner. The absorption measurements of the metals were performed under the conditions recommended by the manufacturer. A Cole–Parmer microfiltration apparatus with membrane filter (0.45 µm pore size manufactured by Micro Filtration Systems, MFS) was used for the filtration of the aqueous phase before metal determination.

Results and Discussion

In this study, the bark samples of *P. brutia* collected from 30 different stations, in industrial, suburban, roadside, rural and control areas throughout Western Anatolian Region, in Turkey were investigated to identify the pollution level of the region by analysing the density of some heavy metals.

As a result of this study it was detected that the mean zinc concentration found in the study area ranges between 8.4 and 14.1 µg g^{-1} (Table 1). The minimum mean zinc value was determined as 8.4 µg g^{-1} in control areas, and the maximum mean value was determined as 14.1 µg g^{-1} in both industrial areas and roadsides. Accumulation of Zn in areas where there are less anthropogenic activities is less than in industrial areas and roadsides. This result leads us to reach a conclusion that in such areas the origin of Zn accumulation is anthropogenic activities.

Heavy metals occur regionally in natural soils. Of particular concern is, however, soil pollution with heavy metals introduced by human activities [22]. For example, zinc occurs naturally in air, water and soil, but as a result of human activities its concentrations are rising unnaturally. Most zinc is added during industrial activities, such as mining, and waste combustion and steel processing in automotive and electrical industries. Moreover, recent developments in hardware industries make their contribution to zinc deployment in the environment. Some soils are heavily contaminated with zinc, and these are to be found in and around industrial areas, or where sewage sludge from industrial areas has been used as fertilizer [23].

The results of this study showed that from the zinc pollution point of view, the least pollution levels were determined in the control and the rural study stations, than suburban, and the most polluted stations were in industrial areas and raodsides. The level of Zn accumulation in the industrial areas and roadsides were close to each other.

According to Bowen [24], land plant intervals for zinc are between 20–400 µg g^{-1}, dry weight. In this study, as a result of investigating the bark samples collected from 30 stations, only a few results taken from some stations in industrial areas and roadsides were in between Bowen's limits. The zinc concentration of the rest of the stations were below these limits. That means that in our study area, there is no considerable zinc pollution.

The results of Manganese trace element investigated in this study revealed that the accumulation of Mn ranges between 3.78 ile 24 (µg g^{-1}, dry weight) (Table 1). Mn accumulation values in five study stations were not considerably different from each other.

Table 1. Mean concentrations (± standard error of mean) of manganese and zinc (µg g^{-1}, dry weight) in the bark of *Pinus brutia* in the study area.

Site	N	Element (µg g^{-1} dry weight)			
		Mn		Zn	
		Mean concentration	SE*	Mean concentration	SE*
Control	4	19.1	5.12	8.4	1.70
Rural	6	22.9	6.42	8.8	2.08
Suburban	6	21.4	6.11	12.9	2.04
Roadside	6	19.9	3.28	14.1	5.09
Industry	8	24.0	5.22	14.1	2.82

* standard error of mean

Like many trace elements, a grey-white, chemically-reactive heavy metal, manganese and manganese compounds exist naturally in the environment as solids in the soil and as small particles in water. Manganese may also be present in small dust-like particles in the air. It is a valuable element for the human beings. For example, it is used in the production of batteries, in dietary supplements, and as ingredients in some ceramics, pesticides, and fertilizers. However, its principal value is derived from its role in steel production.

It is also an essential micronutrient throughout all stages of plant development. It is important for vital plant functions [25], but can be toxic when present in excess in the environment. Humans, as a result of industrial activities and burning fossil fuels, are the source of unnatural manganese in the environment. Among the sources of airborne manganese, iron- and steel-producing plants, power plants, coke ovens, and dust from uncontrolled mining operations can be counted [26].

Bowen [24] stated that acceptable Mn content limits for plants are between 20-700 (µg g^{-1}, dry weight). Evaluation of the results taken from this study showed that our results were close to the Bowen's minimum limit. Therefore, we can reach a conclusion that our study area is not polluted by Mn.

Mulgrew and Williams [27] stated that coniferous trees indicate pollution over a longer time period, and since bark is exposed to air pollutants either directly from the atmosphere or from stemflow, tree bark is appropriate in indicating longer term air pollution. Moreover, depend upon the type of the tree, the deployment of heavy metal content and ways of accumulation show a great variety. For example, in some trees heavy metals are filtered out by the leaves from the air, while in others they are taken up by their crown or by their roots. According to Rademacher [28], Mn or Zn are mainly taken up by the root system and are than transported from there to the crowns, since they are highly mobile elements. Therefore, it is better to investigate its deposition in the crowns.

In conclusion, in this study, heavy metal pollution of the study area from Mn and Zn trace elements point of view were identified by investigating the bark of *P. brutia.* Therefore, we can claim that this study demonstrates that barks of Turkish red pine can be used as a biomonitor for detecting the heavy metal pollution in a specific area**.**

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INDUSTRIAL SOLID WASTE MANAGEMENT IN TURKEY

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Types of waste generated by the industrial activities do not show major differences throughout the world. Considering its rapid growth mode, waste generation rate in Turkish industry is expected to exceed the waste generation rates of the developed countries because of the use of relatively older technologies and lack of regulatory enforcement. Currently, there is no reliable industrial waste inventory in Turkey. The objective of this study is to present an overview of industrial waste management in Turkey.

Introduction

Industrial waste production in Turkey is increasing, as it is in many other countries. The composition of municipal solid waste (MSW) is fairly well known in Turkey today through studies and measures taken by waste management componies, waste management associations and universities. However, no detailed analysis of the amount of industrial waste produced or its composition has been carried out.

Turkey is a rapidly developing country with an increasing standart of living, with a population of over 68 million. Turkey, located in the eastern rim of Europa, is a country with the total area of ca. 779,542 km^2. With the rapid industrialization and economic development, heavy evniromental loadings in Turkey caused some serious enviromental pollution such as illegal dumping of industrial wastes.

From the viewpoint of the preventive and sustainable regulations on industrial waste management in the developed countries Turkey’s goverment began to actively adopt source reduction and recycling/use as a strategy of industrial waste management in the environmental/financial regulation development and implementation promotion phases.

Generation of Industrial Solid Waste

Industrial wastes in Turkey are generated from a variety of industries. Using waste generation factor data, State Statistics Institute estimated that about 17.4 million tons of industrial wastes were generated in 2004. Figure 1 shows the amount of solid waste generated industrial activities from 1994 to 2004.

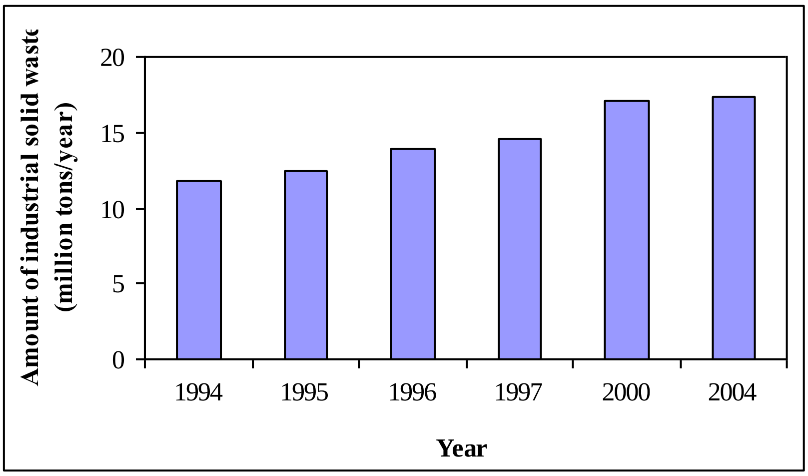

Figure 1. Amount of solid waste generated industrial activities, 1994-2004
(State Statistical Institute, 2005)

According to the estimation of State Statistics Instutite, approximately 1.2 million tons of the industrial waste is hazardous. Based on the data of Table 1, the major sources of industrial waste are the chemistry industry, followed by the textile industry, paper industry and metal products industry, machinery industry, respectively.

Classification of Industrial Solid Wastes

The composition and type of industrial wastes usually depend on the characteristics of each industrial activity (Abduli, 1996). In some cases a subclass specifying the origin of the wastes is also included (Casares et all., 2005):

- Paper and cardboard, including office and packaging materials,
- Glass, including bottles from the eating establishments, packaging and construction wastes, car windshields, manufacturing lamps, mirrors, window panes, and glassworks,
- Textiles, including clothing industry wastes and upholstery ,
- Metals, including packaging and construction materials, automobile mechanics and metal sector transformation processes in metal works,
- Plastics, including packaging and various other wastes,
- Wood, including splinters, sawdust, and other residues from the wood sector activities,
- Inerts, including demolotion wastes, sand, gravel and other wastes,
- Municipal solid wastes from bars, restaurants and food sector industries,
- Used tyres,
- Hazardous wastes, including car oil, printing ink, paint, batteries, varnish, soluble cutting emulsion and disinfectants.

There is no available data for industrial solid waste composition in Turkey. The only available waste inventory data complied by the Turkish State Statistical Institute in 1992 is for manufacturing industry. These values are presented Table 1.

Table 1. Quantity of industrial waste generated in Turkey, 1992 (Zanbak, 1998)

Industry Category	**Quantity (ton/year)**
Food	4,701
Textile	130
Forestry	5,450
Paper	90,169
Chemistry	1,674,894
Sand/Rock	12,292
Metal Products	73,301
Machinery	12,686
Others	100

A case study from Turkey was carries out for Samsun in 2005. Table 2 presents industrial solid waste composition in detail.

Table 2. Industrial solid waste composition in Turkey (Akdemir and Ergun 2005)

Industry Category	**Number of Establishments**	**Waste Quantities**	
		kg/day	**%**
Food wastes	18	1111	11.10
Paper/cardboard	100	118	1.18
Plastics	120	362	3.62
Textiles	84	57	0.57
Leather	89	597	5.96
Rubber	90	91	0.91
Wood	99	3822	38.18
Misc. organics	80	53	0.53
Glass	9	132	1.32
Metals	876	2546	25.43
Dirt, ashes, brick, etc.	166	1060	10.59
Other Inorganics	80	61	0.61

Industrial Waste Treatment/Disposal

According to Turkish State Statistical Institute in 2004 45% of approximately 17.4 million tons of industrial solid waste is sold, of which 8% recovered and reused, and 47% disposed off (Figure 2).

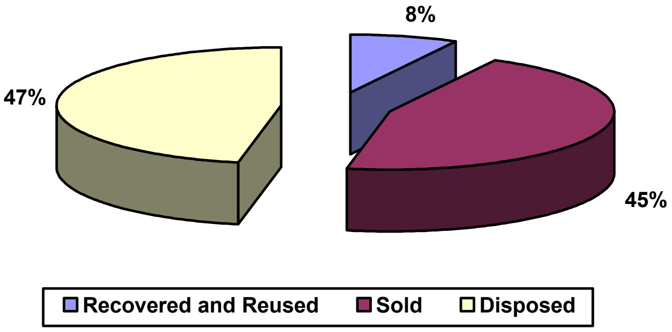

Figure 2. Industrial waste management practices in Turkey (State Statistical Institute, 2005)

Currently, land disposal is reported to be the most common method of industrial waste management. However, it should be noted that at the time of this waste survey, there was no hazardous waste disposal service facility licensed under applicable regulations in Turkey; meaning that landfilling operations were realized at unregulated dumping grounds. However, this should not be misinterpreted as a malicious act of the industry against the environment; rather, as an incorrect and desperate industry practice due to unavailability of waste management facilities, public's lack of environmental awareness and lack of regulatory enforcement.

Basically, industrial waste disposal act, is the legal basis of various regulations, is shown in Figure 3. To achieve the aim of sustainable development, an enterprise shall incorporate the concept of environmental protection into the proceeding activity at the planning stage. Based on the regulatory framework for industrial solid waste management, an enterprise shall also promote cleaner production, prevent and reduce pollution, save resources, recycle reusable resources, and use materials and services that are beneficial mitigation of environmental loading (Tsai and Chou, 2004).

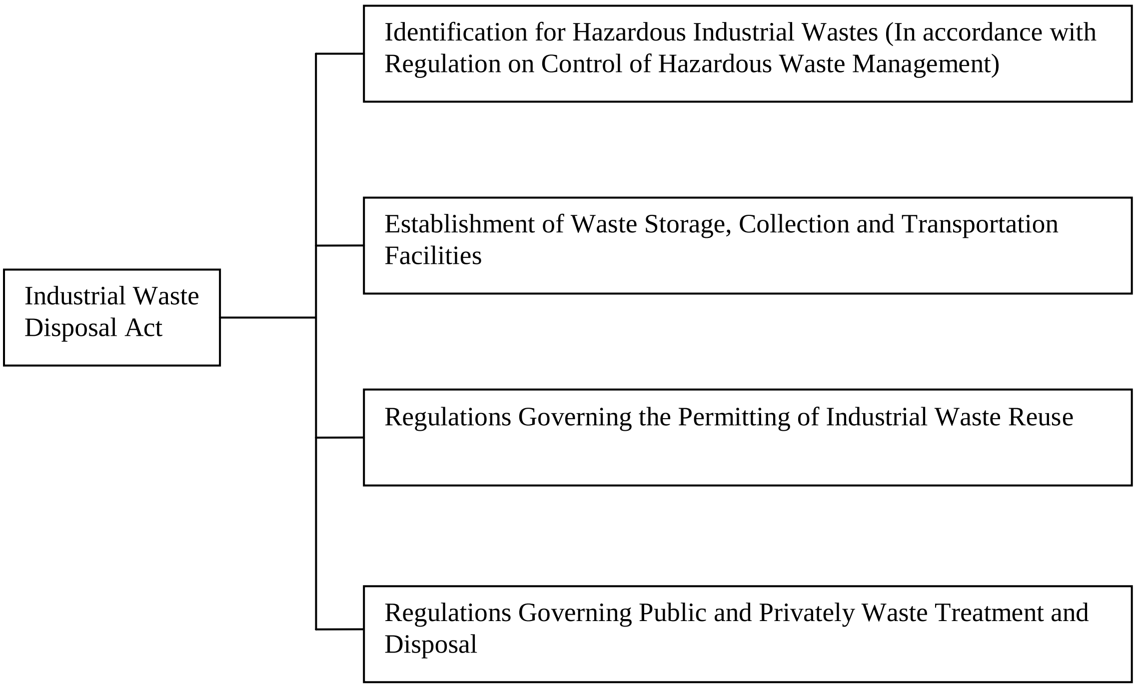

Figure 3. Regulatory framework for industrial waste management in Turkey

Conclusions

According to the principles of source management, this law also requires that the industrial enterprises should adopt some measures to reduce resource consumption, eliminate waste generation and popularize resource reuse/recycling sush as choosing pollution prevention or cleaner production technologies, adopting necessary measures to reduce waste geneation for raw material usage, and recycling used raw materials due to the loss of original effectiveness of these material.

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PROCEEDINGS

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MT-12: Global Warming: How Much of a Threat?

VOLUME 7

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DEVELOPING COUNTRIES AND THE CHALLENGE OF CLIMATE CHANGE

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There is a growing concern that the earth climate is warming up as a result of the human influence and this change could lead to several irreversible grave consequences which would pose serious challenges particularly for the developing countries.

Generally speaking the global warming is expected to give rise in sea level and more moisture in the atmosphere resulting in higher temperatures and higher humidity. Climate change needs to be worked out in greater details and with more understanding at the regional level. The global climate models provide overall trends. It is the regional level models which can describe the impact of climate change on the socio-economic situation in various countries and regions. In Pakistan, we have started a systematic study to develop a measure of competence in the regional climate modeling, watershed modeling and crop simulation modeling. We are looking into how the water picture in the Indus Basin area will emerge in the coming decades with enhanced temperature and altered water situation. The paper will give a resume' of the results achieved so far and the difficulties that are faced in a country like Pakistan to undertake work in the science of climate change and its impact. Measures involving enhanced international cooperation will be proposed for capacity enhancement of developing countries to cope with the adverse impacts of global warming and associated extreme climate events.

1. INTRODUCTION

Carbon dioxide, water vapor and other greenhouse gases provide the warmth to make our planet liveable. Atmospheric carbon dioxide comes from animal and plant respiration and from oxidation of complex organic substances i.e. decay of plants, biological waste etc. It is removed from the atmosphere by photosynthesis in plants and it also dissolves in oceans. A natural carbon dioxide cycle maintained a balance with the amount of carbon dioxide taken out of the atmosphere by plants equalized by amount put back into atmosphere by respiration and decay in the absence of anthropogenic interventions.

It is commonly believed that the anthropogenic enhancement of the greenhouse effect began as a result of the industrial revolution of the eighteenth century. This is not exactly true; human intervention became a factor in climate thousands of years ago through deforestation and agriculture. Human ability to affect climate assumed importance with increase in population and change in lifestyles. The industrial revolution provided the technology to use fossil fuel for energy production and transportation. This brought about socio-economic development and also provided means for military dominance by the industrialized countries. With the increasing use of fossil fuel more and more man-made greenhouse gases were released to the atmosphere. The human foot-print thus began to deepen and disturb the balance of carbon in the atmosphere. The trend in the increase of CO_2 during the last 30 years is shown in Figure 1.

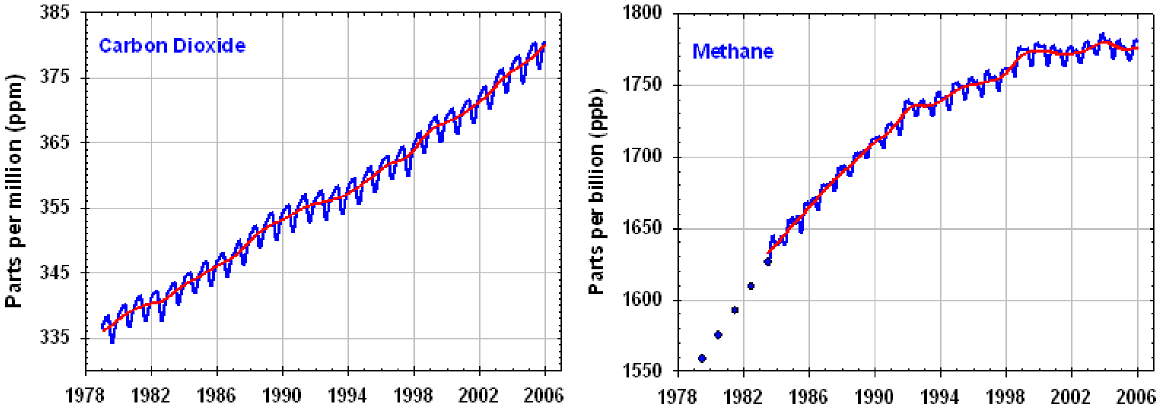

Figure 1: Increasing trend in Green House Gases

Another important greenhouse gas is methane. The significance of methane as a greenhouse gas is that it produces 21 times as much warming as CO_2 and plays a vital role in the enhanced greenhouse effect. The increase in the concentration of the greenhouse gases in the atmosphere (Table 1) is increasing resulting in warmer climate.

Table 1: Pre-industrials and post-industrial trends in GHG's

Green house Gas	**Pre-Industrial Concentration 1860**	**Concentration In 2006**	**% increase**
Carbon dioxide	288 ppm	380 ppm	31 %
Methane	750 ppb	1780 ppb	138 %

The phenomenon of climate change is a source of concern among the scientists, as they believe that the warming will lead to more warming and at a far quicker pace. As the planet gets warmer, glaciers and ice sheets in the polar regions and on high mountains have been rapidly melting resulting in more water and less ice or snow. This results in more warming because ice and snow reflect radiation while water has much less reflectivity and more absorption. Secondly oceans absorb carbon dioxide and act as sinks. The absorption of CO_2 in oceans will decrease as they get saturated in CO_2 leaving more of it in the atmosphere which would result in enhanced greenhouse effect leading to more warming. Thirdly, warmer land will provide more CO_2 to the atmosphere because of enhanced respiration. Finally a warmer atmosphere would hold greater water vapor which is a greenhouse gas. Thus it is feared that the global warming may have spiral increase resulting in accelerated warming. The rise in average global temperature during the last century is shown in Figure 2.

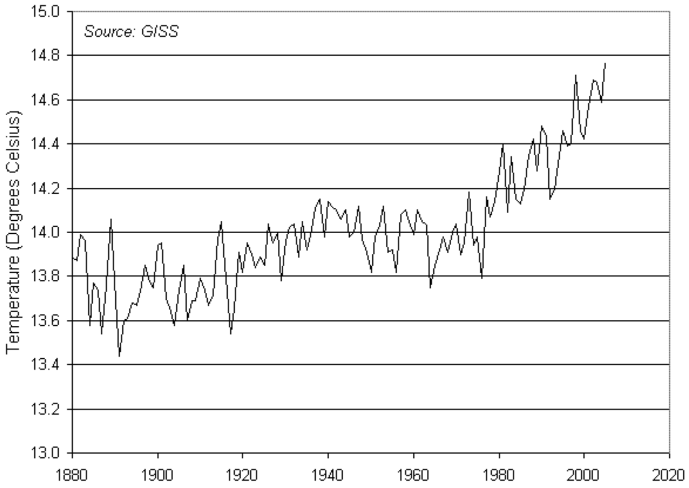

Figure 2: Average Global Temperatures, 1880-2005

During the last three decades, the temperatures have been climbing remarkably. The 1990's was the warmest decade since the mid 1800's when the record keeping started. The hottest years recorded came in quick succession 1998, 2001, 2002, 2003, and 2005.

The global warming will have profound effect on the world's climate and will result in melting of polar glaciers and ice sheets, rise in sea level, warming of oceans resulting in severe hurricanes and increase in extreme climate events. This will adversely alter the availability of water resources and agricultural production. This would also be disruptive for the economies especially of the developing countries in view of the fact that the carbon dioxide once released to the atmosphere will remain there for long period of hundreds of years. Global initiatives are needed to face the challenge posed by climate change.

Global mitigation initiatives such as Kyoto Protocol have not been effective because of reluctance by the producers of greenhouse gases to curb their emissions. Adaptive measures are best realized at the national and local levels to cope with the challenge of climate change. Success in this area requires understanding of the science of climate change and its impact on various socio-economic sectors.

In Pakistan, we made a late start and it was only in 2002 that an activity called "Global Change Impact Studies Centre (GCISC)" started functioning. The main areas of research are climatology, water and agriculture. Figure 3 illustrates the approach adopted at GCISC in the light of the mandate given to it by the Government.

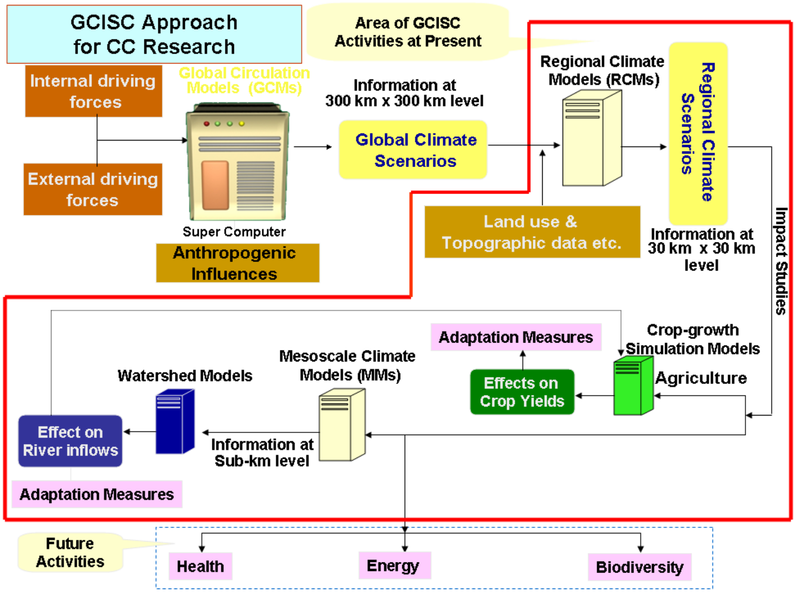

Figure 3: GCISC's approach for CC research

2. RESEARCH AT GCISC

A. CLIMATOLOGY SECTION:

Use of Simulation Models for Climate Change Scenario Development and Impact Assessment Studies at GCISC

At GCISC we have been pursuing climate change research aimed at developing climate change scenarios for Pakistan, making use of both Global Circulation Models (GCM's) and Regional Climate Models (RCM's) as outlined below.

Use of Global Circulation Model Outputs

The Intergovernmental Panel on Climate Change (IPCC) has established a Data Distribution Centre (DDC) where the output data of a number of GCM's corresponding to different GHG build-up scenarios have been stored and made accessible through internet. Using this facility, GCISC has been engaged in analyzing the outputs of 6 different GCM's (**Table 2**) for which the model outputs corresponding to the IPCC scenarios A2 and B2 (**Table 3**) spanning the period from 1960 to 2100. The analysis is being done over five different sub-regions of South Asia, as shown in **Figure 4**. The data has been analyzed for the validation of the selected GCM's over South Asia Region, and then development of climate change scenarios for the region for 2020s, 2050s and 2080s.

TABLE 2: GCM's whose Outputs are being analyzed at GCISC.

NO.	**COUNTRY OF ORIGIN**	**CENTRE OF ORIGIN**	**MODEL**	**RESOLU-TION**
1	Canada	Canadian Centre for climate modeling and Analysis (CCCma)	CGCM2	3.7°x3.7°
2	Germany	Max Planck Institute für Meteorology (MPIfM)	ECHAM4/ OPYC3	2.8°x2.8°
3	UK	Hadley Centre for Climate Prediction and Research (HCCPR)	HadCM3	2.5°×3.8°
4	Australia	Australia's Commonwealth Scientific and Industrial Research Organization (CSIRO)	CSIRO-Mk2	3.2°×5.6°
5	USA	Geophysical Fluid Dynamics Laboratory (GDFL)	R30	2.2°×3.8°
6	Japan	Center for Climate System Research National Institute for Environmental Studies (CCSR / NIES)	CCSR/NIES AGCM + CCSR OGCM	5.6°×5.6°

Note: - All the data was first regrided to 1° x 1° resolutions for comparison.

TABLE 3: Some Characteristic Features of IPCC Scenarios A2 and B2

Feature	**A2**	**B2**
Global Economic Growth	Low	Low
World Population	Very High	Medium
Technological Development	Very Low	Low
Emphases on Environmental Issues	Low	High
Disparity between Developed and Developing Countries	High	Medium

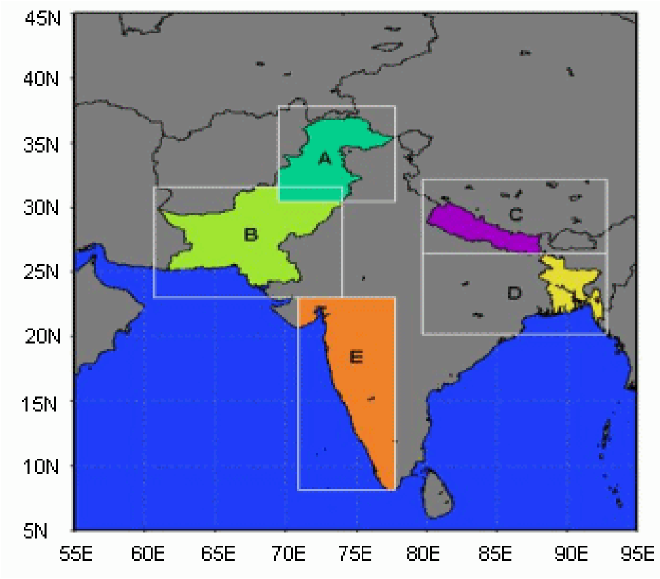

Figure 4: Selected Domain of South Asia Region with the five selected Sub-regions

For the development of climate change scenarios for the 5 South Asian sub-regions corresponding to the projected global changes of temperature and precipitation in the IPCC A2 and B2 scenario, three time slices of 30-year periods centered around 2020s (2010-2039), 2050s (2040-2069) and 2080s (2070-2099) were chosen. Climate changes during the winter (DJFM) and summer (JJAS) seasons compared to the baseline period, as projected by the ensemble of the 6 selected models, using the average values of their outputs for the above mentioned 30-year time slices in the future, were worked out for each selected sub-region. For each sub-region, time series of the ensemble's output data were also generated to look at the monthly and seasonal variations of temperature and precipitation over time. The ensemble results on annual basis for northern and southern Pakistan are summarized in **Table 4**.

Table 4: Projected changes in temperature and precipitation over Northern and Southern Pakistan in IPCC A2 and B2 Scenarios, based on analysis of ensemble output of 6 GCM's (namely: CGCM2, ECHAM4/OPYC3, HadCM3, CSIRO-Mk2, R30, CCSR, and CCSM/PCM1)

Use of Regional Climate Models

GCM's provide information about the global climatic conditions e.g. temperature, precipitation etc. with rather coarse resolution (300km x 300km), and still require weeks and months of operation on super computers. For high spatial resolution work it is particularly useful to make use of the RCM's (30km x 30km) in combination with the GCM output and high resolution information in topography, land use pattern etc obtained from US Geological Survey via internet. Another nice feature of RCM's is that they are designed for operation on a PC like Pentium-4.

At GCISC two different RCM's are currently in use. These are: RegCM3 developed by the Abdus Salam International Centre for Theoretical Physics (ASICTP), Italy and PRECIS, developed by the Hadley Centre (HCCPR) / United Kingdom Met Office (UKMO). These two models are very suitable for climate change studies at the regional scale, GCISC has close collaboration with both ASICTP and the Hadley Centre and both these institutions have provided us necessary data and technical support for their respective models. For meso-scale climate studies, GCISC is making use of the MM5 and WRF models (with resolution of about 1 km x 1 km) developed by the National Centre for Atmospheric Research (NCAR), USA. Both these models are well documented and are being widely used throughout the world, which makes it relatively easy to get the required technical support.

Time Period	**Global Average Temp. Change (°C)**	**Temp. Change (°C)**		**Precip. Change (%)**	
		Northern Pakistan	**Southern Pakistan**	**Northern Pakistan**	**Southern Pakistan**
IPCC Scenario A2					
2020s	0.64	1.00	1.03	1.03	36.8
2050s	1.65	2.69	2.48	2.74	41.3
2080s	3.05	4.98	4.34	1.95	52.5
IPCC Scenario B2					
2020s	0.79	1.14	1.24	-0.33	37.5
2050s	1.56	2.50	2.37	1.16	45.8
2080s	2.32	3.75	3.47	3.61	44.9

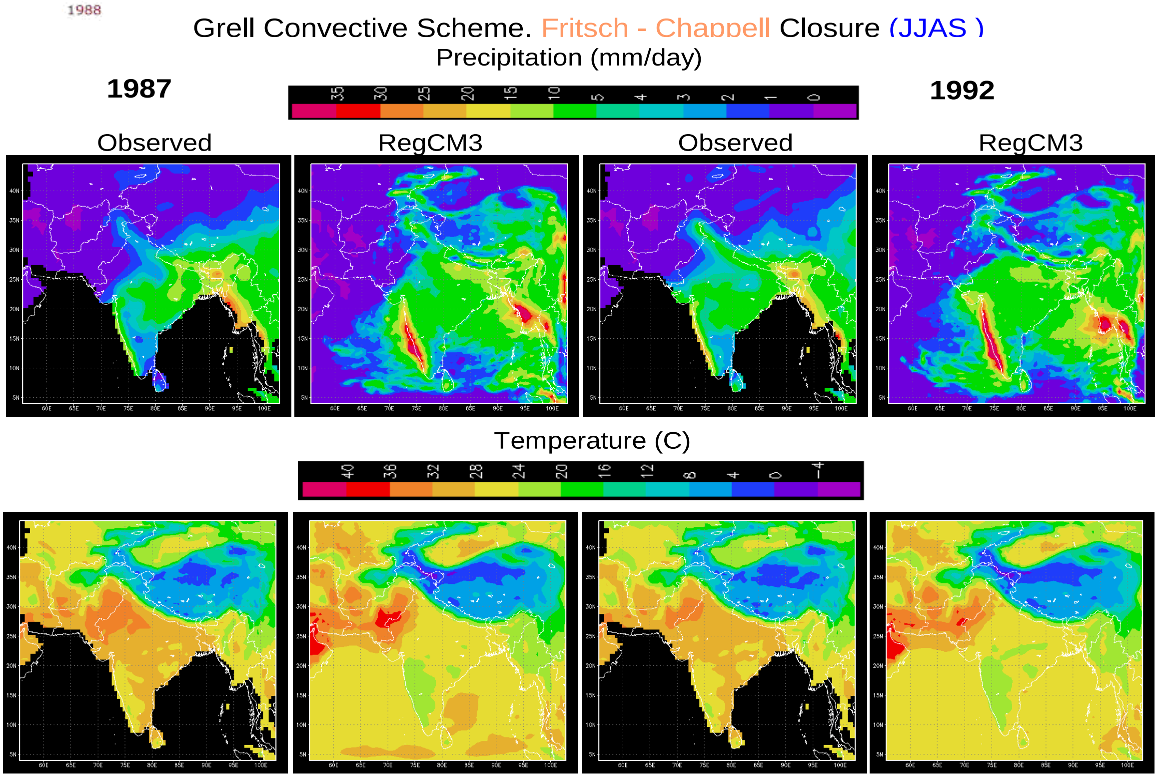

Figure 5: Simulation by RegCM3 of Precipitation and Temperature in summer (JJAS) over South Asia Region in two different years: 1987 (a particularly dry year in Pakistan) and 1992 (flood year in Pakistan)

A number of experiments were conducted to validate the performance of RegCM3 and PRECIS over the South Asia region. These include, inter alia, simulation of various observed extreme events, testing of different convective schemes in the case of RegCM3, testing of different domain sizes, experiments to resolve problems in precipitation patterns over Nepal etc. The results of one such validation experiment with RegCM3 showing the performance of the model are shown in **Figure 5.**

Table 5 summarizes the combinations of RCM’s and the corresponding GCM data and also lists the time slabs being used in the simulation runs now in progress at GCISC for the development of climate change scenarios for the South Asia region. Of these the PRECIS–HadAM3P combination runs for the 30-year period 2071-2100 have been completed and the output is now being analyzed, in particular with a view to develop climate change scenarios for 5 sub-regions of Pakistan, as shown in **Figure 6**.

Table 5: Combinations of RCM's and GCM Outputs and Time Slabs in Use for Scenario development work

Driving GCM	**RCM**	**Base Period**	**Future Period**	**Status (Runs completed for each simulation)**
ECHAM	RegCM3	1961-1990 (30 years)	2039-2069, 2071-2100 (30+30=60 years)	14 years
FVGCM	RegCM3	1961-1990 (30 years)	2071-2100 (30 years)	14 years
ERA40 (Reanalysis data)	RegCM3	1961-1990 (30years)	NIL	10 years
HadAM3P	PRECIS	1961-1990 (30 years)	2071-2100 (30 years)	30 years
ERA40 (Reanalysis data)	PRECIS	1961-1990 (30years)	NIL	20 years
ECHAM	PRECIS	1961-1990 (30 years)	2039-2069, 2071-2100 (30+30=60 years)	To be started next month

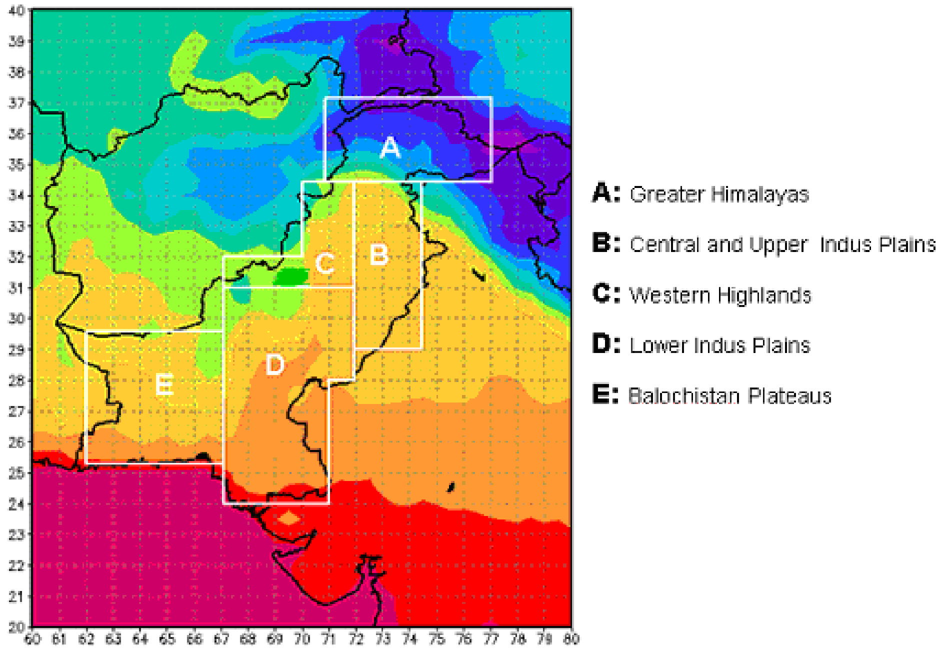

Figure 6: Five sub-regions of Pakistan for which RCM based climate change scenarios are planned to be developed

B. WATER SECTION

Use of Hydrological Simulation Models:

In order to conduct studies on the impact of climate change on water inflows in the Indus River System (IRS) (**Figure 7**) in Pakistan (comprising Indus, Jhelum, Chenab and Kabul rivers). GCISC first identified a set of four hydrological models (**Table 6**), which varied in complexity and were readily available to it, along with some technical support, through its international contacts. The key input parameters for these models are topography, vegetation cover, soil characteristics, glacier cover and meteorological factors like temperature, precipitation etc. They can all be operated on a P-4 Pentium Computer.

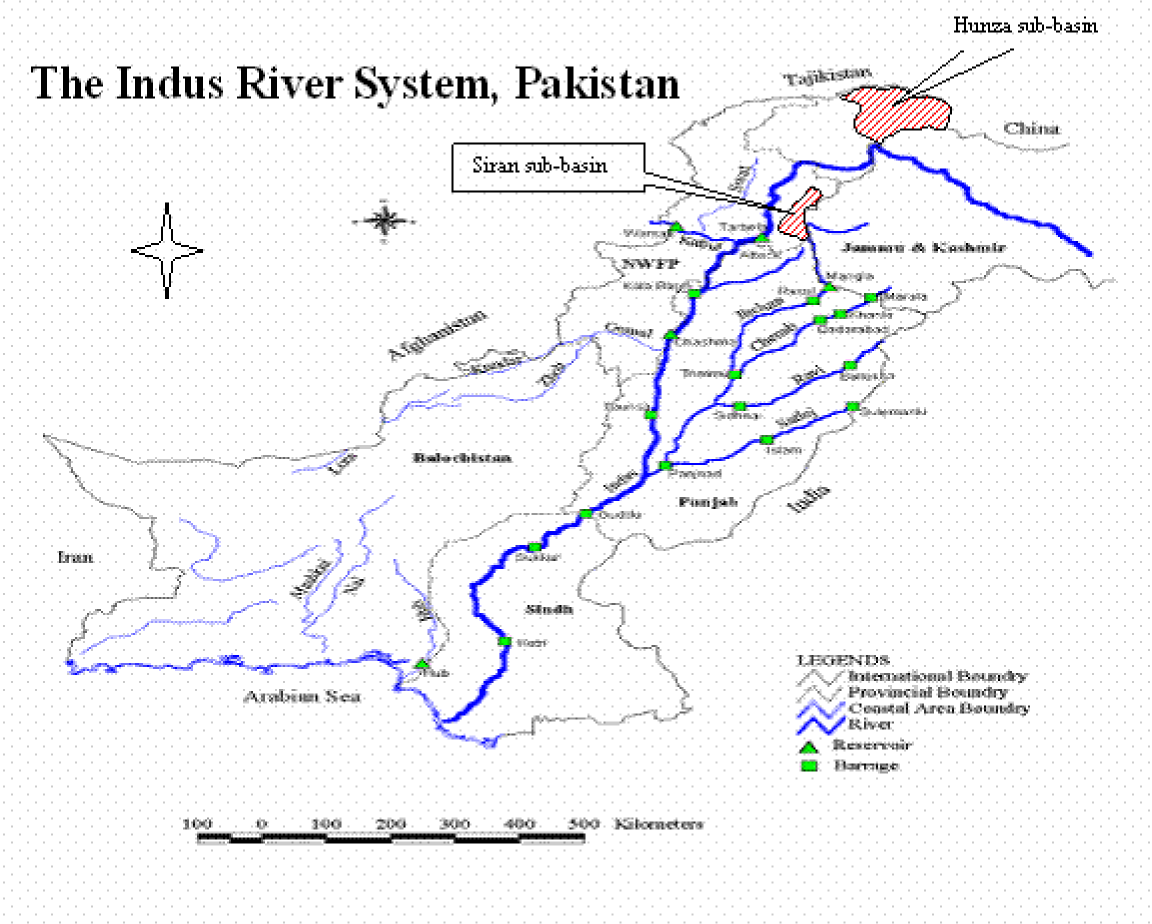

Figure 7: Indus river system

It is worth mentioning here that the hydrological system of Upper Indus Basin (UIB) is quite complex: It has a rapidly changing topography and combines runoff from glaciers, snowmelt and rainfall; these are further complicated by variable snow cover in space and time and by the upward migration of melting temperatures with altitude; glacier melt is the largest component of water supply in the rivers of the UIB; the estimated relative contributions of flows from glaciers, snow and rain are around 60%, 35% and 5% respectively. Of the 4 models listed in Table 5, after initial testing for their suitability for the UIB, two models i.e. University of British Columbia (UBC) and Distributed Hydrological Soil Vegetation Model (DHSVM) were selected for further work and are now undergoing calibration and validation process in various sub-regions of UIB.

Table 6: Hydrological Models Explored at GCISC

S. No	**Model Name**	**Type of model**	**Developed by**
1.	Brook90	Fully Lumped	US Forest Service U.S.A.
2.	Hydrologic Engineering Center's Hydrologic Modeling System (HEC-HMS)	Lumped/ Distributed	U.S. Army Corps of Engineers Hydrologic Engineering Center, U.S.A.
3.	University of British Columbia (UBC) Watershed Model	Semi-distributed	University of British Columbia, Canada
4.	Distributed Hydrology Soil and Vegetation Model (DHSVM)	Fully Distributed	University of Washington, U.S.A.

The UBC model has been calibrated and validated for Hunza sub-basin with glacier, snow and rain components and the DHSVM for Siran sub-basin with no glacier component. The performance of both these models is very encouraging as, in spite of there being only a small number of meteorological stations providing the input data, reasonably good simulated flows have been obtained. The calibration results of UBC for Hunza and of DHSVM for Siran sub-basins are shown in **Figures 8** and **9** respectively. Efforts are now in progress to calibrate these models for the entire UIB.

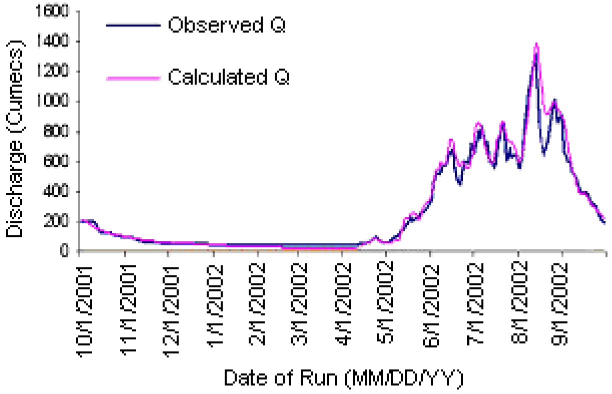

Figure 8: Observed and Simulated Hydrographs of Hunza River at Dainyour using UBC Watershed Model and high altitude weather data.

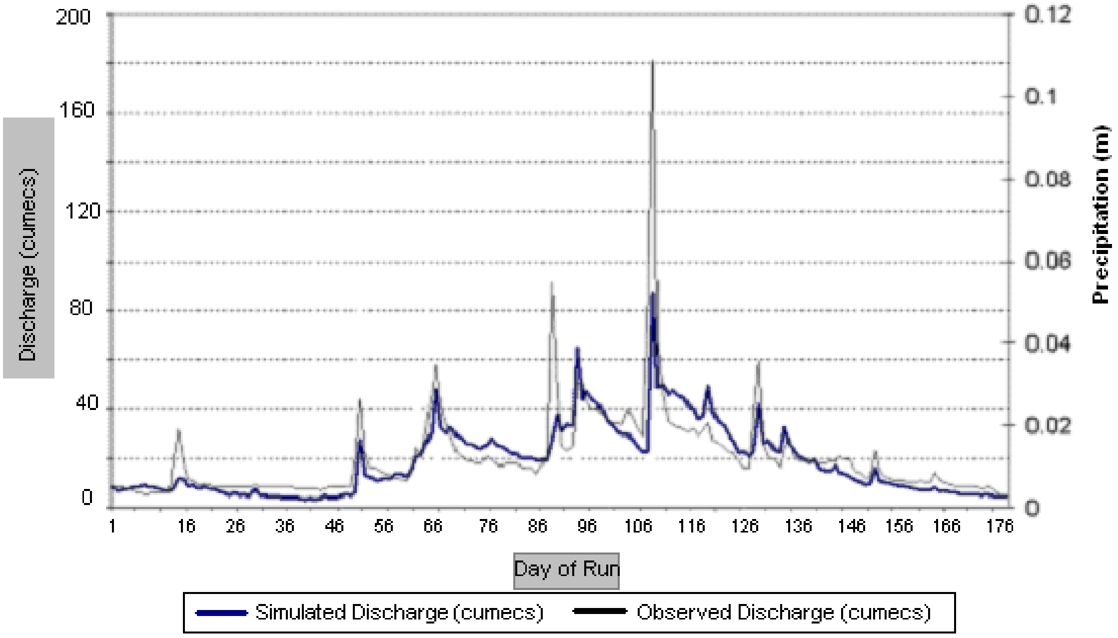

Figure 9: Observed and DHSVM Model Simulated Hydrographs of Siran River at Phulra, Jan-June

Once the UBC and DHSVM models have been calibrated and validated for the entire UIB, studies will be undertaken by using them to assess the impact of climate change on IRS inflows, initially corresponding to some hypothetical climate change scenarios, and later on in line with the climate change scenarios developed by the Climatology Section of GCISC based on its studies using RCM’s.

C. AGRICULTURE SECTION:

Use of Crop Simulation Models

Pakistan's economy is heavily dependent on agriculture sector which is highly climate sensitive**.** Changes in climate, particularly an increase in temperature coupled with a decrease in precipitation, would have very serious negative impact on the future of agriculture. In order to make quantitative assessment of the likely impacts of changes under future climatic conditions in various agro-climatic zones of the country, one needs to make use of appropriate Crop Simulation Models after the same have been tested, calibrated and validated for the specific varieties of crops under consideration and for the agro-climatic conditions of the region under study. GCISC has been very fortunate in getting access to a number of well known families of crop simulation models along with the technical advice and support. These are listed in Table 6. They are all based on a Decision Support System for Agro-Technology Transfer (DSSAT) developed by the University of Georgia. DSSAT and its associated models can be operated on a Pentium-4 computer. **Table 7** lists those DSSAT-based crop simulation models which are currently in use at GCISC.

Table 7: DSSAT Based Families of Crop Simulation Models acquired by GCISC

Model	**For**
CERES (for Cereals)	Corn, Wheat, Rice, Barley, Sorghum, Millet
CROPGRO (for Grain Legumes and Fiber crops)	Soybean, Peanut, Dry Bean, Chickpea, Cotton
CROPSIM (for Root Crops)	Potato, Cassava
Oil Seed Crops	Sunflower
Vegetables	Bell pepper, Cabbage, Tomato

The input requirements for using the crop simulation models are:

1. Provision of Relevant crop and climate parameters
    - Agronomic parameters
    - Climatic parameters of crop
    - Soil inputs
2. Calibration and validation of crop simulation models
3. Adoption of appropriate climate change scenarios for future climate

The two most important food crops for Pakistan are wheat and rice. Wheat is grown in all parts of Pakistan whereas rice is mostly (93%) grown in the irrigated areas of Punjab and Sindh. At GCISC, CERES-Wheat and CERES-Rice crop models have been calibrated and validated for specific varieties and selected agro-ecological zones. The CERES-Wheat model was calibrated and validated for wheat variety Inqalab, which is the dominant wheat cultivar in Pakistan covering more than 70% of the wheat area in the semi-arid and arid regions of the Punjab province. The CERES-Rice model was calibrated and validated using data taken from the semi-arid irrigated area of Faisalabad for Basmati Super cultivar.

These models have been used to assess the impact of climate change on the yields of Wheat and Rice corresponding to the GCM based scenarios for Northern and Southern Pakistan developed by the Climatology Section of GCISC **(Table 8)**.

Table 8: Impact of rise in temperature on wheat growing season length in Northern and Southern parts of Pakistan

Temperature (˚C)	**Growing Season Length (Days)**			
	Northern Pakistan		Southern Pakistan	
	Mountainous Region (Humid)	Sub-Mountainous Region (Sub-humid)	Plains (Semi-arid)	Plains (Arid)
Baseline	246	161	146	137
(increase over baseline) **1**	232	155	140	132
2	221	149	135	127
3	211	144	130	123
4	202	138	125	118
5	194	133	121	113

The results of the model based analysis on the yields of wheat and rice corresponding to the GCM based climate change scenarios for Pakistan are shown in **Figures 10** and **11**. In the absence of any change in crop varieties and agricultural practices, the average yield of wheat in Pakistan will decrease by 2080's by about 3.6% under the scenario A2 and 5.2% under the scenario B2.

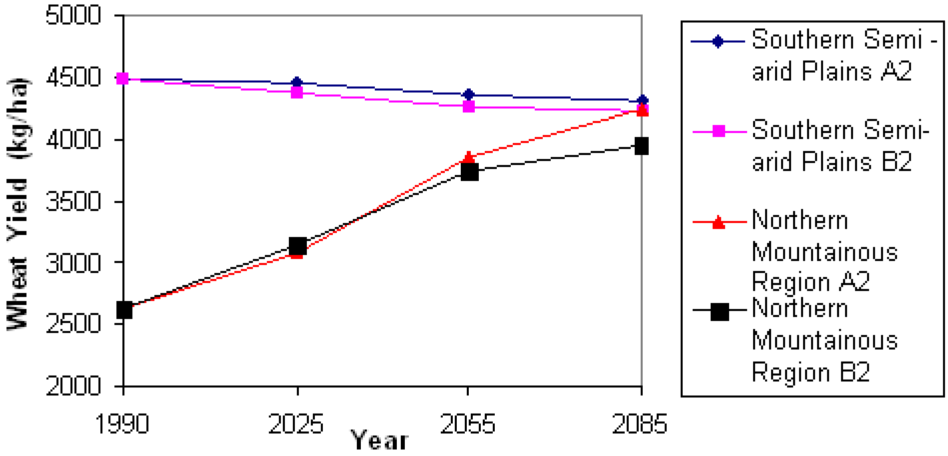

Figure 10: Wheat Yield in Northern mountainous region and Southern Semi-arid Plains of Pakistan under A_2 and B_2 Scenarios

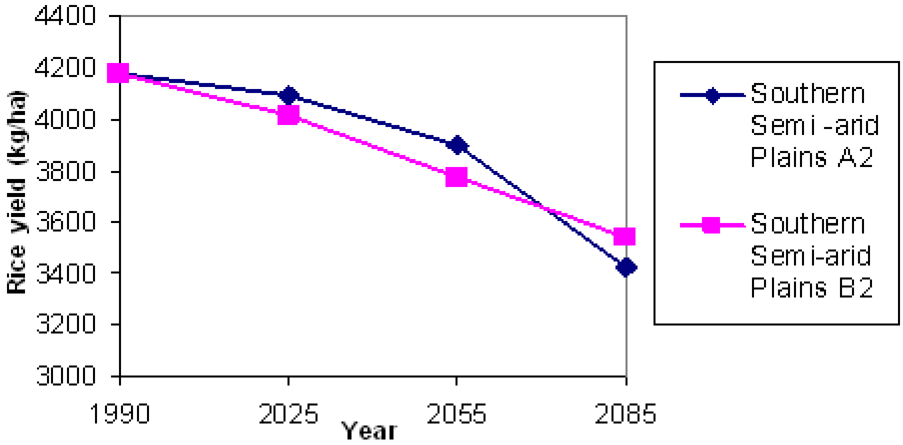

Figure 11: Rice Yield in Southern Semi-arid Plains of Pakistan under A_2 and B_2 Scenarios

For rice, the yield of Basmati Super variety grown in Southern Semi-arid Plains will decrease by 18% and 15% by 2080's under the scenarios A2 and B2 respectively, resulting in the corresponding reduction in overall production of rice in country by 9.3% and 7.9% respectively. We will undertake work later on in line with the climate change scenarios developed by GCISC based on its studies using RCM's.

3. CONCLUSIONS

We have achieved some modest success at GCISC. We have faced difficulties in attracting suitable qualified manpower. We have used simulation models developed by others rather than develop our own models. There also is a weakness in authentic local data in all areas viz. climate, water and agriculture. We are constantly striving to overcome these deficiencies. Other developing countries may be facing similar problems and sharing the experience could be mutually beneficial.

In 2005 the Prime Minister of Pakistan decided, at our recommendation, to establish a Prime Minister's Committee on Climate Change comprising Federal Ministers of Environment, Water and Power, Food and Agriculture, Science and Technology, Planning and Special Advisor to the Prime Minister with GCISC as the secretariat of this Committee. This important decision has helped the GCISC to raise its stature. The functioning of GCISC under the Committee will be helpful in not only bringing awareness of Climate Change to the highest echelons of the Government but also prepare the country planning for adaptation and mitigation on sound scientific basis.

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GLOBAL WARMING THREAT ON WATER RESOURCES AND ENVIRONMENT

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Global warming, greenhouse effect and the climate change problems are long-term anthropogenic consequences that are expected to threaten water related demand and supply patterns in the near future. It is, therefore, necessary to identify these problems linguistically on logical basis so as to take the necessary precautions, mitigation strategies after the vulnerability possibilities awareness. Climate change has become at the focus of many scientific, engineering, economic, social, cultural, and global nuisances, which awaits rational remedial solutions with less cost. This paper presents the possible views about the water resources and environmental vulnerability against the climate change by presenting rather detailed information concerning the engineering water systems, extreme events such as floods and droughts and groundwater recharge. The major conclusions are documented on the basis of previous studies with the prospects of future developments. The main emphasis is given on how to combat with the climate change challenge concerning the water resources and environment including the use of renewable energy alternatives. Last but not the least, linguistic (verbal) information is furnished with the concept of fuzzy logic.

Key words: *Climate, change, droughts, energy, floods, groundwater, impact, sedimentation, thread, variation, water resources.*

1.Introduction

Climate is defined as the average of weather events over a long time spans and large regions. It is caused by changes in the atmospheric circulation, sunshine radiation, wind direction and speed, ocean currents, precipitation, pressure and temperature. In local climatic signatures especially temperature and the precipitation records and variations provide basic initial information. Additionally it is the sum total of the weather experienced at a place in the course of the year and over the years. It comprises not only those conditions that can be described as 'near average' or 'normal' but also extremes and all the variations. The climate signature of any place can be identified on the basis of five factors, namely, radiation, heat transport, moisture transport, transport of matter, and finally, near ground surface conditions.

Climate is effective not only on the human life, culture and civilization but equally valid on the animal, plant and materials of all types natural and artificial. For instance, food types, shelter, clothing, protection of human life all depend on the climate and its variation. On the contrary, human, and animal affect the weather and consequently the climate by meddling the water courses, fertile lands, genuine atmospheric composition due to urban and industrial activities. This indicates that there is an interaction on both sides between the life and climate. Nature is gifted for the life on the earth suitable hydrologic, lithologic, biologic, and weather environments, which are in balance with each other temporally and spatially and even tolerable in such a balance to a certain extend, but when the limits of allowance is approached or transgressed then the environment may start to react adversely. It is, therefore, necessary to care for the weather and especially climate by trying to limit the undesirable effects on the atmosphere, which is the domain for the weather and climate events to take place and shape. Any deterioration in climate pattern results on unpleasant consequences on the life in vital environment.

In search for life in other planets the first question is whether the climate is suitable for the survival of any organism or creature. Water is the major agent in the development and sustenance of climate and it is the first element that is sought at the surface of the concerned planet or water vapor in its atmosphere. For the survival of creatures climate is not the only important factor but also other factors are necessary. Among such factors it is possible to summarize the following points.

1) Water must be available in liquid form as an essential solvent for living processes. Life cannot exist and continue except under the conditions of condensing steam and melting ice, which constitute the local hydrological cycle for water agents transportation,

2) The rotation period of the planet should be such that the days and nights cannot oversize each other. This means that nights do not overcool and days do not overheat,

3) The sun radiation must be intercepted in a harmonious manner by having low orbital eccentricity in order to avoid excessive differences in the insolation as the planet moves between perihelion to aphelion,

4) There must be convenient proportions between the chemical constitutions of atmosphere, hydrosphere and lithosphere which allow suitable activity in biosphere environment. For instance, methane and ammonia were abundant at the early atmosphere of the earth which did not allow life sustenance.

The IPCC Second Assessment Report (Santer et al., 1996) on climate change noted that although few would argue that completely unambiguous detection and attribution of climate change had already occurred, the 'balance of evidence suggests a discernible human influence on global climate'. Some evidence indicating that 20th century global mean temperature was at least as warm as any other century since at least 1400 AD. Data prior to 1400 are too sparse, at the moment, to allow the reliable estimation of global mean temperature.

Climate change will affect the availability of water, as well as its quality, distribution, the complex infrastructure and systems in place to manage water and existing climate variability. There is very little literature about how different climate changes may affect the infrastructure and complex systems built to manage water resources. At the same time, significant knowledge gaps remain and far more research is needed. Priorities and directions for future work should come from water managers and planners as well as from the more traditional academic and scientific research community.

The cycling of water in its various states solid, liquid, and gaseous is a primary process within the earth's climate system. Information on variability of states and fluxes over time is crucial for the understanding of the sustainability of local, regional, national, and international economies and ecosystems. It is essential to establish rates of cycling, changes in these resulting from human intervention, and the consequences of those changes for regional fresh water availability. It is a priority scientific objective to establish how much of the variability in the water cycle is predictable over a range of time and space scales.

There are many opportunities to adapt to changing hydrologic conditions, and the net costs are sensitive to the institutions that determine how water is managed and allocated among users.

How should rainfall change as the climate changes? This is a key question that could have a substantial impact on society and the natural environment, as it can directly affect availability of fresh water, the quality of potable water, drought and floods. Usually the only measure of rainfall cited is rainfall amount. Yet most of the time it does not rain. So just a little thought makes us realize that we need to be concerned also with how often it rains: the frequency; and how hard it rains when it does rain: the intensity or rainfall rate, as well as the amounts. Also, it turns out that making these distinctions allows us to make more sensible statements about the likely changes and how to examine the data on rainfall. Rainfall intensity is an essential factor in many engineering design procedures such as risk assessments, culvert design, and inundation maps. It is necessary to elaborate about the impact of climate change on these factors in the coming decades.

When the temperature increases, so does the water-holding capacity of the atmosphere. This is why we tend to use relative humidity as a measure of moisture as it signifies the percentage of moisture the atmosphere can hold rather than the absolute amount. At very cold temperatures, the atmosphere can hardly hold any moisture, in effect it gets freeze dried, and so liquid water amounts from snow at temperatures below freezing are quite small. Of course, enhanced evaporation depends upon the availability of sufficient surface moisture and over land; this depends on the existing climate. Surface moisture comes directly from evaporation as well as through transpiration in plants, together called evapotranspiration. However, it follows that naturally-occurring droughts are likely to be exacerbated by enhanced potential evapotranspiration (drying).

Further, globally there must be an increase in precipitation to balance the enhanced evaporation but the processes by which precipitation is altered locally are not well understood. Precipitating systems of all kinds (rain clouds, thunderstorms, extra-tropical cyclones, hurricanes, etc) feed mostly on the moisture already in the atmosphere at the time the system develops, and precipitation occurs through convergence of available moisture on the scale of the system. Hence, the atmospheric moisture content directly affects rainfall and snowfall rates, but not so clearly the precipitation frequency and thus total precipitation, at least locally. Thus, it is argued that global warming leads to increased moisture content of the atmosphere which in turn favors stronger rainfall events. In other words, when it rains it should rain harder than it used to under similar circumstances. This is exactly what is being observed to be happening in many parts of the world, thus increasing risk of flooding. It is further argued that one reason why increases in rainfall should be spotty is because of mismatches in the rates of rainfall versus evaporation. Rain dries out the atmosphere unless the winds bring in more moisture from remote areas, and the weather system runs out of moisture.

An increase in atmospheric moisture may lead to increased relative humidity and increased clouds, which could cut down on solar radiation and reduce the energy available at the surface for evaporation. Those feedbacks are included in the climate models and alter the magnitude of the surface heat available for evaporation in different models but not its sign. The rainfall rates and frequencies as well as accumulations are important in understanding what is going on with precipitation locally. The accumulations depend greatly on the frequency, size and duration of individual storms, as well as the rate, and these depend on atmospheric static stability (vertical structure) and other factors as well. In particular, the need to vertically transport heat absorbed at the surface is a factor in convection and extra-tropical weather systems, both of which act to stabilize the atmosphere. Increased greenhouse gases also stabilize the atmosphere. Those are additional considerations in interpreting model responses to increased greenhouse gas simulations.

Changes in runoff, the source of a region’s renewable water supply, are the direct result of changes in precipitation and evaporation (which is strongly influenced by temperature).

Uncertainties as to how the climate and hydrology of a region will change in response to a global greenhouse warming are enormous. However, one of the more likely impacts involves areas where precipitation currently comes largely in the form of winter snowfall, and where streamflow comes largely from spring and summer snowmelt. A warming would likely result in a distinct shift in the relative amounts of snow and rain and in the timing of snowmelt and runoff. A shift from snow to rain could increase the likelihood of flooding early in the year and reduce the availability of water during periods of peak demand, especially for irrigation.

The water resources are an integral part of the global hydrologic cycle. Precipitation originates as evaporation from land and the oceans. Soil moisture is used by plants, which return more moisture to the atmosphere. Water that does not evaporate or transpire or seep into aquifers runs off to form the nation’s streams and rivers. Snow stored in winter in the mountains provides water for rivers and deltas in the spring and summer. Storms bring extra moisture; droughts arise from protracted periods of low rainfall, all as part of our natural climate. Climate change is just one of a number of factors influencing the hydrological system and water resources.

If we are to understand why floods and droughts occur, we must begin with the air we breathe. Climate is the fundamental link between the floods (droughts) and the atmospheric changes. Everyday in different parts of the world storms break and rivers burst their banks. In arid and semi-arid regions, however, the sky remains relentlessly clear for months as animals die, reservoirs dry up and groundwater storages are in continuous depletion. Over the years, season after season, one learns what to expect from the weather and consequently he/she starts to make interpretations about the present climate situations on the basis of previous experience. This gives one the ability to make climate change statements. With time, the cumulative experiences of storm, wind, and heat coalesce into a sense of climate, an important component of our sense of place. Although this "sense of place" is invaluable to us as individuals, it does not offer scientists or society much of a foundation for the broader picture of a global climate, much less any insight into how climate might be changing or how it affects our lives.

Detection of climate change requires demonstrating that the observed change is larger than would be expected to occur by naturally inherent fluctuations alone. An observed variation in climate is highly unusual in a statistical sense. Attribution of change to human activity requires showing that the observed change cannot be explained by natural forced or unforced causes. Climate change impacts are observable through numerical measurements and/or linguistic expressions in a fuzzy manner. Assessments of the statistical significance of the observed global mean temperature trend over the last century have detected a significant change and shown that the warming is unlikely to be entirely natural in origin.

1) The two most key climate variables are temperature and precipitation and their numerical measurements are necessary in a systematic manner temporally, 2) Past climate variable records in terms of time series provide an objective basis for climate variability and change assessments,

3) Time series plots may reveal hidden or obvious trends which may be observable by naked eye or better by the application of competent statistical methodologies. Increasing or decreasing trends may indicate the climate impact provided that other side effects are isolated,

4) People make their decision about the climate change based on basis of their daily experience on climate. They make statements as "climate is changing" "the rainfall occurrences become more frequent compared to decadal past"

5) Observations on snow occurrence indicate that in some parts of the world the snow events have decreased,

6) Flood and drought frequency as well as magnitude variations especially in the

7) Observations of the relevant human inputs to the atmosphere (i.e. greenhouse gases, sulphate aerosols).

2. Effect of Climate Change on Water Availability

Climate is only one of many factors influencing the future supply and demand for water. Indeed, population, technology, economic conditions, social and political factors, and the values society places on alternative water uses are likely to have more of an impact on the future availability and use of water than changes in the climate. Even in the absence of human-induced changes in the climate and hydrological cycle, there is cause for concern over the adequacy of water supplies. Demands are outpacing supplies, water costs are rising sharply, and current uses are depleting or contaminating some valued resources.

Humans are influencing the global climate and, thereby, altering the hydrological cycle, however inadvertently. Greenhouse warming will have the following future effects on fresh water resources and on their management.

1) The timing and regional patterns of precipitation will change, and more intense precipitation days are likely.

2) General circulation models (GCMs) used to predict climate change and suggest that a 1.5 to 4.5^0 C rise in global mean temperature would increase global mean precipitation about 3 to 15 percent.

3) The regional distribution is uncertain; precipitation is expected to increase in higher latitudes, particularly in winter. This conclusion extends to the mid-latitudes in most GCM results.

4) Potential evapotranspiration rises with air temperature. Consequently, even in areas with increased precipitation, higher evapotranspiration rates may lead to reduced runoff, implying a possible reduction in renewable water supplies.

5) More annual runoff caused by increased precipitation is likely in the high latitudes. In contrast, some lower latitude basins may experience large reductions in runoff and increased water shortages as a result of a combination of increased evaporation and decreased precipitation.

6) Flood frequencies are likely to increase in many areas, although the amount of increase for any given climate scenario is uncertain and impacts will vary among basins. Floods may become less frequent in some areas.

7) The frequency and severity of droughts could increase in some areas as a result of a decrease in total rainfall, more frequent dry spells, and higher evapotranspiration.

8) The hydrology of arid and semiarid areas is particularly sensitive to climate variations. Relatively small changes in temperature and precipitation in some areas could result in large percentage changes in runoff, increasing the likelihood and severity of droughts and/or floods.

9) Seasonal disruptions might occur in the water supplies of mountainous areas if more precipitation falls as rain than snow and if the length of the snow storage season is reduced.

10) Water quality problems may increase where there is less flow to dilute contaminants introduced from natural and human sources.

The impact of climate change on water resources is dealt with in more detail in the Second Assessment Report of the IPCC issued in 1995 and in the Report of the Second International Conference on Climate and Water held in 1998, which made a number of recommendations as.

1) research priorities (data networks, problems of scale, need for interdisciplinary dialogue),

2) research management (large scale land-surface experiments, advanced planning for remote sensing, communication with decision makers and the public),

3) project design and management (effect of climate change, broad dialogue on practical operational problems, conflict resolution on water issues), and

4) policy formulation (national planning based on up-to-date information, respect for local culture and level of development, involvement of all stakeholders at an early stage).

Drinking water sources contain various natural and anthropogenic effects and contaminants. A low concentration of these contaminants is not harmful for human activities and besides removal of all the contaminants is costly. Provided that the contaminant levels are less than specific standards they do not present harmful effects. In general, human activities such as physical activity, body weight and temperature play significant role in drinking water consumption rates depending on the environmental temperature levels. Most often human activity variables are given in crisp numerical interval classifications for water consumption calculations. In practice, expression of water consumption is made by words such as low, medium, high, extremely high, etc. Hence, rather than crisp (certain) values fuzzy (uncertain) quantities are effective.

While future water demand depends as much on consumer preference (or individual unit consumption) as it does on population, much less attention has been given to consumer preferences which can be determined by market purchase analysis and varies from place to place with cultural, environmental, economical and other features. Additionally, the impact of climate change on the consumptions also expected to play significant roles.

Variability and uncertainty in drinking water consumption encompass a multiplicity of concepts, and the precise meaning of these terms varies across disciplines (Richard et al., 2000). These concepts depend on issues that distinguish between inherent physical or natural characteristics and limitations of knowledge or understanding, hence leaving the planner with uncertain, incomplete, imprecise and vague information, i.e. fuzzy data. Uncertainties are natural and refer to observed or measurable differences attributable to diversity in a population, e.g., members of population exhibit variability with respect to their weight and daily water demand. Imprecision is defined as a degree of uncertainty across an exposed population due to inter-subject differences in exposure conditions, rates of intake depending on environmental and body temperatures, inhalation rates (physical activity) per unit body mass, uptake fraction, retention characteristics, biotransformation and sensitivity (Raucher, et al.,2000). Of course, all these conditions are a function of environmental climate variability including micro and macro climate changes.

Logically, drinking water consumption depends not only on the measured qualities, but vaguely on the social variables such as the human weight, activity and temperature. In practice, all these variables are presented in table forms with crisp interval classification. On the other hand, all studies on drinking water consumption data are available in the forms of short-term surveys with uncertainties. Most often, it is not possible to have enough numerical data but rather supplementary linguistic data as the consumer's opinion. There is no any other approach than the fuzzy logic and system modeling to treat such linguistic (verbal) data sources. This may be a source of uncertainty in the consumption rate estimations because of the subjective nature of the survey techniques. However, they include general tendencies at least for the drinking water consumption rates. In the same manner description of climate change and trends can be expressed as low, medium, high, extreme, etc.

While future water demand depends as much on consumer preference (or individual unit consumption) as it does on population, much less attention has been given to consumer preferences which can be determined by market purchase analysis and varies from place to place with cultural, environmental and other features. Future preference trends will result from intersection between the introduction of new goods and services and the changes in the means to purchase and time to enjoy them.

Climate change will affect the availability of water as well as its quality, distribution, and form. Large changes in the reliability of water yields from reservoirs could result from small changes in inflows (high confidence). There is a growing literature about how different climate changes may affect the infrastructure and complex systems built to manage water resources. Research has been conducted on potential impacts over a wide range of water-system characteristics, including reservoir operations, hydroelectric generation, navigation, and other concerns. At the same time, significant knowledge gaps remain and far more research is needed. Priorities and directions for future work should come from water managers and planners as well as from the more traditional academic and scientific research community.

3. Effect of Climate Change on Extremes

Perhaps one of the greatest interests in weather and climate relates to extremes of climate. Due to inadequate monitoring as well as prohibitively expensive access to weather and limited data held by the world's national weather and environmental agencies, only limited reliable information is available about large-scale changes in extreme weather or climate variability. The time-varying biases that affect climate means are even more difficult to effectively eliminate from the extremes of the distributions of various weather and climate elements. There are a few regions and climate variables, however, where regional and global changes in weather and climate extremes have been reasonably well-documented. Inter-annual temperature variability has not changed significantly over the past century.

There is a risk of increased flooding in many parts of the world that experience large increases in precipitation (medium confidence). The Intergovernmental Panel on Climate Change concluded in 1996, that: "the flood related consequences of climate change may be as serious and widely distributed as the adverse impacts of droughts" and "there is more evidence now that flooding is likely to become a larger problem in many temperate regions, requiring adaptations not only to droughts and chronic water shortages, but also to floods and associated damages, raising concerns about dam and levee failure."

A widespread increase in the risk of flooding for many human settlements (tens of millions of inhabitants in settlements studied) from both increased heavy precipitation events and sea-level rise.

Extreme events, such as droughts and floods are related to climate variability and change. The climate change causes some areas to suffer more frequent and severe droughts, while other places to have more frequent and severe flooding. These changes virtually reflect their impacts on freshwater resources. The impact of drought on groundwater resources is obvious, but the impact of flooding may be less so. One impact of flooding is a significantly increased risk of groundwater contamination.

Hydrologists and climatologists have long been aware of the role of regional climate in the prediction of floods or in understanding drought. With our growing sense of a variable climate, it is appropriate to reassess these concepts of flood and drought, not as isolated events, but as phenomena connected on a worldwide scale.

Floods and droughts are not aberrations. Floods are initially more conspicuous than droughts because they can occur over days or weeks instead of months or years. Droughts require a more persistent weather pattern before they are recognized. We commonly assume that they are end members of the spectrum of possible meteorological conditions for a given locality. Another emerging perspective, however, is that floods and droughts arise from conditions that are somehow different than the established norm. Climate may not turn out to be a smooth continuum of meteorological possibilities after all, but rather the summation of multiple processes operating both regionally and globally on differing time scales. Floods and droughts are neither random nor cyclic. The extremes of flood and drought occur within the context of climate, a context that is both local and global. One must understand the geography and meteorological response of a given watershed to understand its history of flooding. One should also look beyond basin boundaries to appreciate the coherent patterns that influence weather regionally.

There is the likelihood of abrupt changes in the climate system such as the collapse of the ocean thermohaline circulation, inception of a decades-long mega-drought, or rapid melting of the major ice sheets.

3.1 Floods

A flood is an overflowing of water from rivers onto land not usually submerged. They also occur when water levels of lakes, ponds, reservoirs, aquifers and estuaries exceed some critical value and inundate the adjacent land, or when the sea surges on coastal lands much above the average sea level. Nevertheless, floods are a natural phenomenon important to the life cycle of many biotas, not the least of which is mankind. Floods are the most destructive of natural disasters and cause the greatest number of deaths.

Catastrophic floods can explode suddenly out of a single summer thunderstorm. Flooding, however, can also be caused by a months-long build-up of moisture, such as the fast melting of a heavy winter's accumulation of mountain snow or soil saturated by high seasonal rainfall. All floods, of course, are shaped by the basin through which they flow.

Spatial and temporal scales of floods are generally linked to the corresponding scales of the flood generating rainfall coupled with weather and climate change conditions.

Many measures can be used by societies to cope with floods. They are usually classified into two major groups as engineering structural and non-structural measures. Furthermore, these measures can be combined together in order to maximize the effects of the alleviation of the floods risks.

Structural measures of the flood management can be defined as the measure that alters the physical characteristics of the floods. They usually involve engineering hydraulic structures as dams, reservoirs and retarding basins, channel and catchments modifications, levee-banks, flood proofing, etc.

On the other hand, non-structural measures alter the exposure of lives and properties to flooding (flood forecasting and warning, flood insurance, planning controls, public information and education, etc.)

It is worthy to remember that floods, after all, are periodical events, so that in between these events people forget their effects. For this reason it is important to increase awareness to the public of this problem. Increasing possibility of future climate change effects make this point more significant than before.

The alternating sequence of wet and dry years is difficult to comprehend, let alone predict. A tantalizing pattern links drought and its inverse, flooding, in many places around the world. Floods in one location and drought in another, so obviously different, often exist within similar global configurations of climate.

Floods do not just happen because of rains only. Floods happen because rain falls on saturated ground, because warm rain falls on an existing snow-pack, because rain falls heavily throughout an entire basin, or because the basin has been changed (either naturally or otherwise) so as to retain or heighten floodwaters that would have otherwise rolled on through without making a mess. Floods are usually more localized than droughts, both temporally and spatially because they require these specific pre-existing hydrologic and meteorological conditions.

Spring melting of winter snow is always a time of high river flow. In many regions, river channels shape themselves to accommodate these annual events, building banks and gradually raising floodplain terraces in response to each year's high water. Melt waters will usually be released from the snowbound mountains in an orderly progression as springtime temperatures begin to rise. Floods will occur if temperatures rise faster than expected or if rain falls on snow that is already near its melting point. Destructive flooding does not always have to follow high precipitation.

Floods are fickle, requiring very specific conditions beyond merely humid weather. A flood might hit one basin yet inexplicably ignore another basin nearby. Whether widespread or local in scale, floods are set up by large-scale atmospheric processes recently including possible climate change effects. Whether the flood occurs or not when those conditions are present is another matter that befuddles flood forecasters.

By 2025, one-third of the population of the developing world is expected to face severe water shortages. Yet, even in many water-scarce regions, large amounts of water annually flood out to the sea. Some of this floodwater is committed flow to flush salt and other harmful products out of the system and maintain the ecological aspects of estuaries and coastal areas (Seckler, et al., 1998).

3.2 Droughts

Droughts are manifestations of climatic fluctuations associated with large scale anomalies in the planetary circulation of the atmosphere. They imply precipitation absence or weak precipitation occurrence during a long time over large areas. It is very difficult to identify and to clearly determine the onset as well as termination point. It is a creeping phenomenon and its effects accumulate slowly and tend to persist over longer periods of time. The local and regional climate features are important in drought generation. This subsidence originates an adiabatic compression which leads to an increase of temperature and therefore to a reduction of the relative humidity. The subsidence further produces an inversion of temperature, which increases the static stability of the atmosphere and so prevents the formation of sufficiently thick clouds to generate precipitation. Since at the start the air is already dry, the relative humidity decreases further as the air mass subsides. The formation of clouds becomes difficult or if formed they dissipate fast by evaporation of cloud drops or crystals in the dry environment.

People start to feel drought when there is not enough water. When drought comes everybody is concerned, if it lasts everybody tries to do his/her best for the combat, but when it passes away everybody forgets except those who have been hurt (Yevjevich, et al., 1983).

In spite of all the inconveniences that drought cause, it is not yet sufficiently understood in terms of characterization and impact assessment. There is no general accepted definition of drought. Current definitions are based on different disciplines such as meteorology, hydrology, agriculture, geography, water resources development, water supply, industry, navigation, recreation, etc. From social and economic points of view the definition of drought should consider not only water supply but also water demand. Hence, drought depends on the water use practices and the population. Drought appears when there is significant temporal or spatial water shortage in an area. Droughts are basically economic and social phenomena.

Drought occurrences result mainly from variations inherent to atmospheric circulation. It may depend also on such factors as the transport of volcanic ash and dust, which reduce the solar radiation reaching the earth's surface.

Drought is more than a simple lack of rainfall. Drought is a persistent moisture deficiency below long-term average conditions that, on average, balance precipitation and evapotranspiration in a given area. Not all droughts are created equally. Similar moisture deficits may have very different consequences depending on the time of year at which they occur, pre-existing soil moisture content, and other climatic factors such as temperature, wind, and relative humidity. Drought can be defined in terms that go beyond the meteorologist's rainfall measurements.

Hydrologic drought occurs when surface water supplies steadily diminish during a dry spell. If dry conditions continue, groundwater levels could begin to drop. Various drought characteristics such as duration, magnitude, and intensity are related to each other in a region (Sirdaş and Şen, 2003).

Agricultural drought occurs when a moisture shortage lasts long enough and hits hard enough to negatively impact cultivated crops. Soil conditions, groundwater levels, and specific characteristics of plants also come into play in this functional definition of drought.

Ecologic drought is detrimental to native plants that do not have the benefit of irrigation. Drought depends on the persistence of dryness over months or years.

The crop yield in a year can be compared with its long-term average and drought intensity can be classified linguistically in a fuzzy manner as nil, mild, moderate, severe, or disastrous, based on the difference between the current yield and the average yield. Various researchers in different parts of the world have developed drought indices that can also be included along with the weather and climate variables to estimate crop yield. For example, Boken and Shaykewich (2002) modified Wester Canada Wheat Yield Model (Walker, 1989) drought index using daily temperature and precipitation data and Advanced Very High Resolution Radiometer (AVHRR) satellite data. The modified model improved the predictive power of the wheat yield model significantly. The performance of the regression techniques have been found to have improved significantly by including satellite data based variables.

Climate data during a growing season cannot be used for obtaining the long-term estimates simply because the long-term estimates are required prior to even sowing of the crop. As the yield is known to be influenced most by weather and climate conditions during the growing season, it is a common practice to estimate yield using climate data. Attempts to obtain long-term estimates that do not employ climate data are limited (Şen and Boken, 2005).

Aridity is a permanent climatic feature. Drought is an extreme event of a time and area process. In driest zones, the variability of precipitation is the highest.

Economic consequences of droughts are more important for humid regions because of unpreparedness of people to recurrent drought events and the large investments in agriculture may undergo large losses from droughts. Economic losses caused by droughts are mainly the reduction in the production of crops, cattle, industrial goods, poor navigation and hydro-power. Among the secondary effects of droughts are soil erosion and consequent dust storms, forest fires, plant diseases, insect plagues, decrease of personal and public hygiene, increased concentration of pollutants, degradation of water quality, harmful effects on wildlife, and deterioration in the quality of visual landscape.

In contrast to floods, droughts start in a comparatively sudden manner, have a relatively short duration and are restricted to local influences. While floods, earthquakes and cyclones are disasters associated with extreme high events, drought is the result of the low extreme as non occurrence of sufficient water. They seldom cause dramatic losses of human life except through famine.

Temporary of permanent migration have been a common form of social adjustment to droughts through history.

One of the dramatic long-term impacts of droughts, combined with the human activities, is the degeneration of productive ecosystems into desert in the process called desertification. Desertification is not exclusively as a consequence of drought, but it may be accelerated by droughts through phenomena as wind action in dry years, soil erosion in drought and post drought periods, and particularly through human activities that are responsible for poor management of land, soil, crops and herds. The desertification areas reflect more of the solar radiation than the original land by causing changes in thermal regime of the atmosphere that in turn may tend to extend or intensify droughts.

Throughout the history drought has been the companion of humanity. Over years drought impacts have been felt in agriculture, water supply. Industry, pollution control, energy, recreation and a host of other activities related to water and society.

3.2.1 Drought impacts

Droughts have socio-political, economic and environmental impacts which are interrelated with each other. Drought effects are intricately related to the environmental economic and social fabric of a given region or an entire nation. Its consequences are population shifts and/or reduction, alteration of the social structure, large economic hardship and significant environmental perturbations. In order to better understand the drought concept the following four different events must be considered.

1) Aridity: It is a permanent natural condition and a stable climatic feature of a region.

2) Drought: It refers to a temporary feature of the climate or to regular of unpredictable climatic changes.

3) Water Shortage: It is understood mostly as a man-made phenomenon reflecting the concern with temporary and small area water deficiencies, and

4) Desertification: It is a part of an alteration process in the ecological regime often associated with aridity and/or drought but principally brought about by human-made activities which change the surrounding environment to a significant degree.

Droughts represent temporary imbalance in the irradiative transfer with characteristics that it is persistent lower than average precipitation with uncertain frequency, duration and severity; has unpredictable consequences; represents overall diminished water resources, and has diminished average carrying capacity of ecosystem.

Among the drought effects are deterioration of farm and rangelands, increase wind erosion, reduction in natural flora and fauna, air quality deterioration, brush and pest infestations, and strained water supply.

Responses to droughts necessitate resource use regulation, rationing and/or recycling, institutional measures. Possible social consequences of droughts may be bulleted as follows.

1) Agricultural: Loss of income, increased indebtedness, bankruptcy, and dislocation.

2) Regional: Regional instability, migration intensity increase, unemployment increase, and regional economic sector disruptions.

3) National: Increased government payments to agricultural sector, foreign trade losses, rising prices, health effects and food shortage, and

4) Worldwide: Severe health effects, disruptions in world social order, international conflicts, starvation, and famine.

The biosphere may respond fast, e.g. to droughts, but also very slowly to imposed changes, such as the climate change.

4. Effect of Climate Change on Groundwater Recharge

The effect of climate change on streamflow and groundwater recharge varies regionally and between climate scenarios, largely following projected changes in precipitation.

Groundwater is the major freshwater source especially for arid and semi-arid regions, but unfortunately there has been very little attention or study on the potential climate change effects on these freshwater resources. Most of the works are concentrated on humid regions. Aquifers in arid and semi-arid regions are replenished by floods at possible recharge outcrop areas through fractured and fissured rocks, solution cavities in dolomite or limestone geological setups as well as through main stream channels of Quaternary alluvium deposits. At convenient places along the main channel engineering infrastructures such as levees, dikes, successive small scale groundwater recharge dams may be constructed for groundwater recharge augmentation. The groundwater recharge areas must be cared for isolation from fine silt accumulation after each flood occurrence or at periodical intervals. Furthermore, flood inundation areas are among the most significant groundwater recharge locations in arid and semi-arid regions. Accordingly, their extents must be delimited by considering future climate change effects.

Understanding the relative importance of climate, vegetation, and soils in controlling groundwater recharge is critical for estimating recharge rates and for assessing the importance of these factors in controlling aquifer vulnerability to contamination. Understanding the role of climate and vegetation in controlling recharge will also be valuable in determining impacts of climate change and land use change on recharge.

The aquifers that are in contact with present day hydrological cycle will be affected by climate change. These are referred to as unconfined or shallow aquifers. On the other hand, deep and especially confined aquifers are not in contact with the present day hydrological cycle and consequently their effect from climate change is virtually negligible. They include fossil groundwater storages.

Groundwater recharge depends on several factors such as infiltration capacity, stochastic characteristics of rainfall and climate factors. The spatial and temporal distribution of the rainfall mainly controls the natural groundwater recharge. In arid regions, recharge occurs through the ephemeral streams, which flow through the wadi course but most of the water is absorbed in the unsaturated zone before reaching the aquifer. In semi-arid regions, the recharge is irregular and occurs only in the periods of heavy rainfalls. In humid regions, recharge is mainly in the winter period. In the summer period, most of the rainfall becomes soil moisture and evaporates. In cold areas the melting of ice suddenly recharges the groundwater.

Unsaturated zone has a unique capability in helping to assess impacts of climate change on groundwater resources. The potential impacts of climate change can be assessed by focusing on porous, fractured and karstic (carbonate rock, dolomite, limestone) aquifer systems. Especially, fractured and karstic aquifers are the most responsive to changes in recharge as typically they have low specific yields (i.e. they have drainable porosities) in comparison with porous flow systems. Karstic rocks are soluble and the aquifers might show exacerbated water table lowering if predicted increases in atmospheric CO_2 contents along with temperature rise induce rapid enlargement of fracture apertures and enlargement in the solution cavities. Dissolution of carbonate rocks (karstic media) might become more vigorous by time and accordingly the hardness of groundwater sources is expected to increase, leading to possibly unacceptable water quality.

As a result of climate change, in many aquifers of the world, the spring recharge retreats towards winter with more or less the same rates, but summer recharge declines dramatically. Understanding the relative importance of climate, vegetation, and soils in controlling groundwater recharge is critical for estimating recharge rates and for assessing the importance of these factors in controlling aquifer vulnerability to contamination. Understanding the role of climate and vegetation in controlling recharge will also be valuable in determining impacts of climate change and land use change on recharge.

There are two types of groundwater recharge processes, namely, direct and indirect. Direct groundwater recharge mode is more sensitive to climate change than indirect natural recharge. Direct recharge can be defined as water added to the aquifer through the unsaturated zone by direct percolation of rainfall at the spot where it falls. Indirect recharge occurs where water fulfils the soil moisture deficits and evapo-transpiration process before reaching to groundwater reservoir. Indirect recharge occurs from percolation to the aquifer following surface water runoff (surface water category) and localization (localized category) in joints, poundings, and lakes or through the wadi beds. Indirect recharge produced as a result of infiltration during flood pulses is considered as the most important contribution to the groundwater table in wadi channels. The amount of water that is added to the aquifers by such processes is much larger than the direct recharge. Small local floods merely compensate for soil moisture deficits and evapo-transpiration particularly during dry season and therefore the amount of water that goes to the water table will not be a significant contribution. While comparing direct and indirect recharge, Simmers (1990) concluded the following:

1) Estimates of direct recharge can be more reliable than indirect recharge.

2) With increasing aridity, direct recharge becomes less significant while indirect recharge more in terms of total recharge to an aquifer.

3) Recharge occurs to some extent even in the most arid regions, although increasing aridity decreases the net downward flux with greater time variability.

4) Successful groundwater recharge estimation depends on first by identifying the probable flow mechanism and important features influencing recharge for a given locality.

Coupled with the changes in the hydrological cycle and probable inducement of climate change basic elements, the groundwater recharge is also interactively affected due to the following events.

1) Changes in precipitation, evapo-transpiration, and runoff are expected to influence recharge. It is possible that increased rainfall intensity may lead to more runoff and less recharge.

2) Sea-level rise may lead to increased saline intrusion of coastal and island aquifers, depending on the relative position of sea-level to the groundwater table level.

3) Changing in precipitation imply changes in CO_2 concentrations, which may influence carbonate rocks dissolution and hence formation and development of karstic groundwater aquifers.

4) Natural vegetation and crops changes reflection of climate change may influence recharge.

5) Increased flood events contribute to unconfined aquifers in arid and semi-arid zones and hence they affect groundwater quality in alluvial aquifers of wadis.

6) Changes in soil organic carbon may affect the infiltration properties above aquifers and consequently the groundwater recharge.

The above mentioned factors indicate that the groundwater-focused organization should take interest in global climate change issues in order to protect the groundwater resources effect from the implications.

Due to the global warming, a smaller proportion of the winter precipitation falls as snow. The spring snowmelt peak therefore is reduced while the flood risk in winter is probably increased. In summer, mean monthly groundwater recharge and streamflow are reduced by up to 50% potentially leading to problems concerning water quality, groundwater withdrawals and hydropower generation (Eckhardt and Ulbrich, 2003). Some water supplies could become unusable due to the penetration of salt water into rivers and coastal aquifers as sea level rises. Changes at the surface water resources frequency and magnitude would influence the aquifer storage replenishment through natural recharge. Water quality may also respond to changes in the amount and timing of precipitation.

Coastal aquifers may be damaged by saline intrusion as salty groundwater rises due to sea-level rise. The movement of the salt-front up in aquifers would affect freshwater pumping plants near the coastal line.

Relative sea-level rise adversely affects groundwater aquifers and freshwater coastal ecosystems (high confidence). Rising sea level causes an increase in the intrusion of salt water into coastal aquifers. Other impacts of sea-level rise are likely to include changes in salinity distribution in estuaries, altered coastal circulation patterns, destruction of transportation infrastructure in low-lying areas, and increased pressure on coastal levee systems.

Higher sea levels associated with thermal expansion of the oceans and increased melting of glaciers will push salt water further inland in rivers, deltas, and coastal aquifers (very high confidence). It is well understood that such advances would adversely affect the quality and quantity of freshwater supplies in many coastal areas.

Another great advantage of groundwater is that as water slowly percolates down into the aquifer it is usually purified of biological pollutants. Thus, groundwater is usually the best source of drinking water, especially in arid, semi-arid and rural areas of developing countries where water treatment facilities or desalination plants are not available. In water resources poor countries, such as the Arabian Peninsula countries, the desalination plants are used to maintain groundwater resources as strategic planning assets for future generations or emergency situations (Al-Sefry, et al., 2004). Groundwater resources assessment for any purpose in arid region wadi drainage basins requires uncertainties to be taken into calculation. Among these uncertainties the climate change impact may well be accounted for future planning, operations and managements. Unfortunately, deterministic crisp approach does not open way for risk assessments under uncertain climate, recharge, and aquifer and drainage basin properties. In arid regions, wadis have Quaternary depositions of different facies and grain size distributions depending on the paleogeologic environmental processes. Consequently, any measurement at a point may be significantly different than other points within the same wadi. For instance, several aquifer test lead to different hydrogeologic parameter estimations, and the rainfall variability has temporal and spatial trends. Hence, rather than regional average parameter values, their probabilistic consideration gives rise to determination of any parameter value under an acceptance certain risk level such as 10 %. It is necessary to manage the groundwater resources under such risk levels. The application of the methodology is presented for wadi Fatimah that lies in the central western part of the Kingdom of Saudi Arabia (Al-Sefry, et al., 2004).

The critical issue facing many groundwater aquifers today is that the volume of water withdrawal exceeds long-term recharge, resulting in rapidly declining groundwater levels in many areas. Closely related to this is the key issue of managing groundwater access and utilization, since groundwater is a common property concern with individual benefits and collective costs.

The rainfall and infiltration elements of the hydrological cycle in arid regions indicate temporal and spatial variations in a random and sporadic manner. Such variations may be exacerbated groundwater replenishment facilities.

Groundwater recharge estimation has become a priority issue for both developed and underdeveloped countries, especially in dry areas like central Africa, where rainfall is both temporally and spatially irregular. The rapid agriculture and industrial growth in such areas has dramatically changed the groundwater resources withdrawal pattern. Groundwater withdrawal in excess of recharge has lowered the hydraulic heads in the aquifers, and resulted in increased pumping energy costs and reduced the rate of removal. Continual withdrawal in excess of recharge and possible climate change effects will in time ultimately remove all of the recoverable water.

In arid and semi-arid regions, the recharge component in any groundwater balance assessment presents difficulties for direct measurement in the field. It is more difficult, especially, at the upstream portions, because of inaccessibility by routes, heterogeneity in climate variability and porous medium properties. In dry climates the recharge component of hydrologic cycle becomes the most significant element after the rainfall occurrences, but its direct calculation is not possible. The recharge rates in arid and semi-arid regions are small but this small amount must be estimated with care and accuracy. The groundwater storage rates in alluvial aquifers of the middle and lower wadis depend on recharge amount, and consequently, the human activities (domestic, agricultural and man-induced climate change) for survival can be developed based on the storage volumes without significant problems. On the other hand, now in the Middle East, there are plans for strategic exploitation and use of groundwater resources, especially, on the western regions along some potential wadi courses. This makes the recharge estimation more important for such arid and semi-arid regions of the country. Consideration of these difficulties, especially, during the last decade led many researchers to use the simple method of chlorine mass balance (CMB) approach in groundwater recharge estimation studies. This is based on the assumption that the chloride concentrations in the rainfall and recharge area are in steady state balance, i.e., input is equal to output without chloride storage change during a time period, which is taken as a storm duration, month or year. Such a simple and very ideal situation is further physically simplified, and then the recharge estimation is obtained provided that there are field records on rainfall amount and chloride concentrations in the rainfall and groundwater. In thousands of geochemistry studies within the wadis, the chloride is found only in negligible amounts, except after a rainfall event (Bazuhair et al., 2002, Subyani and Şen, 2004). The long-term rainfall and its chloride concentration amounts have a balanced situation, i.e., steady-state condition. This implies stable and long-term averages, as the classical CMB method requires. A hidden assumption is that the fluctuations around the average rainfall and chloride records must be very small so that they are negligible, however by the consideration of climate change such small but accumulatively effective increments must not be ignored.

The average recharge rates, calculated by chloride mass-balance method in the central western wadi aquifer systems along the Red Sea range from 0.52 to 11.57 mm/yr or 0.35 to about 7% of average annual rainfall (Bazuhair, et al., 2002).

All studies related to the estimation of groundwater recharge must be based on strong foundation of comprehensive hydrologic and climatologic data of the study area; otherwise the calculated recharge rates will have large uncertainties. Information about rainfall amount, seasonality, intensity, duration and distribution is of prime importance because infiltration of rainfall is the main source of groundwater recharge. Besides this, there are several factors, which govern the rate of groundwater recharge such as aquifer depth, infiltration capacity of the unsaturated soil profile, confining layers in the wadi beds, slope of the land surface and aspect, temperature, wind, and relative humidity. Unfortunately, in many methods of groundwater recharge estimation we use the literature-derived values of some variables without knowing the reliability of the data.

Rainfall-based annual recharge maps should be prepared for active aquifer monitoring. The quantity of recharge to an aquifer must be considered in any integrated management program as equivalent to the "safe yield" or quantity of groundwater that could be withdrawn form an aquifer on a sustainable basis. This type of maps will be very helpful in evaluating the effects of climate variability on groundwater recharge and exploitable groundwater resources. Many researchers believe that climatic conditions mainly govern the recharge rates, although vegetation and soils also interactively control the groundwater recharge.

As the rainfall is the main source of groundwater recharge, our understanding of the Middle East and the south eastern Asia spring and summer monsoon mechanism should be developed in order to utilize the water resources more effectively. The onset and withdrawal dates of monsoon rains and their spatial distribution over the southwest of Arabian Peninsula must be studied and published, in order to utilize the undammed floodwaters by establishing the weirs on the major wadis for retaining floodwater for artificial recharge purposes. The groundwater can be stored behind subsurface dams for future exploitations.

Unsaturated zone has a unique capability in helping to assess impacts of climate change on groundwater resources. The potential impacts of climate change can be assessed focused on fractured carbonate aquifer systems (having variable degrees of fracture development, i.e., karstification) because,

1) fracture flow aquifers are the most responsive to changes in recharge as typically they have low specific yields (i.e., they have drainable porosities) in comparison with inter-granular flow systems,

2) carbonate rocks are soluble and the aquifers might show exacerbated water table lowering if predicted increases in atmospheric $C0_2$ contents along with temperature rise induce rapid enlargement of fracture apertures;

3) if dissolution of carbonate rocks does become more vigorous then potentially the hardness of groundwater could be expected to increase, leading to possibly unacceptable water quality.

Application of the climate change scenarios and software is necessary to forecast changes in aquifer geometries, hydraulic parameters (permabilities, storage coefficients), flows, water balances and water quality.

One of the major advantages of storing water in aquifers is that it can be stored for years, with little or no evaporation loss for use in drought years as a supplementary source of water supply. It also has the advantage that storage can be near or directly under the point of use and is immediately available through wells and pumps on demand. The groundwater mixture procedure can be used in order to augment the groundwater potentiality even under the climate change conditions (Şen, et al., 2003)

5. Engineering Systems and Dams

Among the altered hydrological aspects are dam operations, historical and current forest management practices (higher runoff associated with altered forest structure, composition), urban development, historical and current forest management practices, agricultural runoff, hydroelectricity generation, highway construction and culverts.

More importantly, the prospect that a global warming will alter in unknown ways local and regional supplies and demands reinforces the need for institutions that facilitate adaptation to whatever the future brings and promote more efficient water management and use.
There are four major ways of storing water, namely, in the soil profile, in underground aquifers (including underground dams), in small reservoirs and in large reservoirs behind large dams. Storage in the soil profile is extremely important for crop production, but it is relatively short-term storage, often only sufficient for a period of days. Other three kinds store water for periods of months, in small reservoirs, or years, in aquifers and large reservoirs. Aquifers, small and large reservoirs all serve an indispensable role in water storage and each alternative has strong comparative advantages under specific conditions of time and place. If it is possible to do so substantial gains can be achieved by combining all three storage technologies in an integrated engineering system. Any configuration consisting of a set of engineering storage structures for water resources management is referred to as an engineering system.

Engineering structures include dams, reservoirs, weirs, levees, aqueducts, dikes, wells, kanats, culverts, canals, distribution pipe network, treatment and desalination plants etc., which help human to cope, adopt, operate and manage inherent temporal and/or spatial variability in water resources planning, design, operation, management and maintenance. To the average citizen engineering structures are largely invisible and taken for granted. Yet they help insulate people from wet and dry years and moderate other aspects of our naturally variable climate. Indeed the engineering structures help us to almost forget about our complex dependences on climate.

Water resources engineering systems are major social engineering units that are essential for individuals, societies, countries and humanity, in general. The development of any country is measured with the water resources system availability and adaptation to natural (droughts and floods) and man-induced variations (including climate change).

Engineering systems help to manage the water resources utilization according to demand and supply side requirements in the best possible (optimum) manner. Climate change can be regarded as one of the accumulating variability. Different management alternatives are developed and applied in water sector over many years, but they do not take into account the climate change effects explicitly. However, some water resources managers become to care about the climate change effects, which will become rather significant in the coming decades especially in the mid-latitudes and some subtropical climate belts of the world. If reservoirs are full after a wet period then a short-lived summer flood may not end a water resources drought caused by prolonged lack of dam inflows. Hence, droughts are not dependent on possible climate changes only but critically on the water resources system characteristics and especially on their management.

Climate change will affect the complex infrastructure of engineering systems in place to manage the society's water and existing climate variability. It is not that the construction of additional dams which indicates the development level of a country, but rather an efficient management program of the existing dams.

The potential impact of climate change on the hydrologic regime is a crucial question for water resources engineering system management. Potential change in hydrologic regime resulting from changed climate is an important topic in contemporary hydrology and water resources management.

An understanding of mechanisms linking large-scale climate variability with regional conditions also forms the basis for reducing the uncertainty associated with assessing regional impacts of climate change over decadal-to-centennial periods. A region-specific ability to project the consequences of global change is now required, for example, by decision-makers concerned with long-term fixed capital investments in infrastructures such as dams, water diversion systems, and flood damage mitigation systems that are vulnerable to shifts in hydro-climatic regime.

The IPCC (2000) review of climate impact studies suggests large differences in the vulnerability of water resource systems to climate variables. Isolated single-reservoir systems in arid and semiarid areas are extremely sensitive. They lack the flexibility to adapt to climate impacts that could vary from decreases in reservoir yields in excess of even more than 50 percent at one extreme to increased seasonal flooding at the other. In contrast, highly integrated regionally interconnected systems are inherently more robust.

Changes in the quantity, quality, and timing of runoff stemming from greenhouse warming would affect in-stream water uses such as hydroelectric power generation, navigation, recreation, and maintenance of ecosystems. These changes might also affect in-stream water demands, directly or indirectly. For example, changes in streamflows would alter actual and potential hydroelectric power generation through dams, which in turn would affect the demand for substitute sources of electricity. Maintaining minimum in-stream flows to protect an endangered species or recreation benefits when supplies become scarcer requires major adjustments in the use of water. On the other hand, protecting off-stream uses could threaten the sustainability of some aquatic ecosystems. Tradeoffs between in-stream and withdrawal water uses would increase if water supplies became scarcer or more variable as a result of climate change. The optimum and sustainable maintenance of streamflow volumes is possible through a rational, integrated and inter-regional management programs.

Climate change has the potential to either aggravate or alleviate an area's water situation. On balance, however, the impacts are likely to be adverse because the existing water infrastructure and use are based on an area's past climate and hydrology records. During most of this century, dams, reservoirs, pumps, canals, and levees provided the primary means of adapting to climate and hydrological variability and meeting the growing demands for water. While the focus was on supply-side solutions, institutions that establish opportunities as well as incentives to use, abuse, conserve, or protect water resources were slow to adapt to the challenges of growing scarcity, rising in-stream values, and the vulnerability and variability of supplies.

In recent decades, however, the high financial and environmental costs of water projects, along with limited opportunities for building additional dams and reservoirs to develop new water supplies, have shifted the focus away from new construction to improved management of existing supplies and facilities, and also toward demand management. New infrastructure may, in some instances, eventually prove to be an appropriate response to climate-induced shifts in hydrological regimes and water demands. But it is difficult to plan for and justify expensive new projects when the magnitude, timing, and even the direction of the changes at the basin and regional levels are unknown. Narrowing the range of uncertainty for improved water planning, operation and management depends on a better understanding of

1) the processes governing global and regional climates;
2) the links between climate and hydrology;
3) the impacts of the climate on unmanaged ecosystems;
4) the impacts of ecosystem change on the quantity and quality of water; and 5) the impacts of increased atmospheric CO_2 on vegetation and runoff.

In the meantime, the possibility that a warming could result in greater hydrological variability and storm extremes should be considered in evaluating margins of safety of long-lived structures such as dams and levees that are under consideration anyway. In particular, low-cost structural and managerial modifications that ensure against the possibility of a range of climate-induced impacts should be sought. Unlike the structural supply-side approach, demand management that introduces additional incentives to conserve and opportunities to reallocate supplies as conditions change does not require long lead times, large financial commitments, or accurate information about the future climate. Integrated management of existing supplies and infrastructure at the river basin and watershed levels offers a potentially cost-effective means of increasing reliable supplies and resolving water conflicts in many regions. While the prospect of climate change adds another element of uncertainty to the challenge of matching future supplies with demands through different storages (dams, weirs, dikes, etc.), it does not alter what needs to be done to ensure that water is managed and distributed wisely.

In general, climate change is expected to lead to more precipitation coupled with more evaporation, but the important question is how much of this precipitation will end up at water deficit areas? If not then regional management of water engineering infrastructures comes into view with sustainable water distribution programs. On the other hand, probable precipitation increase in some areas and decline in others is another indication for regional water resources distribution to needed areas through an efficient management programs.

The main solution for reducing the local and regional vulnerability to climate change requires improved water resources engineering systems management prior to any capacity increase with new engineering structure design and construction (dams). In this manner the existing supplies will be used efficiently. Long-term management studies will also indicate for the necessity of engineering structures, if any for the region. Efficient management strategies should include regulations and technologies for directly controlling land and water use, incentives and taxes for indirectly affecting behavior, the construction of new dams and pipelines to boost supplies, and improvements in water-management operations and institutions. Other adaptation measures can include removing levees to maintain flood plains, protecting waterside vegetation, restoring river channels to their natural form, and reducing water pollution.

Vast and complex infrastructure of dams and pipes can be planned and built to provide justified fresh water resources distribution based on an effective management program which takes into account a multi-purpose optimization helping to industry, disposal of wastes, transportation facilities, hydroelectricity generation, crops irrigation, and floods and droughts risk reduction.

The vulnerability and sensitivity of water engineering systems and management rules, the strengths and weaknesses of technologies and policies might help to cope with adverse impacts and take advantage of possible beneficial effects.

Certain aspects of water resources and engineering infrastructure are very sensitive to both climate and to how to manage complex water systems. It is, therefore, necessary to have mediators in the form of engineering structures (such as dams) in order to offset or diminish the sensitivity to various expected and unexpected changes in the future. Changes in management of the engineering systems requires understanding what changes would be most effective and then applying the will and direction of those responsible. Water managers and policymakers must start considering climate change as a factor in all decisions about water investments and the operation of existing facilities and systems.

A continued reliance solely on current engineering practice may lead to make incorrect and potentially dangerous or expensive decisions. Conventionally, water resources system operation and distribution practices should be designed and for the most part are operated assuming that future climatic and hydrologic conditions will look like past conditions, which is no longer true. Accordingly, two of the most important coping strategies must be to try and understand what the consequences of climate change will be for water resources and to begin planning for and adapting to those changes through real-time operation and management programs. Dynamic management strategies of dams can be effective in mitigating the adverse impacts of climate change, but such policies need to be implemented before such changes occur to maximize their effectiveness.
Such management studies are available on a dynamical daily basis for Istanbul city including European and Asian sides' dams in an integrated manner (Şen and Kadioğlu, 2000).

Water engineering systems including more than one dam are highly developed and water managers have a long history of adapting to changes in supply and demand. Past efforts have been focused on minimizing the risks of natural variability and maximizing system reliability.

Many of the approaches for effectively dealing with climate change are little different than the approaches already available to manage risks associated with existing variability. Tools for reducing these risks have traditionally included supply-side options such as new dams, reservoirs, and pipelines, and more recently, demand-management options, such as improving efficiency, modifying demand, altering water-use processes, and changing land-use patterns in floodplains. This work is going on largely independently of the issue of climate change, but it will have important implications for the ultimate severity of climate impacts.

Sole reliance on traditional dam management responses is a mistake. First, climate changes are likely to produce, in some places and at some times, hydrologic conditions and extremes of a different nature than current systems were designed to manage. Second, climate changes may produce similar kinds of variability but outside of the range for which current infrastructure was designed and built. Third, relying solely on traditional methods assumes that sufficient time and information will be available before the onset of large or irreversible climate impacts to permit managers to respond appropriately. Fourth, this approach assumes that no special efforts or plans are required to protect against surprises or uncertainties.

The role of subsurface dams must not be forgotten in the management of groundwater resources especially in arid and semi-arid regions where evaporation losses are high. Records of past climate and hydrological conditions are no longer considered to be reliable guides for the future water resources system design, operation and management. The design and management of both structural (dam, weir, dike, etc) and non-structural water-resource systems should allow for the possible effects of climate change, but little professional guidance is available in this area. Further research by hydrologists, civil engineers, water planners, and water managers is needed to fill this gap, as is broader training of scientists in the universities. There should be a systematic re-examination of engineering design criteria and operating rules of existing dams and reservoirs under conditions of climate change. Information on economic sectors most susceptible to climate change is extremely weak, as is information on the socioeconomic costs of both impacts and responses in the water sector. More work is needed to evaluate the relative costs and benefits of non-structural management options, such as demand management and water-use efficiency, or prohibition on new floodplain development, in the context of a changing climate.

The flexibility of large storage structures is further reduced when they are multipurpose and potentially conflicting demands (for example, hydropower generation and irrigation) exist. Other factors limiting the flexibility of large dam operations are the many parties and levels involved in their management and countless institutional prerequisites.

Small dams have the advantage of being operationally efficient. They are flexible, close to the point of use and require relatively few parties for management. Because of these attributes, they can be responsive to demands, the supply to demand mismatch can be small and managerial and institutional issues are easier to handle.

Large surface dams have the advantage of greater yield relative to the available inflow than small reservoirs, and their yield is generally more reliable. This is because of lower evaporation loss fractions in large reservoirs are due to their greater depth. Large dam reservoirs are more complex to operate than small reservoirs and groundwater systems from the standpoint of meeting the needs of the individual user.

If climate changes, as a result of global warming manifests, the need for freshwater storage will become even more acute. Increasing storage through a combination of groundwater and large and small surface water facilities (dams) is critical to meeting the water demands of the twenty-first century.

In spite of uncertainties, current evidence justifies consideration of reservoir emissions in international climate change policies and mechanisms as well as their inclusion in national emissions inventories.

Just as dams are impacting global warming, a changing climate holds major implications for the safety and performance of dams. Increases in the severity and frequency of droughts would reduce hydropower production and water storage. Increased floods threaten dam safety and may increase reservoir sedimentation. Climate change will add to existing stresses on riverine ecosystems from dams, canalization, pollution and watershed degradation. The safety of existing dams needs to be reassessed in the light of possible precipitation changes. Feasibility and impact studies for future dams should allow for the hydrological uncertainties of a warming world.

Adaptations to increased morphological dynamics such as erosion and accretion also include physical and institutional aspects. Physical adaptations would focus on protection against bank erosion and dredging of navigation channels which suffer from increased sedimentation. River training and bank protection have long been practiced in Bangladesh, in particular on a local scale. The scale of the rivers in this context is also significant, and the priority of such measures is low. Due to increases in the runoff volumes (partially due to climate change) some rivers may show a continuous increase in river width, which is partly compensated by a decrease in river depth. Monitoring and predicting morphological changes become more and more important to prepare for anticipatory measures to protect the increasingly important engineering infrastructure. Knowledge and experience to analyze the morphological behavior of the rivers has growing interest but still inadequate for proper management and has to incorporate the impacts of climate change. Other institutional arrangements include programs to relocate the victims of erosion. At present, erosion victims often move to low lying lands that are hardly gained from accretion.

On the other hand, climate changes cause alternate freezing, thawing and expands soil, increases moisture content and decreases cohesion thus facilitating dislodgement, dispersion and transport.

Soil type, topography and soil cover are among the passive forces affecting erosion and transport of sediment from land surface. Soil mass and soil constituents as the soil characteristics provide the main factors for the sedimentation. Soil mass properties are the permeability, volume change and dispersion properties, moisture content, and frost susceptibility. Permeability determines percolation rate and affects infiltration and runoff rates. Volume change and dispersion properties cause soil swelling looses and dispersion of soil thereby reducing the cohesion and facilitating dislodgement and transport. Moisture content reduces cohesion and lengthens erosion period by increasing the period of precipitation excess.

6. Environmental Prospects

It has been stated by Dunn (1986) that several problems have arisen from the increased use of energy. For example, oil spillages result from the tanker transportations. Burning of various energy resources has caused global scale carbon dioxide rise due to especially fossil fuels. If the necessary precautions are not considered in the long run, this gas in the atmosphere could exceed the natural levels and may lead to climate change. Another problem is big scale air pollution in large cities, especially, during cold seasons. Use of fossil fuels in automobiles causes exhaust gases that give rise to another sort of air pollution as well as the surface ozone concentration increases, which are dangerous for human health and environment. Air pollution leads to acid rains that cause pollution of surface and groundwater resources, which are the major water supply reservoirs for big cities.

In order to reduce all these unwanted and damage full effects, it is consciously desirable to shift towards the use of environmentally friendly, clean and renewable energy resources, especially, the solar energy alternatives. It seems that for the next few decades, the use of conventional energy resources such as oil, coal and natural gas will continue, perhaps at reduced rates with the replacement of renewable sources to a certain increasing rate. It is necessary to take the necessary measures and developments toward more exploitation of solar and other renewable energy alternatives by the advancement in the research and technological progress. Efforts will also be needed in conversion and moving towards a less energy demanding way of life.

Use of energy is not without penalty in that energy exploitation causes many undesirable degradation effects in the environmental surrounding and life. It is, therefore, necessary to reduce the environmental impacts down to a minimum level with the best energy usage. If the energy consumption goes at present level with present energy sources which are mainly of fossil types, then the future prospective cannot be expected as sustainable or without negative impacts. It has been understood by all the nations since about 1970s that the energy usage and types must be changed towards cleaner and environmentally friendly sources so as to reduce both environmental and atmospheric pollutions. Sustainable future development depends in a major scale on the energy sources pollution potential. The criterion of sustainable development can be defined as the development, which meets the needs of the present without compromising the ability of future generations to meet their own needs. Sustainable development within a society demands a sustainable supply of energy in addition to an effective and efficient utilization of energy resources. In this regard, solar energy provides a very potential alternative for future prospective development. The major environmental problems are classified by Dincer (2004) as follows,

1) major environmental accidents,
2) water pollution,
3) maritime pollution,
4) land use and sitting impact,
5) radiation and radioactivity,
6) solid waste disposal,
7) hazardous air pollution,
8) ambiant air quality,
9) acid rain,
10) stratospheric ozone depletion, and finally,
11) global climate change leading to greenhouse effect.

The last three items are the most widely discussed issues all over the world. The main gaseous pollutants and their impacts on the environment are presented in Table 1. Herein, plus and minus signs indicate proportional and inversely proportional effects whereas ± implies either effects depending on circumstances.

At present, large-scale fossil energy production is cheaper than the available solar energy generation alternatives. However, conventional energy generation technologies based on fossil fuel have reached maturity leaving little room for significant cost reduction. Indeed, current research on these technologies is mainly concerned with pollution abatement (e.g. clean coal technologies or the use of hydrogen) rather than with improving fossil fuel conversion efficiencies, which are nearing their theoretical limits. Similarly, the important progress in energy conservation serves mainly to mitigate the rapid increase in energy demand, but does not contribute directly to reduce the production costs of fossil energy. In contrast, solar technologies still have large potential for improvement, pending appropriate research and development studies. Moreover, the true price of fossil energy must include scarcity and pollution components to allow a valid evaluation of social costs and benefits of alternative energy options.

Table 1. Main gaseous pollutants

Gaseous pollutants	Greenhouse effects	Stratospheric ozone depletion	Acid precipitation	Smog
Carbon monoxide (CO)	+	±		
Carbon dioxide (CO_2)	+	±		
Methane (CH_4)	+	±		
Nitric oxide (NO) and Nitrogen dioxide (NO_2)		±	+	+
Nitrous oxide (N_2O)	+	±		
Sulfur dioxide (SO_2)	-	+		
Chlorofluorocarbon(CFCs)	+	+		
Ozone (O_3)	+			+

The long term sought energy sources are hoped to have the following important points for a safer and pleasant environment in the future.

1) Diversity of various alternative energy resources both conventional and renewable with steadily increasing trend in the renewables but steadily decreasing trend by time in the conventional energy resources,

2) Quantities must be abundant and sustainable for the long future,

3) Acceptable cost limits and compatible prices with strong economic growth,

4) Energy supply options must be politically reliable,

5) Friendly energy resources for the environment and climate changes,

6) Renewables are domestic resources that help to reduce the important energy alternatives,

7) They can support small to medium scale local industry,

The renewable energies are expected to play an active role in the futures energy share because they satisfy the following prerequisites.

1) They are environmentally clean, friendly and do not produce greenhouse gases.

2) They should have sufficient resources for larger scale utilization. For instance, the solar energy resources are almost evenly distributed all over the world with maximum possible genera table amounts increasing towards the equator.

3) Intermittent nature of solar and wind energy should be alleviated by improving the storage possibilities

4) Cost effectiveness of the renewables is one of the most important issues that must be tackled in a reduction direction. However, new renewable energies are now, by and large, becoming cost competitive with conventional forms of energy.

Hydropower is an already established technological way of energy generation. In the industrial and surface water rich countries the full scale development of hydroelectrical generation by turbines at large scale dam sites are already exploited to the last limitations, and consequently, smaller hydro systems are of interest in order to gain access to the marginal resources.

Wind power is by now is reliable and established technology which is able to produce electricity at cost competitive with coal and nuclear. On the other hand, solar energy applications in buildings are of interest for heating, cooling and day lighting. Furthermore, solar electricity production from photovoltaics has already made great advancements since the beginning of 1980’s.

Economic growth and prosperity rely heavily on adequate energy supply at reasonably low costs. Unfortunately, energy is the main source of pollution in any country on its way of development. It is well known, by now, that the SO_2 emission from the fossil fuels is the main cause of acid rain as a result of which more than half the forests in the Northern Europe have already been damaged. On the global scale, increase in the emission rates of greenhouse gases and in particular CO_2 represents colossal treat to the world’s climate. Various theories and calculations in the atmospheric research circulations have already indicated that over the last half century, there appeared a continuously increasing trend in the average temperature value up to 0.5 ^{o}C. If this trend continues in the future, it is expected that in some areas of the world, there will appear extreme events such as excessive rainfall and consequent floods, droughts and also local imbalances in the natural climatic behaviors giving rise to unusual local heat and cold. Such events will also affect the world food production rates. In order to decrease degradation effects on the environment and atmosphere, technological developments are sought since 1973 oil crisis.

It has been recently realized that renewable energy sources and systems can have a beneficial impact on the following essential technical, environmental, and political issues of the world. These are:

1) major environmental problems such as acid rain, stratospheric ozone depletion, greenhouse effect and smog,
2) environmental degradation,
3) depletion of the world's non-renewable conventional sources such as coal, oil, natural gas,
4) increasing energy use in the developing countries, and
5) world population increase.

7. Conclusions

Although previous studies in the literature are comprehensive as for the basic understandings of the climate change and implications on hydrological cycle components and water resources but there are still many gaps, uncertainties and unanswered questions, which can be summarized as follows.

1) Cost effectiveness of various climate change impacts such as floods, droughts, mismanagements,
2) there have been a few studies that have summarized potential response strategies and assessment how water managers might respond in practical applications,
3) there are different trends in different parts of the world and even among sub-areas of the same region, but unfortunately such regional variations have not been taken into consideration through regional water resources management. Climate change is expected to affect the regional integrated water resources planning, operation and maintenance.
4) Although soil moisture is related to probable climate change but infiltration capacity as one of the significant hydrological component for the groundwater resources storage is not addressed with the perspective of groundwater storage increase or decrease on decadal time scales.
5) The significance of infiltration and flood for groundwater recharge in arid and semi-arid regions are not assessed by considering the climate change
6) Artificial groundwater recharge enhancement possibilities can be mentioned due to climate change. Especially fractured medium and karstic region (solution cavity) groundwater recharge can be related to climate change. For instance, the effect of warmer rainfall on solution cavities should play role in the expansion of solution cavities and consequently groundwater recharge,
7) Drainage basin areas are considered as they appear in humid regions, but arid wadi concept and fresh water resources are not covered at all,
8) The rate of groundwater recharge estimate by using carbon-14 isotopes are mentioned, but the same estimation in arid regions by chloride concentration is not considered,
9) Rather than the trend as the indication of climate change, it is preferable in future studies to consider the breaking of record.
10) Flash flood appearances in arid and semi-arid regions are not covered from the climate change point of view,
11) Sedimentation is mentioned very briefly in the previous studies, hence it is necessary to present a more detailed calculation,
12) Adaptive real-time reservoir and fresh water distribution must be presented through an effective management project,

13) Multi-purpose and multi-dam operation and management studies must be considered with the effects of climate change future studies,

It is expected that the future studies will cover the following points towards more comprehensive understanding and application of climate impact.

1) New scenarios for future climate change effectiveness. These are gathered in the Special Report on Emission Scenarios (SRES),

2) Different application of SRES scenarios on water resources availability and management assessments,

3) Climate change and variability increased effects including more illuminating and detailed knowledge on extreme events (floods, droughts), engineering aspects, management strategies,

4) Strategic planning of fresh water resources storages under the effect of different SRES scenarios,

5) New techniques and suggestions for adaptation against the climate change related man-made influences,

6) In fresh water resources assessment, the role of technological developments and especially desalination plants in arid regions must be considered,

7) The effect of climate change on expected flood inundation maps must be documented,

There are increasing or decreasing trends in streamflow discharge, which may be partially due to climate change effect but this effect cannot be quantified definitively. Climate change glacier retreats towards winter season are observable and this is obvious in streamflow timing in many areas. Rather than streamflow variable only an integrated assessment of different hydrological elements must be evaluated simultaneously in order to arrive at more sound evidence of climate impact through detectable trends.

A growing number of studies suggest that climate changes will increases the frequency and intensity of the heaviest precipitation events, but there is little agreement on detailed regional changes in storminess that might occur in a warmed world. Contradictory results from models support the need for more research, especially to address the mismatch between the resolution of models and the scales at which extreme events can occur.

The current state-of-the-science suggests that plausible climate changes, projected by general circulation models, raise a wide range of concerns that should be addressed by national and local water managers and planners, climatologists, hydrologists, policymakers, and the public.

Little work has been done on the impacts of climate change for specific groundwater basins, or for general groundwater recharge characteristics or water quality. Some studies suggest that some regional groundwater storage volumes are very sensitive to even modest changes in available recharge.

Variability in climate already causes fluctuations in hydroelectric generation. Climate changes that reduce overall water availability will reduce the productivity of hydroelectric facilities. Reliable increases in average flows would increase hydropower production. Changes in the timing of hydroelectric generation can affect the value of the energy produced. Specific regional impacts are not well-established.

Catchments with a substantial snow-pack in winter are expected to experience major changes in the timing and intensity of runoff as average temperatures rise (very high confidence). Reductions in spring and summer runoff, increases in winter runoff, and earlier peak runoff are all common responses to rising temperatures. The ability of existing systems and operating rules to manage these changes has not been adequately assessed.

Climate models are still unable to make precise regional predictions. In addition, the hydrological cycle is extremely complex. A change in precipitation may affect surface wetness, reflectivity, and vegetation, which then affect evapo-transpiration and cloud formation, which in turn affect precipitation. Meanwhile, the hydrological system is also responding to other human activities such as deforestation, aforestration urbanization, and the over-use of water supplies.

Little information is available on how climate changes might affect groundwater aquifers, including quality, recharge rates, and flow dynamics. New studies on these issues are needed.

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TRENDS AND VARIATIONS OF AIR TEMPERATURE AND PRECIPITATION SERIES IN NORTHERN CYPRUS

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In this study, seasonal mean, maximum, minimum temperature and normalised precipitation series of Girne (Kyrenia) and Lefkoşa (Nicosia) stations in Northern Cyprus have investigated with respect to the long-term trends and changes. Main conclusions are as follows:

(i) Statistically significant increasing (warming) trends were found in mean temperatures of Girne, while mean temperatures of Lefkoşa were statistically random against to any trend in all seasons; (ii) Statistically significant and the strongest warming trend showed up mainly in minimum temperatures at both stations in all seasons. Observed night-time warming at both stations is stronger than warming in mean temperatures; (iii) Increasing trends in maximum temperatures were not as strong as in mean temperatures at Girne and in minimum temperatures of both stations. Only summer and autumn maximum temperatures were characterized with a significant warming at Lefkoşa; (iv) Warmer than long-term average temperature conditions in the series was detected especially after the year 1990; (v) Although precipitation series did not show any significant trend at both stations, spring precipitation at Girne has tended to decrease and summer precipitation has indicated an increasing trend at Lefkoşa; (vi) Precipitation series were characterized mainly by wetter or drier than long-term average conditions, such as a dry period from 1993 to 2000 in winter precipitation of Girne, and a period of increased summer precipitation from 1992 to 2003 at Lefkoşa.

INTRODUCTION

Climate change, whether its global or regional scale, is one of the most significant and far-reaching challenges that the human societies living in the Earth's surface have faced in the 21st century as it was in the 20th century. The Mediterranean basin takes part mainly in the subtropical zone between the humid mid-latitudes and the dry and hot northern Africa (tropical) zone. It is likely that the risks facing the Mediterranean countries are in two directions: first includes changes in the hydrological cycle and water resources, aridity and desertification conditions, and second consists of increased extreme events such as heat waves, heavy rainfall and floods.

Some previous studies about observed temperature change and variability over the Mediterranean basin and its surroundings could be listed as follows: Estaban-Parra and Rodrigo (1995); Türkeş *et al.* (1995, 1996); Kutiel and Maheras (1998); Ben-Gai *et al.* (1999); Price *et al.* (1999); Brunetti *et al.* (2000); Türkeş *et al.* (2002); Türkeş and Sümer (2004). Main findings and conclusions from some of these studies have been summarized as follows:

Esteban-Parra and Rodrigo (1995) found that mean and minimum temperatures increased and maximum temperatures did not represent any trend in the northern Spanish. Kutiel and Maheras (1998) studied variations in temperature regimes of the Mediterranean at six stations. They found that warming trend was more evident over the western Mediterranean, and the greatest warming trend in winter and cooling trend in autumn for the eastern Mediterranean. Ben-Gai *et al.* (1999) revealed a significant decreasing trend in both daily maximum and minimum temperatures during the cool season and an increasing trend during the warm season. Price *et al.* (1999) found, for two stations of Cyprus, an increasing trend with a rate of about 1°C/100 years in annual mean temperatures. They showed that minimum temperatures generally increased at a larger rate than in maximum temperatures resulting in a decrease in diurnal temperature range (DTR). Brunetti *et al.* (2000) determined that maximum and minimum temperatures were characterized with an increasing trend especially over the southern Italy. Türkeş *et al.* (2002) found general increasing trends for annual, winter and spring mean temperatures particularly over the southern regions of Turkey, and decreasing trends for summer and particularly autumn mean temperatures over the northern and the continental inner regions. Annual, winter, spring and summer maximum temperatures indicated an increasing trend at many stations. Türkeş *et al.* (2002) also showed that majority of urbanized and rapidly urbanizing stations of Turkey have been experiencing a significant night-time warming especially during the warm and dry period of the year. Summer night-time warming rates are generally larger than those in spring and autumn night-time temperatures, whereas night-time warming rates of spring and summer are generally stronger than those in spring and summer daytime temperatures. Night-time warming rates were detected to have been stronger in the Aegean, Mediterranean and South-eastern Anatolia regions, all of which are characterized by the Mediterranean macroclimate type. In a recent study, Türkeş and Sümer (2004) indicated that DTRs significantly decreased at most of the urbanized and rapidly urbanizing stations throughout the seasons except partly in winter.

Precipitation variations over the Mediterranean region are characterized mainly by runs of dry and wet (rainy) periods: generally wet periods are weak, short and infrequent, while dry periods are strong, long and frequent. Some examples for the studies about precipitation changes and trends of the Mediterranean region, especially in the central and eastern Mediterranean are as follows: Kutiel (1996); Türkeş (1996, 1998, 2003); Brunetti *et al.* (2000); Ramos (2001); Norrant and Douguedroit (2006). Kutiel (1996) examined dry and wet years, seasons and sequences at stations of Thessalonica, Athens, Nicosia and Jerusalem, and found that the number of extremely wet years or seasons was double the number of extremely dry years or seasons, while wet sequences are fewer and shorter than dry sequences. Türkeş (1996, 1998) found that annual and winter precipitation series of many Turkish stations decreased, most of which are located over the Mediterranean rainfall region of Turkey. Long-term variations in precipitation series, however, were generally characterized by successive dry and wet periods. For annual and winter precipitation series, wet conditions generally occurred during 1940s, 1960s, late 1970s, early 1980s and mid-late 1990s, whereas dry conditions generally dominated over early-mid 1930s, early-mid 1970s, mid-late 1980s, early 1990s, and 1999/2000 over most of Turkey (Türkeş, 1998, 2003). Brunetti *et al.* (2000) investigated series of annual and seasonal temperature and precipitation representing respectively northern and southern Italy, and revealed that temperature and precipitation trends are almost always anti-correlated except in winter at north, where an anomalous behaviour was evident till about 1980. The result was that the

Italian climate became warmer and drier especially at south since about 1930. Ramos (2001) evaluated precipitation distribution patterns and their changes in the Mediterranean region. He found that annual rainfall did not show a clear tendency, but during the last decade inter-annual variability decreased. Ramos (2001) indicated that percentage of dry years did not increased, while percentage of wet and very wet years decreased. Norrant and Douguedroit (2006) revealed precipitation trends were appear to be significantly diminishing, primarily during winter months, March in the Atlantic region, October in the Mediterranean Spain, December in the Lions and Genoa Gulfs, January, winter and annually in Greece, winter and annually in Italy and winter in the Near East, and increasing in April in two gulfs.

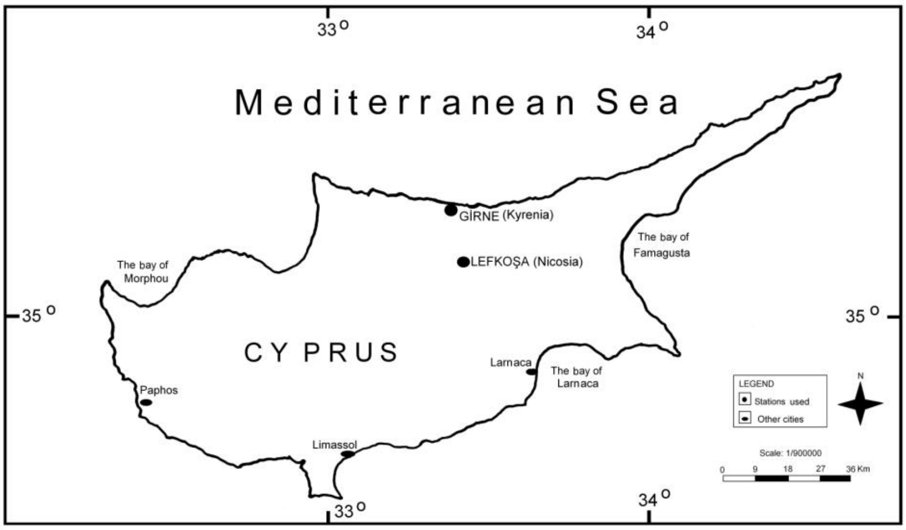

Figure 1. Locations of Girne and Lefkoşa along with other major cities over Cyprus.

Nevertheless, there is still a great gap of information for the climate variability in Northern Cyprus. Thus, main aim of the study is determined as follows:

(1) To analyse seasonal temperature and precipitation series recorded at Girne (Kyrenia) and Lefkoşa (Nicosia) in terms of their homogeneity and randomness characteristics; (2) to detect long-term trends and variations in temperature (mean, maximum and minimum) and precipitation series of Girne and Lefkoşa stations by applying mainly non-parametric time-series methods; and (3) to explain trend features of the series (i.e., nature and magnitude and change points of observed trends).

DATA AND METHODS

We have used monthly mean, monthly mean maximum and minimum temperatures and monthly precipitation totals recorded at Girne and Lefkoşa stations of Northern Cyprus Turkish State Meteorological Administration (Figure 1). Both stations have a Mediterranean type climate with a high seasonality in climatic elements particularly in precipitation. Climatic data of two stations comprise these periods: 1967-2003 for mean temperature series and 1975-2003 for precipitation totals. Maximum and minimum temperature series include the period of 1975-2003 for Girne and 1976-2003 for Lefkoşa. Seasonal precipitation totals were normalised in order to eliminate likely effects of high year-to-year variability in spring and summer seasons and in particular very low rainfall amounts in summer.

For the present study, inhomogeneity means non-climatic strong jumps (step-wise changes) in mean of the series. Homogeneity of the time series was checked with non-parametric Kruskal-Wallis (K-W) homogeneity test (Sneyers, 1990). Although minimum and some mean temperatures series seem to be inhomogeneous, we have made use of them because this non-randomness are very much likely due to observed rapid and statistically significant trends in the series rather than non-climatological stepwise changes, which is main subject of the present study.

Table 1. Long-term trend statistics and their significance levels for seasonal average air temperatures (°C) and normalised seasonal precipitation anomalies of Girne and Lefkoşa stations according to Mann-Kendall rank correlation test, and least squares linear regression (LSLR) approach and Student's *t* test.

	Winter				Spring			
STATIONS/Variables	Mann-Kendall		**LSLR**		Mann-Kendall		LSLR	
GİRNE	$u(t)$	P	β	Student t	$u(t)$	P	β	Student t
Mean temperature	3.6**	0.000	0.074	4.38**	1.79	0.073	0.028	1.84
Maximum temperature	1.54	0.124	0.039	1.55	0.49	0.624	0.013	0.62
Minimum temperature	3.97**	0.000	0.092	4.66**	4.63**	0.000	0.106	7.19**
Precipitation	0.20	0.841	1.395	0.45	-1.73	0.084	-2.073	-2.14*
LEFKOŞA								
Mean temperature	-0.34	0.734	-0.006	-0.43	-0.20	0.841	-0.014	-0.97
Maximum temperature	0.88	0.379	0.034	1.14	1.56	0.119	0.040	1.66
Minimum temperature	2.81**	0.005	0.056	2.81**	4.15**	0.000	0.090	4.92**
Precipitation	-0.59	0.555	-0.038	-0.03	-0.43	0.667	0.112	0.14
	Summer				Autumn			
STATIONS /Variables	Mann-Kendall		LSLR		Mann-Kendall		LSLR	
GİRNE	$u(t)$	P	β	Student t	$u(t)$	P	β	Student t
Mean temperature	4.11**	0.000	0.066	4.91**	2.98**	0.003	0.059	4.306**
Maximum temperature	1.61	0.107	0.025	1.34	1.43	0.153	0.033	1.957
Minimum temperature	5.57**	0.000	0.163	10.7**	5.27**	0.000	0.112	9.096**
Precipitation	-0.36	0.719	0.002	0.01	0.75	0.453	0.653	0.558
LEFKOŞA								
Mean temperature	1.84	0.066	0.012	0.99	-0.04	0.992	-0.006	-0.510
Maximum temperature	2.19*	0.029	0.048	2.84**	1.66	0.097	0.037	2.081*
Minimum temperature	5.26**	0.000	0.115	9.73**	4.27**	0.000	0.084	5.648**
Precipitation	1.61	0.107	0.810	2.04	0.41	0.968	0.483	0.561

(*) Statistically significant trend at the 0.05 level of significance.
(**) Statistically significant trend at the 0.01 level of significance.

We have applied non-parametric Mann-Kendall (M-K) rank correlation test to detect any non-linear secular trend in the mean of series (Sneyers, 1990). Using two-sided test of normal distribution, the null hypothesis of absence of any trend was rejected for large values of $|u(t)|$. Beginning of the secular trends or change points and the significant warming/cooling (dry/wet) periods in temperature (precipitation) series were determined by means of time-series plots of the $u(t)$ and $u'(t)$ values calculated from the sequential analysis of M-K test.

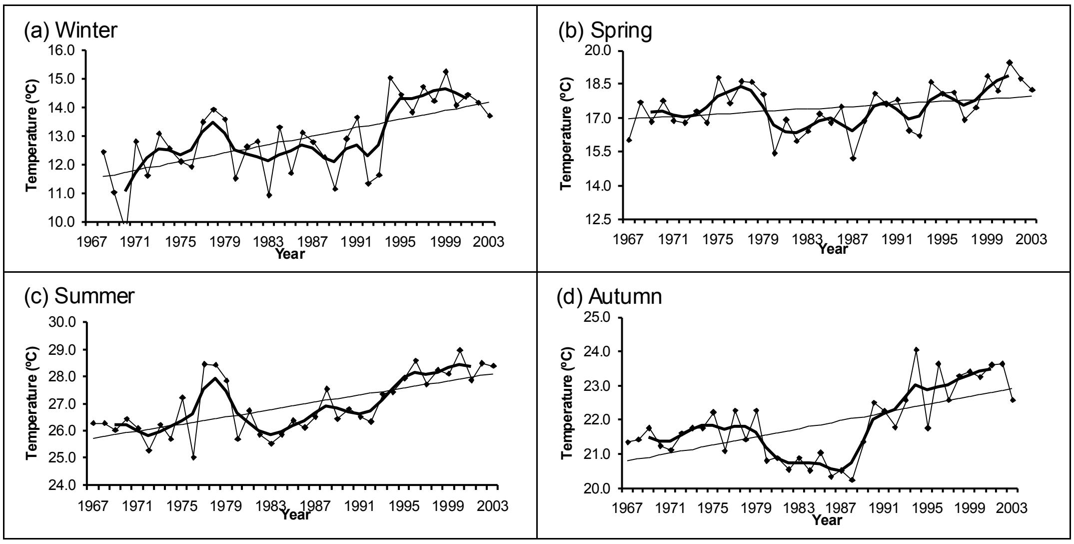

Figure 2. Interannual variations in mean air temperature series of Girne station with the least squares linear fit to trend (—). Year to year variations in the seasonal series are smoothed by using a five-point Gaussian filter (▬▬).

We have made use of least squares linear regression (LSLR) method to detect linear long-term trends in the series. Statistical significance of each estimated β coefficient was tested by Student's t test with (n-2) degrees of freedom according to Student t distribution. The null hypothesis of absence of any trend was also rejected by using two-tailed test for large values of $| t |$.

We have also used a five-point Gaussian filter, as a low-pass filter, to examine the long-term fluctuations visually in the series.

RESULTS OF ANALYSIS

Trends and Variations in Mean Temperatures

Seasonal mean temperatures indicate an apparent increasing trend at Girne (Figure 2). According to both M-K *u*(*t*) test and LSLR approach, these observed warming trends are statistically significant at the 0.01 level of significance in all seasons except that in spring season (Table 1). Observed increasing trend in spring mean air temperatures is not significant in terms of all trend methods.

According to the time-series plots of the *u*(*t*) and *u*'(*t*) values (not given here due to the page limitation), apparent change points have existed in winter, summer and autumn mean temperatures, in addition to the long-term trend in the same series. For mean temperatures of Girne station, beginning point of the significant change on the series was located in the year 1990 for winter and 1993 for summer and autumn seasons. The period of significant warming began in the mid-1990s for winter and summer immediately after the change point, and in the late 1990s for autumn.

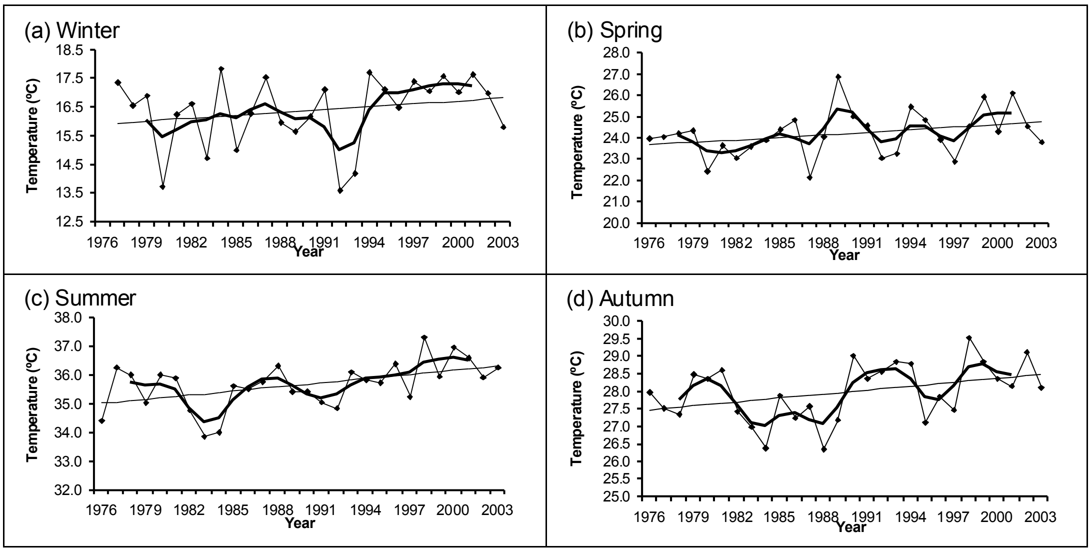

Figure 3. As in Figure 2, but for maximum temperature series of Lefkoşa.

Trends and Variations in Maximum Temperatures

Maximum air temperatures of both Girne and Lefkoşa stations have tended to increase in all seasons except in spring for Girne station. Increasing trends at Lefkoşa station started earlier than at Girne except in winter. Observed increasing trends in maximum temperature series, however, are statistically significant only in summer and autumn seasons at Lefkoşa station (Figure 3). Warming trend is most pronounced for summer maximum temperatures of Lefkoşa, which is statistically significant in terms of M-K test and Student's *t* test made for LSLR approach (Table 1). Summer maximum temperatures of Lefkoşa are significant at the 0.01 level of significance according to Student's *t* test (Table 1).

Even though long-term increasing trends in maximum temperatures of Girne are not statistically significant, some change points were determined in 1993 for winter and 1998 for autumn. At Lefkoşa, change points were detected in 1993 for winter, in 1985 for spring and in about mid-1990s for summer and autumn. Only the trends of spring and summer maximum temperatures have reached a warming period very recently at the end of the series.

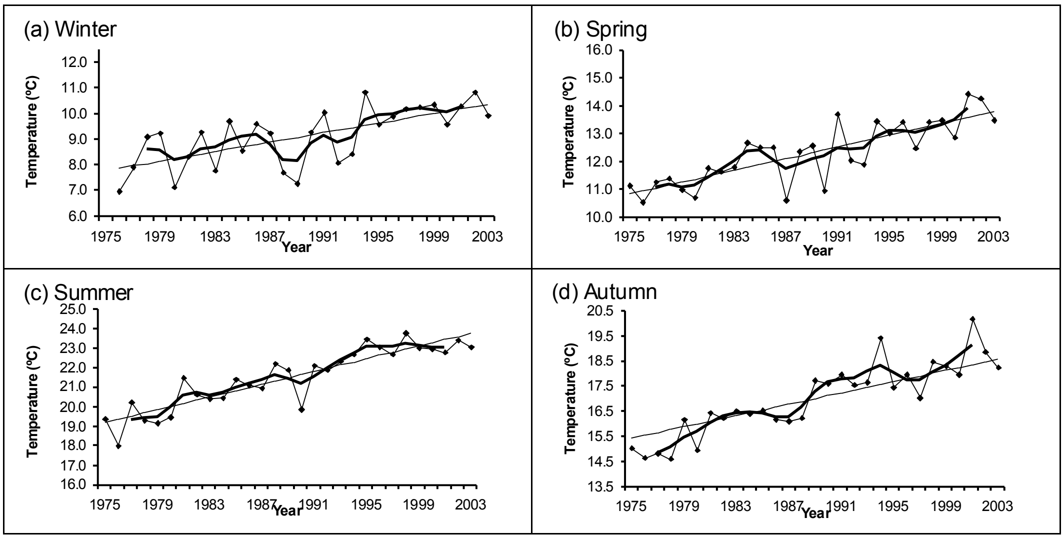

Figure 4. As in Figure 2, but for minimum temperature series of Girne.

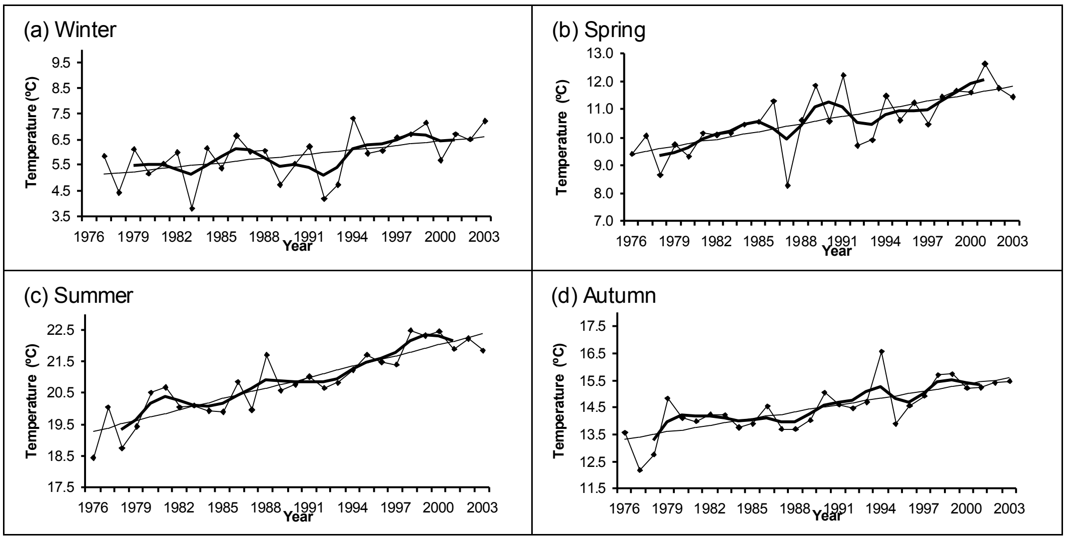

Figure 5. As in Figure 2, but for minimum temperature series of Lefkoşa.

Trends and Variations in Minimum Temperatures

The strongest and the systematic secular increasing trends are dominant in the seasonal minimum air temperatures in Northern Cyprus. All minimum temperature series of Girne and Lefkoşa stations have been clearly characterized by a long-term systematic increasing trend (Figure 4, 5). These observed long-term increasing trends at Girne and Lefkoşa stations are statistically significant for all trend tests at the 0.01 level of significance (Table 1).

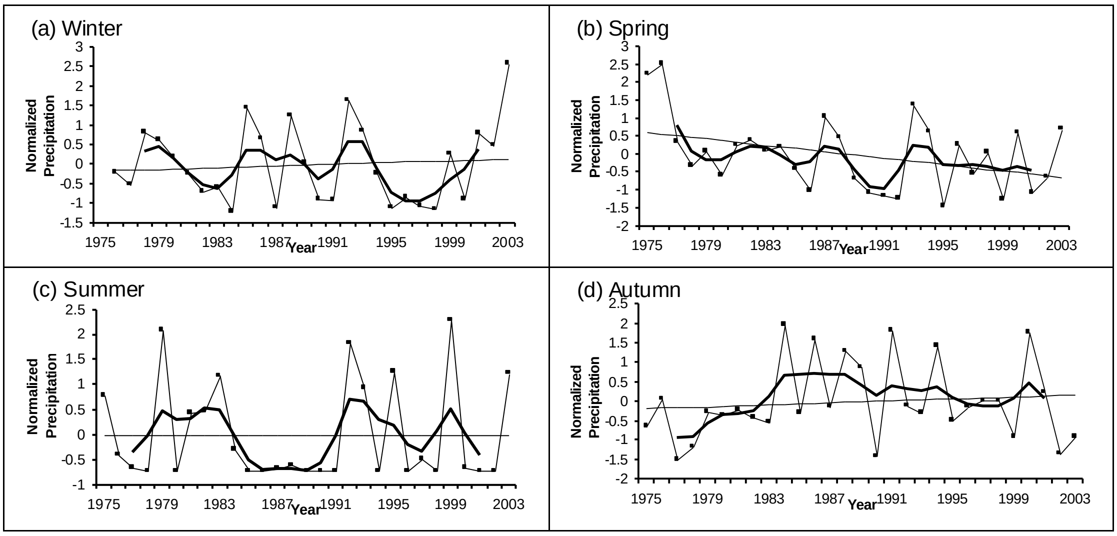

Figure 6. As in Figure 2, but for normalised precipitation anomaly series of Girne.

Apparent change points at Girne were located in 1993 for winter and spring, 1990 for summer and 1989 for autumn. Warming trends in these series also reach 0.95 level of confidence at about those years becoming a significant warming period of minimum temperature series. Similar spatial patterns are seen in minimum air temperatures of Lefkoşa station in comparison with Girne. Only differences found are in the beginning of the change points and thus following warming periods. Change points were detected in 1994 for winter, in 1984 for spring, and in 1991 and 1992 for summer and autumn seasons.

Trends and Variations in Precipitation

Normalised seasonal precipitation series of Girne and Lefkoşa stations are statistically random against to any trend from all trend tests (Table 1). On the other hand, even though they are not significant, normalised spring precipitation at Girne has tended to decrease apparently (Figure 6(b)), while normalised summer precipitation has revealed an apparent increasing trend at the Lefkoşa station (Figure 7(c)).

Winter precipitation anomaly series of Girne station have indicated an increase in recent years following a considerable dry period 1993-2000 (Figure 6(a)). Inter-annual variations of summer precipitation series are characterized by a fluctuation on a stable long-term average (Figure 6(c)), while variations in autumn precipitation series are also climatologically and statistically random against to any trend and serial correlation (Figure 6(d)).

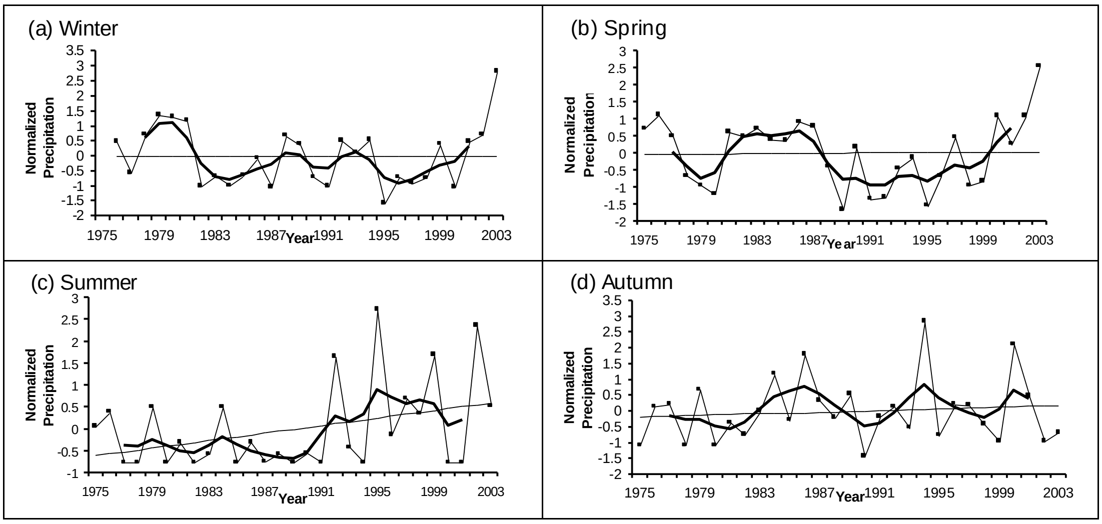

Figure 7. As in Figure 2, but for normalised precipitation anomaly series of Lefkoşa.

Normalised winter and spring precipitation series of Lefkoşa tended to increase in recent years from about 1999 to 2003 (Figure 7(a, b)). In spring, while a low-frequency fluctuation was dominant over the period 1975-1988; following period was characterized by an increased year-to-year variability (Figure 7(b)). Summer precipitation series have tended to increase slightly, and increased precipitation conditions were evident after the change point in 1992 (Figure 7(c)).

CONCLUSIONS

Seasonal mean air temperatures of Northern Cyprus have indicated an apparent increasing trend at Girne. According to the results from M-K $u(t)$ and Student's t tests, these observed warming trends are statistically significant at the 0.01 level in all seasons except that in spring. The beginning point of the significant change on the series of Girne was detected in 1990 for winter and 1993 for summer and autumn seasons. The period of significant warming began in the mid-1990s for winter and summer immediately after the change point, and in the late 1990s for autumn.

Maximum temperatures of Girne and Lefkoşa stations have tended to increase in all seasons except in spring at Girne. Observed warming trend is most pronounced for summer maximum temperatures of Lefkoşa. Change points at Girne were found in 1993 for winter and 1998 for autumn, while change points at Lefkoşa were detected in 1993 for winter, in 1985 for spring and in about mid-1990s for summer and autumn.

The strongest and systematic long-term increasing trends were detected in minimum temperatures of Girne and Lefkoşa in all seasons, all of which are statistically significant at the 0.01 level. Similar spatial patterns are seen at Lefkoşa compared with Girne: change points at Girne were located in 1993 for winter and spring, 1990 for summer and 1989 for autumn, while change points at Lefkoşa were detected in 1994 for winter, in 1984 for spring, and in 1991 and 1992 for summer and autumn.

With respect to temperature trends, there is a close coherence between our results and results of the studies performed for some Mediterranean countries, for example, such as Spain (Esteban-Parra *et al.*, 1995), southern Cyprus (Price *et al.*, 1999), Israel (Ben-Gai *et al.*, 1999), Italy (Brunetti *et al.*, 2000) and Turkey (Türkeş *et al.*, 1996, 2002).

All though they are not significant, normalised spring precipitation of Girne has tended to decrease apparently, while normalised summer precipitation of Lefkoşa has indicated an apparent increasing trend. On the other hand, winter precipitation of Girne has shown an increase in recent years following a considerable dry period occurred during the period 1993-2000. Winter and spring precipitations of Lefkoşa tended to increase during the period 1999 to 2003, and increased precipitation conditions in summer were also evident after the change point in 1992.

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CONTROL OF GREENHOUSE GAS EMISSIONS RESULTING FROM THE TRANSPORT SECTOR IN TURKEY

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This study deals with the estimation of greenhouse gas (GHG) emissions resulting from the transport sector in Turkey according to the UN IPCC methodology in order to investigate the effects of major parameters on the production of GHGs and provide effective solutions to control them.

Road transportation being the key source for GHG emissions within the transport sector has received more attention in the study and IPCC Tier II approach has been used in order to estimate the emissions inventory more accurately using the available data. Other contributers such as railways, domestic aviation and navigation have also been considered.

Some conclusions have been derived from the results of the model used and discussed in the paper.

1. INTRODUCTION

Climate being the average state of atmosphere and underlying land or water, on time scales of seasons, is typically described by the statistics of a set of variables such as temprerature, precipitation, wind, humidty etc. [1, 2]. Climate change refers to long-term fluctuations in temperature, precipitation, wind and other elements of the Earth's climate system which are influenced by the changes in concentration of certain gases in the atmosphere affecting Earth's absorbtion of radiation. [3]

Energy from the sun reaches Earth as a shorter wave length and certain portion of this energy is absorbed while the rest is reflected back into space as a longer wave length thermal radiation. A portion of the terrestrial radiation is absorbed by gases in the atmosphere, warming Earth's surface and atmosphere. This is known as "natural greenhouse effect" and it is essential for life on Earth due to the fact that average surface temperature of the Earth would be 33^{o}C lower than its present value in the absance of this effect. [1, 3, 4, 5]
However, when the atmospheric concentration of greenhouse gases such as carbon dioxide, methane, nitrous oxide etc. increases, problems may arise. Combustion of fossil fuels and some other human activities are the primary reasons for the increased concentration of carbon dioxide and other GHGs since the industrial revolution. During the last two centuries additional release of carbon dioxide by the human activities has been dominant, changing the balance of the CO_2 absorbed by the oceans and terrestrial vegatation, accelerating the rate of climate change. [4, 5]

Transport sector has significant effects on anthropogenic production of greenhouse gases as a result of fossil fuel combustion in internal combustion engines and jet engines. This study is aimed to estimate the GHG emissions produced by the transport sector, analyze and discuss the key sources and produce various senarios for future reductions in transport based GHG emissions in Turkey.

2. METHODOLOGY USED FOR ESTIMATING EMISSIONS

In order to estimate the GHG emissions produced by the transportation sector in Turkey, Intergovernmental Panel on Climate Change (IPCC) Tier 1 and 2/3 approaches are used.[6] Emissions of three direct greenhouse gases, carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) resulting from energy consumption in the transport sector and also indirect GHG emissions such as carbon monoxide (CO), nitrogen oxides (NO_X), non-methane volitile organic compounds (NMVOC) and sulphur dioxide (SO_2) are estimated. Transport sector consists of road transportation, domestic civil aviation, railways and national navigation.

Methods of calculation are based on the IPCC recommendations. In this paper, computations are carried out by using the IPCC Tier 2 approach, except for national navigation, and some modifications are made for road transportation according to the country specific conditions.

Road vehicles powered with internal combustion engines are one of the major sources of pollutant emissions such as CO, unburned HC's, NO_X and particulate matter (PM). These emissions are controlled within emission regulations. CO_2 is also a principal product of combustion and its production is directly related to the amount of fuel consumed. Other GHGs reported in this inventory such as CH_4 and N_2O are produced, again through the combustion process. CH_4 is a hydrocarbon resulting from the incomplete combustion of fuel admitted into the combustion chamber. N_2O is a product during the combustion process resulting from the partial oxidation of nitrogen present in the air and is also produced by catalytic converters.

To calculate emissions from road vehicles, various parameters such as vehicle and engine type, operating characteristics, specifications of fuel consumed, emission control systems, present maintenance conditions, fleet age, etc. have to be considered. In the present approach, initially vehicle fleet is divided into groups according to their categories, fuel type and model year and then passenger cars are grouped by their emission control technologies. For the computations, default values are taken from Revised 1996 IPCC Guidelines for emission factors. Vehicles with a gasoline engine in Turkey posses three different emission standarts being uncontrolled, ECE 15/04 and Euro I. In this study gasoline vehicles according to Euro III are classified as equivalent to the Euro I level. Diesel vehicles on the other habd are considered in a single classification being moderate control. Compiled data is then used in an equation;

$$\text{Emission [kt]} = \text{Emission Factor [g/km]} \times \text{Annual Vehicle Distance [km]} \times 10^{-9} \qquad (2.1)$$

to compute emissions for each vehicle. To calculate total emissions, the emission for each vehicle must be multiplied by the number of vehicles in use, for the year considered. Vehicle fleet of each year is obtained cumullatively by adding newly registered vehicles and subtracting the vehicles removed from registers.

In aviation, activities include all civil-commercial use of airplanes in scheduled and charter traffic for passengers and freight, but military and private aviation activities are not included. Also for national emission inventory, only domestic aviation is considered.

According to the Revised IPCC 1996 Guideliness, aircraft operations are divided into two parts as “Landing and Take-Off” (LTO) and cruise. The LTO cycle includes all activities below the altitude of 914 meters. Single LTO operation consists of both one take-off and one landing. Cruise is defined as activities that take place at altitudes above 914 meters. [6]

Emissions resulting from aircrafts are computed from LTO data of each aircraft model and using the IPCC recommended emission factors total values are calculated annually.

Railway emissions are computed for diesel engined locomotives in Turkey with default emission factors of IPCC, which are expressed as grams of emissons per kilograms of fuel consumed or grams of emissions per MJ of energy consumed. Required conversions are carried out and total fuel consumption data is used to obtain total annual emissions for railways.

To estimate emissions produced by national navigation, Tier 1 approach is used due to insufficient data. Calculation of CO_2 emissions by using Tier 1 approach recommended by IPCC is quite different from the calculation of the other greenhouse gases (CH_4, N_2O, NO_X, CO, NMVOC) and SO_2. For CO_2 and SO_2, the emission factors are estimated using the carbon emission factors, carbon content of fuel and combustion efficiency, but for the others defults from pre-calculated CORINAIR database are utilised.

To find the CO_2 emissons using Tier 1 method, initially fuel consumption values are multiplied by the conversion factors which are net calorific values and energy consumption is obtained. Then using the carbon emission factors of IPCC, the carbon content of the fuel is calculated assuming a combustion efficiency of 99%. Finally, to convert values to carbon dioxide, total oxidised carbon is multiplied by the molecular weight ratio of CO_2 to C which is 44/12. For the rest of GHG emissions, fuel consumption values are converted to energy content and then multiplied by the emission factors given in IPCC Guidelines. For SO_2 emissions, sulphur content in fuel and efficiency of abatement technology values are used.

3. RESULTS OF THE ESTIMATION OF GHG EMISSIONS

Trends in CO_2 and all other GHG emissions resulting from mobile combustion are influenced by national economic conditions and current fuel prices. Influence of economic crisis emerged in Turkey in certain years is clearly observed where fuel consumption values are considerably reduced. Economic crisis also effects the number of new-registered vehicles at those years, but in general total number of vehicles in the fleet, especially passenger cars show an increasing trend.

GHG emission trends are influenced by;

- the increase in number of vehicles in the fleet,
- improvements in vehicle technological that reduced fuel consumption per unit distance travelled,
- developments in consumer behaviour resulting in transportation method changes such as increase in the share of public systems, walking and cycling for short distances,
- changes in traffic flow patterns and conditions. [7]

CO_2 emissions produced by transportation sector in Turkey was 26 million tons in the Kyoto reference year of 1990 and increased approximately by 56% reaching 40.5 million tons in 2004. [8] CO_2 emissions per capita has also increased since 1990 from 0.46 to 0.57 million tons with an increase of 23% in 14 years. Sectoral distribution of GHG emissions is given in Table 3.1.

Table 3.1 Variation of national GHG emissions between 1990 and 2004

SECTORAL REPORT FOR NATIONAL GREENHOUSE GAS INVENTORIES (Gg)							
YEAR: 1990	CO_2	CH_4	N_2O	NOx	CO	NMVOC	SO_2
Transport (Total)	25954	3,37	0,84	263,31	1513,51	211,00	21,24
a. Civil Aviation	904	0,06	0,03	2,92	2,82	0,69	0,28
b. Road Transportation	24035	3,23	0,80	238,41	1499,83	208,09	17,56
c. Railways	516	0,04	0,01	12,04	4,23	0,89	0,49
d. National Navigation	497	0,03	0,00	9,93	6,62	1,32	2,91
YEAR: 2004	CO_2	CH_4	N_2O	NOx	CO	NMVOC	SO_2
Transport (Total)	40457	5,97	2,08	486,24	1811,90	306,85	28,98
a. Civil Aviation	4798	0,07	0,16	16,81	11,91	1,56	1,52
b. Road Transportation	34077	5,79	1,91	436,31	1780,66	301,39	23,01
c. Railways	374	0,03	0,01	8,72	3,06	0,65	0,35
d. National Navigation	1207	0,08	0,01	24,40	16,27	3,25	4,10

CO_2 emission from road transport also increased from 24 million to 34 million tons between 1990 and 2004, while CO_2 emission per capita increases form 0.42 million tons to 0.48 million tons (Figure 3.1).

The trend in total gasoline consumption shows a rapid increase in 1990 - 1996 period and then starts to decrease, while diesel fuel consumption shows a steady increase. *Dieselisation* is a rising trend in Turkey along with most of Europe. Diesel engines are more efficient than equivalent gasoline powered passenger cars and CO_2 emissions are lower per unit distance travelled. Therefore increase in diesel percentage over the whole passenger car fleet would benefit in emission reductions.

Alternative fuel usage with low carbon content also reduces the emission of CO_2. In Turkey, natural gas utilisation in road vehicles is very limited, only application beeing the fleet of city buses in certain districts of Istanbul and Ankara, so the influence and contribution in terms of pollutant emissions is negligible. Short term reduction of GHG emissions would benefit from the increase of these vehicles.

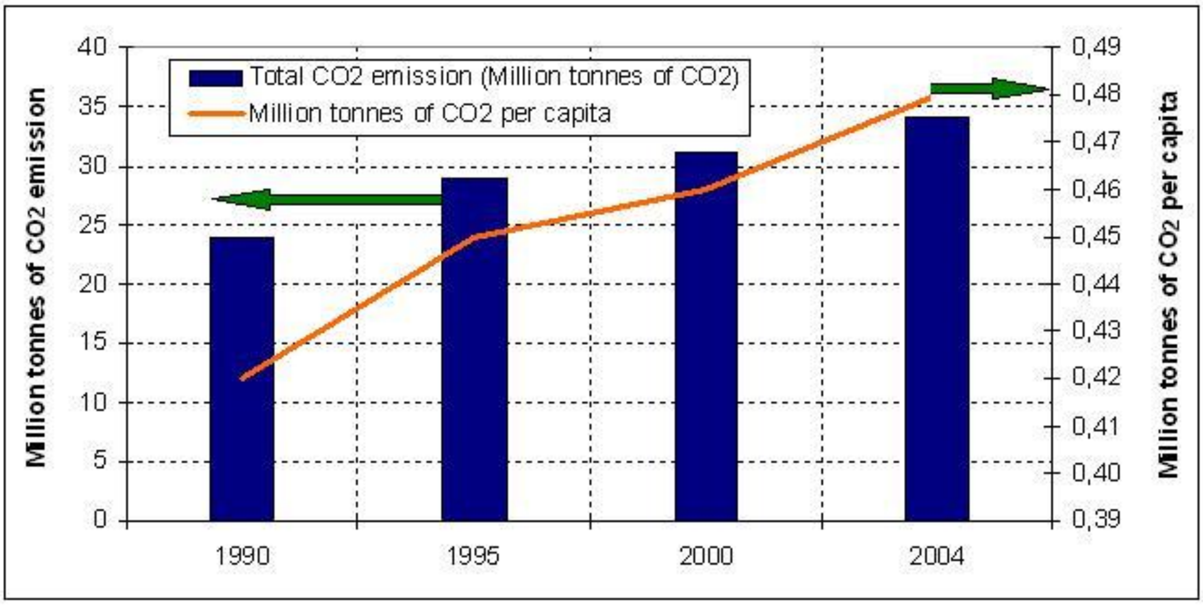

Figure 3.1 Variation of CO_2 emissions per capita and total CO_2 emissions produced by road transport [8]

In Figure 3.2 the contribution of vehicle categories to CO_2 emissions are given. Although the number of gasoline passenger cars increases, it can be seen that CO_2 emissions decrease. The main reasons are the decrease of mileage per vehicle and the development in vehicle technologies for lower fuel consumption.

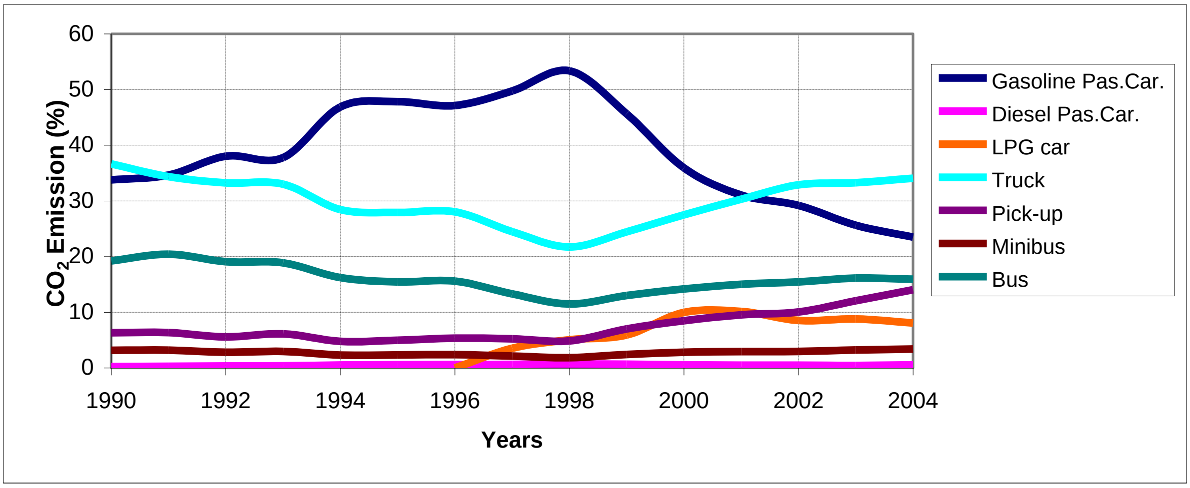

Figure 3.2 Contribution of vehicle classes to CO_2 emissions

Starting from 1994, Euro I emission regulations are put into action in Turkey to reduce CO, unburned HC and NO_X emissions. The advanced technologies used in those vehicles also reduced fuel consumption per vehicle and thus CO_2 emissions.

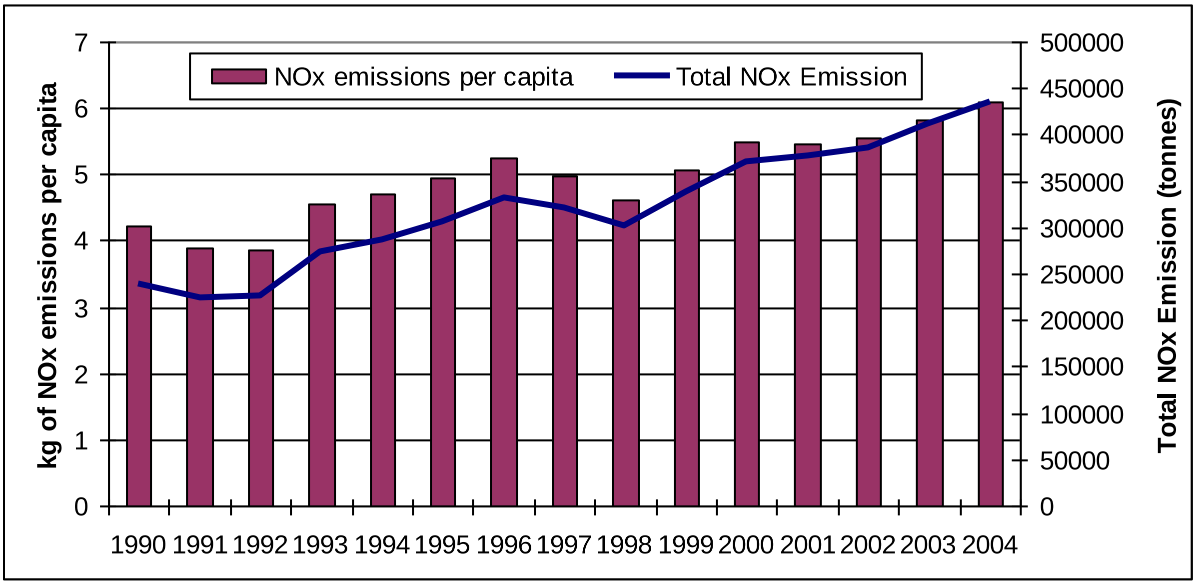

Figure 3.3 Variation of NO_X emissions produced by road transport and NO_X per capita

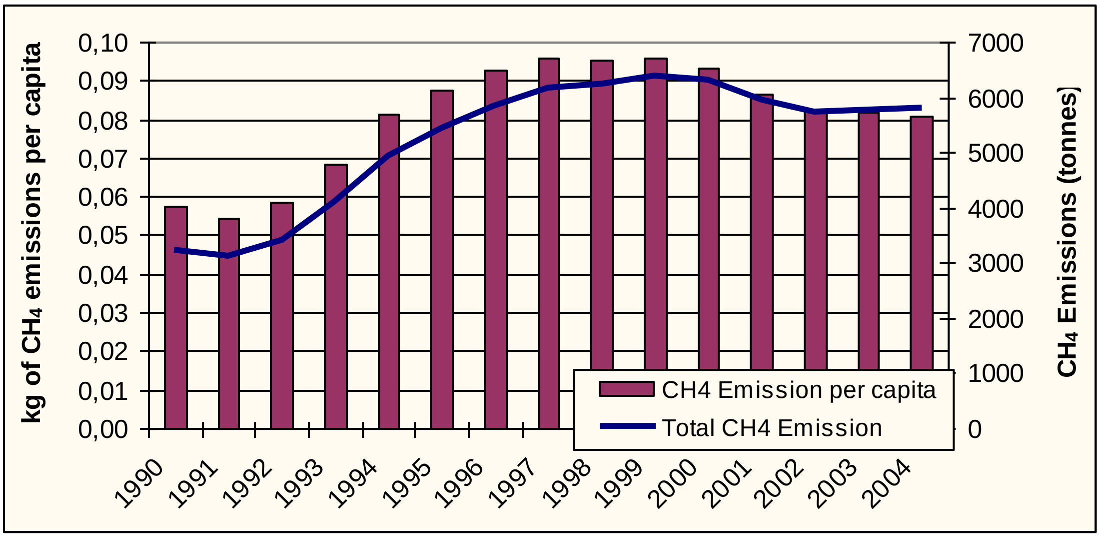

Figure 3.4 Variation of CH_4 emissions produced by road transport and CH_4 per capita

When total CH_4 production is examined, the great portion belongs to gasoline vehicles which produce more CH_4 emissions than diesel vehicles. After the year 1998 due to the fact that fuel comsumption is controlled with advanced technologies, CH_4 esmissions are reduced.

Removing old cars from the registers would bring significant improvement in both CO_2 and other emissions. Indeed, the reduction of CO_2 emissions is observed due to the removal of vehicles from registers by providing taxation advantage to consumers in the years 2003 and 2004. Passanger cars that are deleted from registers add up to 325 481 vehicles in that period and provided up to 4.87% reduction in the CO_2 emissions in those two years. The number of passenger cars with uncontrolled emission technology provides a potential of further gain by the use of a similar application until some 2 500 000 cars are deleted through this method.
In recent years, aviation in Turkey started to develop significantly, increasing the use of aircrafts and becoming second sub sector in transport. This change is almost steady.[8] Figure 3.6 illustrates CO_2 emissions produced by domestic aviation in Turkey and the variation of CO_2 emissions per capita.

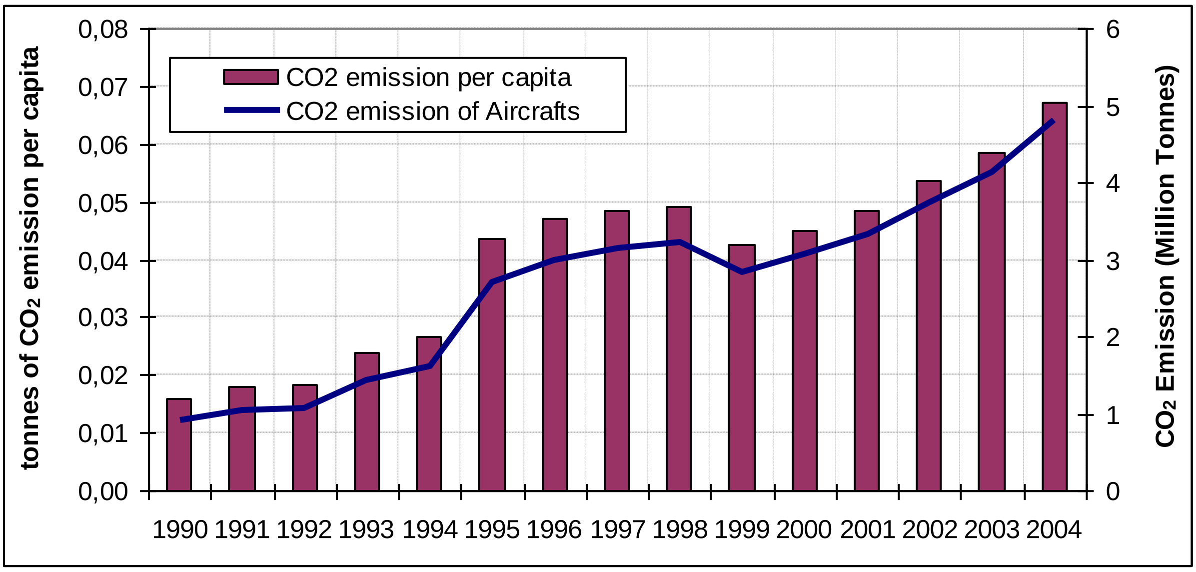

Figure 3.5 The variation of CO_2 emissions produced by aircrafts in 14 year period

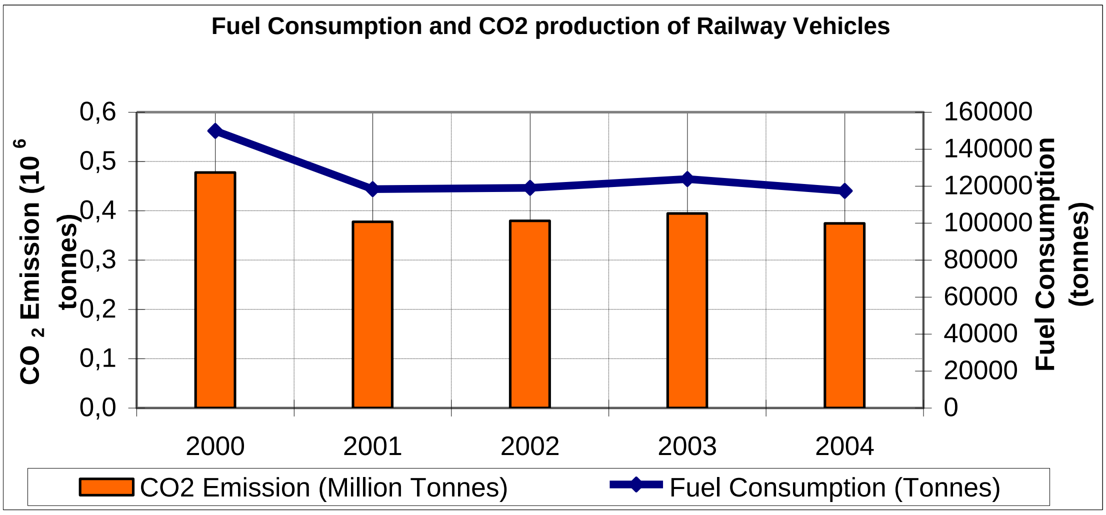

Figure 3.6 Fuel consumption and CO_2 emission production of railway vehicles

Fuel consumption of railway vehicles reduced in recent years. The main reason for this reduction, is the decrease of railway usage. Trains used for urban transport are equipped with electrical systems and locomotives equipped with diesel engines are mostly used for intercity transport. In this study only diesel fuel consumption is considered for GHG emissions.

In order to estimate the GHG emissions resulting from national navigation, Tier 1 approach is used due to the lack of data about navigation and difficulty in processing the small amount of available data. CO_2 emission produced by navigation is especially influenced by freight transport. Navigation usually is not effective for passenger transport in Turkey, except that in some cities urban sea transport is existing. During the final four year period, CO2 production has gone up as a result of the increased use of navigation for freight transport.

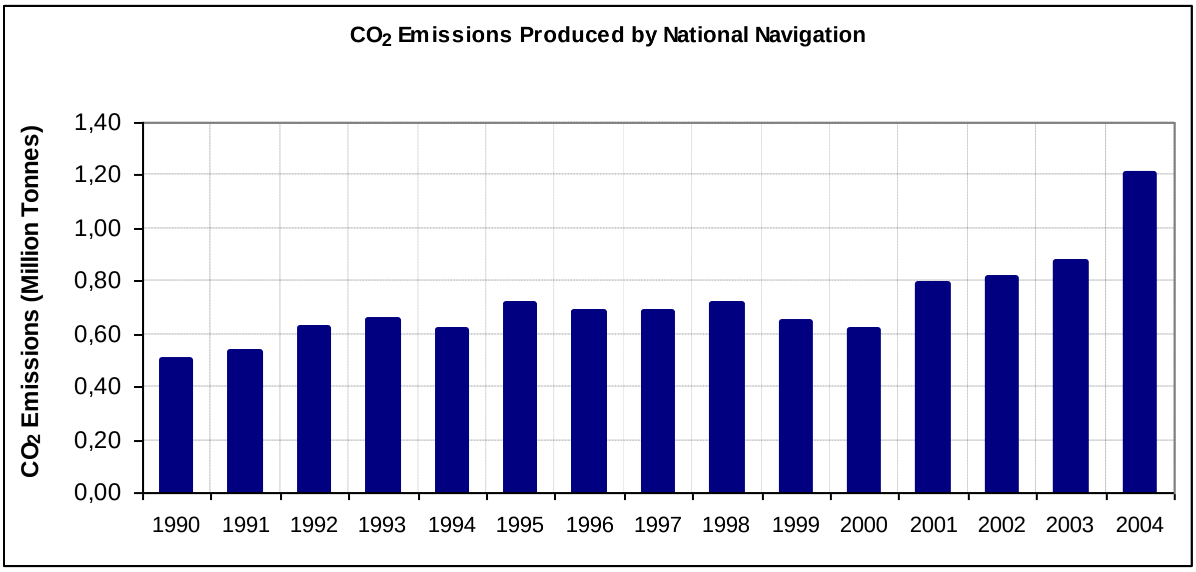

Figure 3.7 CO_2 emissions that are prdouced by national navigation [8]

4. CONCLUSIONS

The GHG emissions resulting from the transport sector in Turkey are in an increasing trend compared to the base year of 1990. The increase in the number of inhabitants and improvements in economical circumstances are the major factors that increases energy consumption which in turn leads to higher GHG emissions.

Total CO_2 emissions produced by transport sector has changed from 26 million tonnes to 40.5 million tonnes in the year 2004 with an increase of 56% compared to year 1990. This corresponds to a change from 0.17 kg CO_2/\$ in the year 1990 to 0.14 kg CO_2/\$ in the year 2004. This improvement shows efficient energy consumption tendancy in the sector. [7] CO2 emissions also incresed from 0.46 ton/capita to 0.57 ton/capita in the same period showing national development rate.

Sustainable transport can be achieved through technological improvement of existing vehicles and engines and also development of new, low pollutant emitting fuels. At the same time demand for transportation has to be managed and reduced by the modification of traffic towards non-pollutant or low-pollutant emitting modes such as public transport, rail systems, bicycles or walk in urban regions.

A significant change in passenger transport systems is required to reduce transport related energy consumption by using vehicles with fuel efficient engines compared to conventional systems. In the long run, hybrid-electric vehicles and electric motors powered by fuel cells are the technological solutions to present problems, but short term achievements would require the development of infrastructure for energy efficient public transportation systems.

The use of information technology for personal communication would also reduce requirement for transportation to reduce energy consumption and GHG emissions.

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REGIONAL CLIMATE CHANGE AND ITS IMPACTS FOR TURKEY

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The aim of this study is to detect regional climate change over Turkey by using both statistical and numerical modeling techniques. The statistical study focuses on two important climate variables – temperature and precipitation. First of all several statistical techniques were applied to find the significant trends. The period for the analysis of the station data is taken as the 1951–2004 interval. One of the primary findings of this study is the significant increasing in temperatures and decreasing in precipitation in the western Turkey. This may possibly due to reduction of cyclone numbers in winter or shifting of cyclone track paths northerly over the area of interest. We also found that minimum (night-time) temperatures have increasing trends in spring and summer seasons, significantly, because of the rapid urbanization after 1980s.

Future simulations for 2100 and 2070 with a regional climate model (RegCM3) based on A2 emission scenario show changes in precipitation and temperature over Turkey. In general, precipitation decreases along the Aegean and Mediterranean coasts and increases along the Black Sea coast of Turkey. It is worth mentioning that the fall precipitation will increase more in the Euphrates basin. The projected temperature increase is higher in the eastern half of the country. In the summer time this pattern is reversed and the western half of the country, especially the Aegean Region will be experiencing temperature increases up to 6 °C; while the area-averaged annual mean temperature increase for the whole country will be estimated to be around 2-3 °C.

1. Introduction

Being regarded as one of the most critical challenges of our century, climate change has been placed at the center of almost every initatives on environmental protection and sustainable development since 1990’s. On the basis of today’s understanding, it is not known that how the global climate system is projected onto the regions, or how the regions contribute to the global system. Unexpectedly large impacts could occur, as they have done in the past, in such a complex system, in response to global change. On the other hand the typically delayed human response to environmental emergencies can result in irreparable damage. Global climate change or its increased variability is expected to alter the timing and the magnitudes of such processes as precipitation, temperature, evaporation and eventually runoff. As a result, regions where floods occur rarely may encounter more frequent events of high flows, while droughts and water scarcity may intensify in the most vulnerable regions like the Mediterranean and the Middle East.

This article includes the results of a study about the climatic changes in Turkey during the last century and the developments in the climate change projection studies conducted at the Istanbul Technical University. This work has two sections: 1) *Statistical analysis*: an attempt has been made to document how the climatic variables such as precipitation and temperature changed in Turkey in the past. 2) *Regional modeling*: Future climate projections have been done through dynamical downscaling.

2. Data Analysis

We obtained longterm precipitation and temperature data (daily, monthly, and yearly averages or totals) from Turkish State Meteorological Service, and performed a quality control procedure and homogenization test on these data sets. Employing Mann-Kendall test, we generated the trends for precipitation and temperature (minimum, maximum and average) time series. In addition, we applied circular statistics approach to monthly precipitation data to characterize seasonality in terms of the average time of occurrence and the seasonality index, and investigated whether/how the seasonality of precipitation changed in Turkey in the past. It is well recognized that variations and trends in most long-term climatological time series are caused not only by the changes in weather and climate but also by the relocation of the stations or the alteration of the instruments, the observing practices or the station environment. Thus, before conducting a study of climate variability or investigation of a possible climate change signal using station data, a quality control and correction of data sets are almost assumed mandatory. The Turkish station data, obtained from the State Meteorological Office of Turkey, are subjected to a quality control before being used in the trend analysis for detection of any climate change signal. Therefore, quality control and homogenization of the Turkish climate data is done by Bozkurt and Göktürk (2006). 113 long station data series are obtained for the analyses after the application of their quality control procedures. Figure 1 shows the distribution of Turkish meteorological stations.

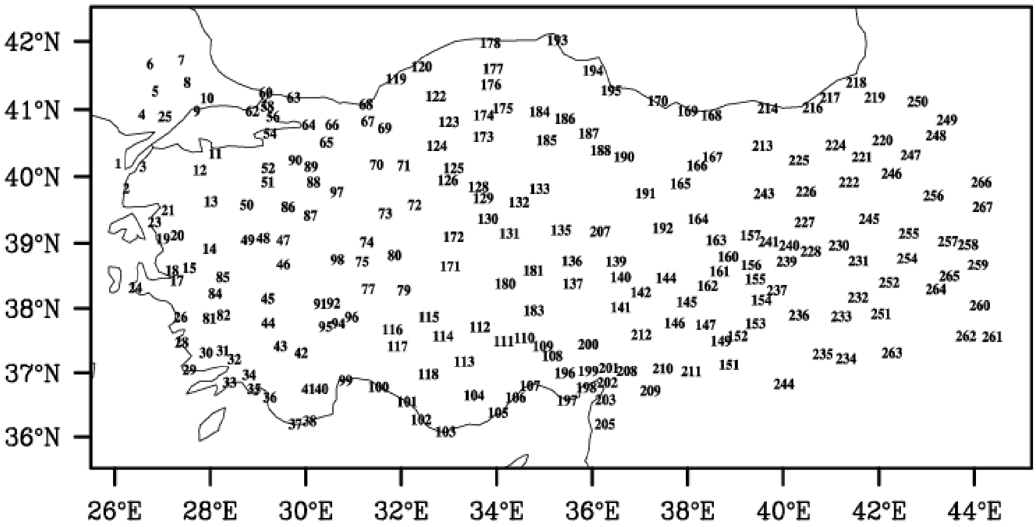


Figure 1. Distribution of meteorological stations in Turkey (Gokturk et al. 2006).

2.a Precipitation

There is no doubt that any persistent change in the patterns of the precipitation, or in the characteristics of the precipitation (e.g., intensity, frequency and duration), would have significant consequences on the environment. Thus, global warming studies pay special attention to this crucial climate variable. There are, however, difficulties in identifying climate change signals in precipitation. Some of these difficulties are related to the quality of the data as precipitation measurements are prone to several types of errors. The length of the precipitation data brings in another difficulty in tracking the climate change signal since precipitation is temporally, as well as spatially, a highly variable parameter. Sometimes it is possible to detect a trend in a 'short' time series of precipitation, which, in reality, could be a part of the long-term variability. Therefore, care has to be taken when interpreting the trend analysis of precipitation data. In the trend analysis, we deployed the commonly used nonparametric Mann-Kendall method to identify significant trends in the quality-controlled station data (e.g., Karaca *et al.* 1995).

Figure 2 illustrates the results of Mann-Kendall trend test for four seasons. Coherent areas of significant changes in precipitation can be seen in both winter and fall seasons. Winter precipitation in the western provinces of Turkey has decreased significantly last five decades. Fall precipitation, on the other hand, has increased at the stations that lie mostly in the northern parts of the central Anatolia. The reason behind these changes is not well understood. They definitely require a comprehensive study, which should also look into the link between cyclone tracks and these changes (Karaca *et al.*, 2000). In the other seasons (spring and summer), there are only a few stations with statistically significant changes, however, they do not show a coherent regional behavior.

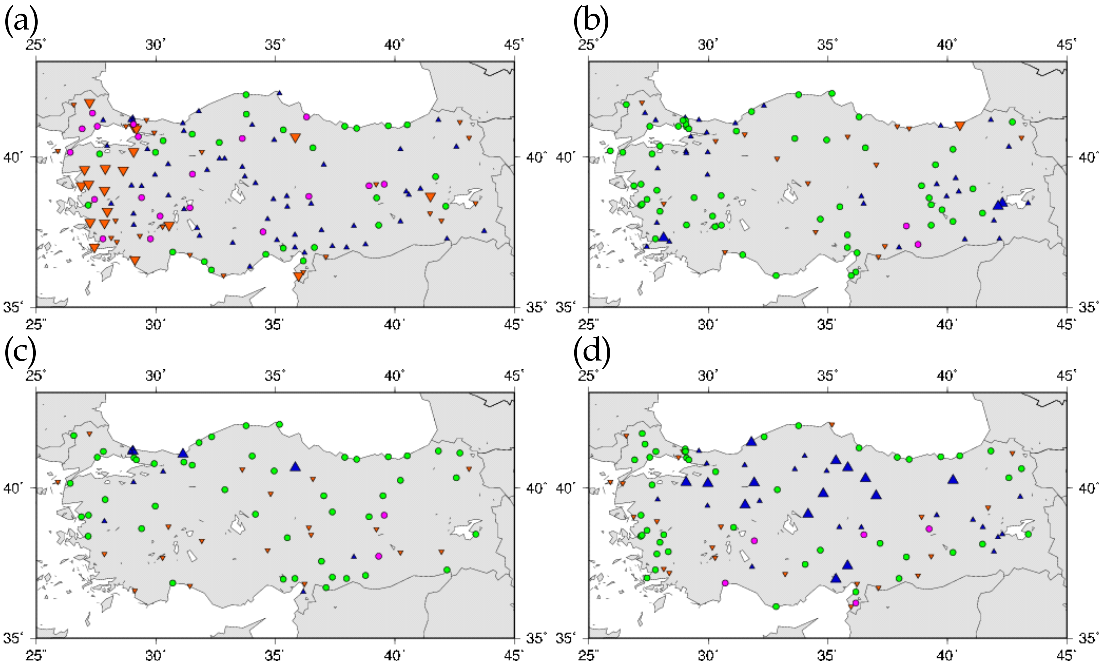


Figure 2 Seasonal precipitation trends for the period 1951-2004. (a) for winter, (b) spring, (c) summer, and (d) fall ● *denotes no trend,* ▲ *significant increase,* ▲*insignificant increase,* ▼*significant decrease,* ▼*insignificant decrease and* ● *insignificant increases and decreases.*

2.b Temperature

Compared to precipitation, temperature is a variable that can be measured easily and more accurately at meteorological stations, therefore the uncertainties coming from measurement errors are of lesser concern for temperature. Nonetheless, the climate change signals in temperature are usually contaminated by the urbanization effects because most of the stations in Turkey or elsewhere have been gradually encircled by the city residential and/or commercial areas. It is, therefore, difficult to separate climate change signal from urbanization effects on temperature time series.

Figure 3 shows the results of Mann-Kendall trend analysis applied to seasonally averaged annual temperature series between 1951 and 2004. The most prominent feature that one can observe is the widespread increase in summer temperatures. Summer temperatures increase mostly in the western and southwestern parts of Turkey. Urban heat island studies (e.g. Ezber et al., 2006, and Karaca et al., 1995) indicate that temperature increase as a result of urbanization is most notable in summer in Mediterranean cities when the region comes under the influence of high pressure systems. Thus, widespread increase in temperature in western stations in Turkey may be mainly related to this phenomenon. Winter temperatures also show a general tendency to decrease in Turkey. It can be noted that the more significant ones are mostly concentrated in the coastal stations. During transition seasons, stations with significant trends are usually sporadic in nature, and they do not show a coherent regional behavior.

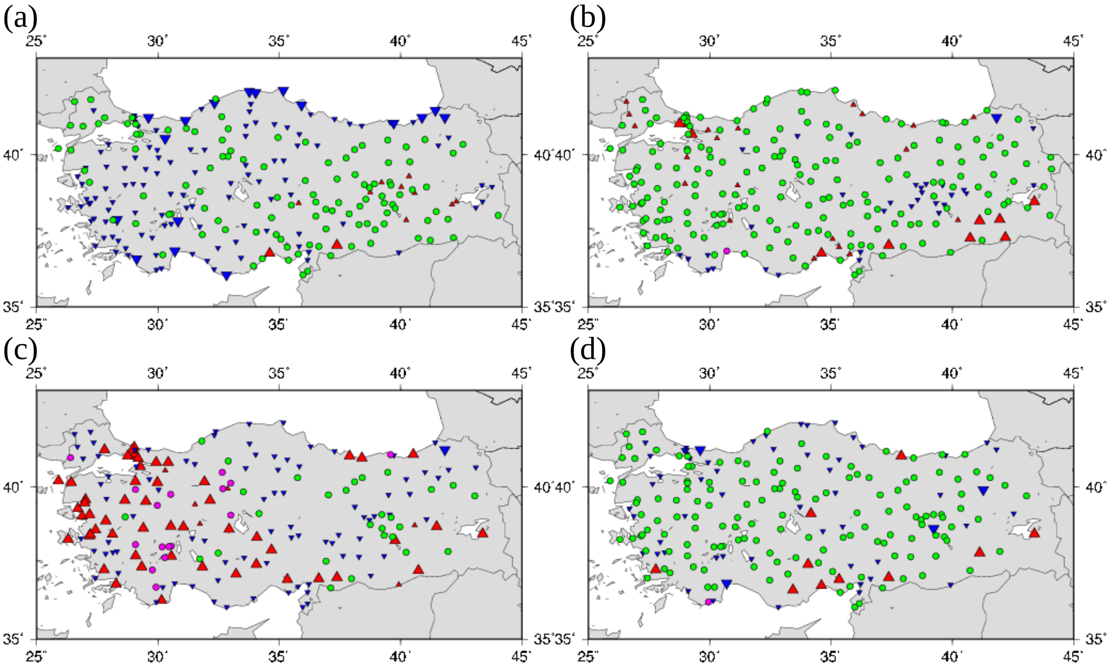
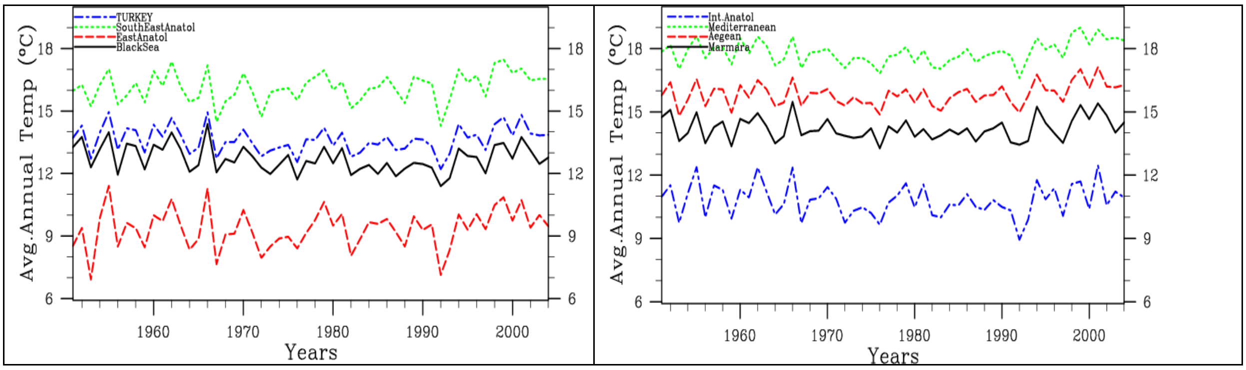


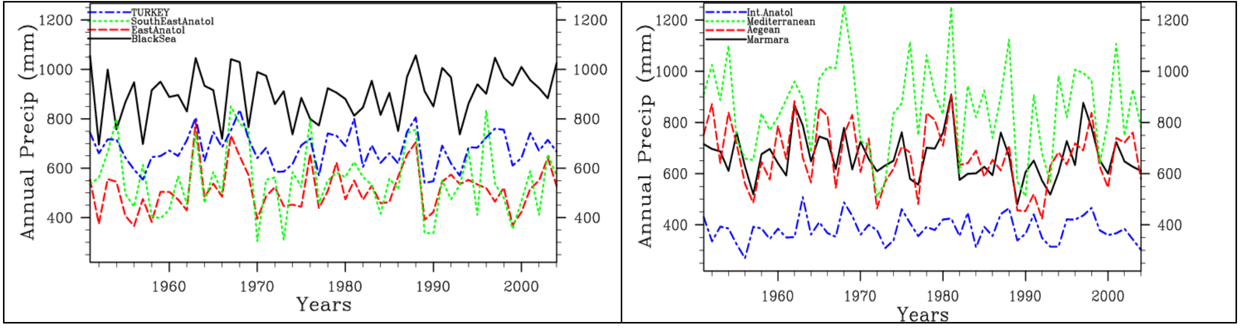
Figure 3 Seasonal temperature trends for the period 1951-2004. (a) winter, (b) spring, (c) summer, and (d) fall. ● denotes no trend, ▲ increase, ▲ insignificant increase, ▼ significant decrease, ▼ insignificant decrease and ● insignificant increase and decrease.



a) b)

Figure 4 Variation of mean temperature of Turkey with seven geographical regions.

Figure 4 shows changes in mean temperature in Turkey with seven geographical regions from 1950 to 2004. There is no resemblence with global mean temperature as it has an increasing trend. In almost all regions the mean temperature has no change from 1950 to 1970. But from 70s to 1990 it decreases slightly. After 1990 it has increasing behaviour as global temperature does.



a) b)

Figure 5 Variation of yearly averaged total precipitation of Turkey with seven geographical regions.

Figure 5 shows the yearly averaged total precipitation of Turkey with seven geographical regions. The total precipitation has a different trend than of the mean temperature. One can easily see that a drought period is observed between 1990 and 2000. After 2000, total precipitation in Turkey has slightly increased as in the Black sea region. One striking result is the large yearly variation in the Mediterranean region. This confirms that the Mediterranean region is most vulnarable and sensitive region in the case of climate change.

3. Regional Modeling

A mesoscale regional climate model is as an important tool associated with climate variability, changes, and impacts at local and regional scales (Giorgi and Bates 1989). As a result, climate models have been applied to numerous studies up to now and they have demonstrated that downscaling skills have been achieved and model deficiencies have been resolved.

The dynamical downscaling studies are performed using RegCM3 regional climate model developed by Giorgi and Bates (1989). A series of tests have been conducted to determine an ‘optimum’ horizontal resolution, and a resolution of 30 km is then chosen. At the moment, two sets of simulations are conducted: control run forced at the boundaries with NCEP/NCAR Reanalysis data and ‘future’ simulation forced by the A2 emission scenario results from the Finite Volume General Circulation Model (FVGCM) of NASA (Lin, 2004). Control runs will cover the ‘standard’ 30-year climatological period, namely 1961-1990. Future simulations cover the interval 2071-2100.

Future simulation with RegCM3 is forced by the general circulation model FVGCM run based on SRES A2 emission scenario. RegCM3 has therefore been modified to take into account yearly variations in CO_2, CH_4, N_2O, CFC11 and CFC12. In general, precipitation shows decreases along the Aegean and Mediterranean coasts and increases along the Black Sea coast of Turkey. Central Anatolia shows little or no change in precipitation. The most severe (absolute) reductions will be observed on the Southwestern Coast; in contrast, Caucasian coastal region is expected to receive substantially more precipitation. These observations are valid both for the winter and the spring totals. In summer there will be not much changes in the amount of precipitation over Turkey. Slight total precipitation increase is expected in the fall season for whole Turkey. It is worth mentioning that the fall precipitation will increase more in the Euphrates basin.

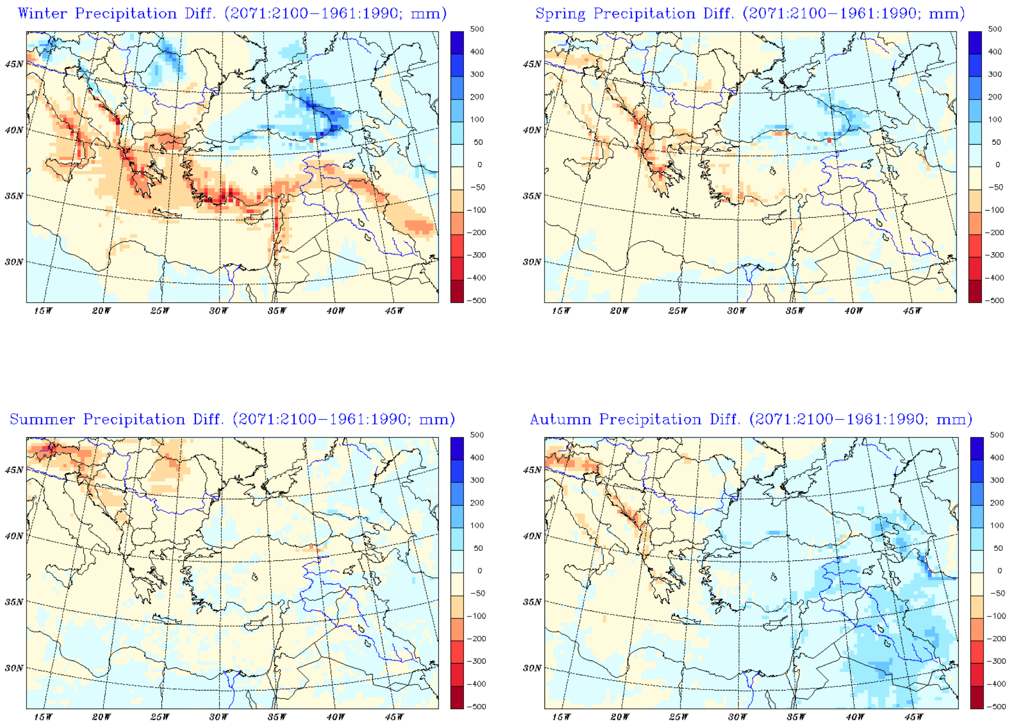


Fig. 6 Climate change projections for Turkey: changes in precipitation for all seasons (Önol and Semazzi, 2006).

Conclusions

Significance of water resources management is much greater in the case of the developing countries than in the developed ones. Over the Eastern Mediterranean region several studies have been conducted on water resources and its importance but none of them has focused on the role of future climate change. Trans-boundary streamflows (Euphrates-Tigris) are the main sources of the water for the region, not only for domestic and industrial usage, but also for energy. To understand present and future climate changes over the Euphrates-Tigris basin, we have focused on the precipitation component of the regional hydrological cycle.

Our primary finding is that the climate anomalies associated with the projected regional global warming tend to manifest themselves in terms of multi-decadal variability North Atlantic Oscillation. More specifically, there is dramatic precipitation increase (approximately 20%) over the northern part of domain of interest (Black Sea). In contrast, the southern part of the domain of interest exhibits the apposite anomaly conditions. We hypothesize that these changes in precipitation could have very significant implications regarding the total hydrological cycle over the region. In spite of the observed cooling trend in the Eastern Mediterranean and the coastal regions of Turkey in 1980s and 1990s, it is expected that mean temperatures will increase by approximately 1.5°C in these regions. The expected increase in temperature and decrease in precipitation will definitely affect: surface and groundwater flows and river regimes; the incidence of floods; sediment and nutrients fluxes to the sea; natural ecosystems and human use of the coastal regions as consequence of sea-level rise, and altered conditions for the fishing industry in the Black Sea, and also tourism and agriculture in the Aegean and Mediterranean coasts.

According to the HadCM3 (Mitchell, *et al.* 2002), a new climate model has assessed the impacts of climate change on temperature and precipitation conditions, natural vegetation, and water resources over Turkey. The so called "second Hadley Center Climate Model" has a climate sensitivity close to the IPCC best estimate value. It is run for two CO_2 emissions scenarios, which stabilise concentrations at 750 ppm and 550 ppm. Changes arising from a business as usual emissions scenario, in which CO_2 and other greenhouse gases increase without mitigation were also used for comparison in that report and referred as "unmitigated scenario". A summary of this model assessment for Turkey is given below:
Annual average temperature by 2070-2099:

- will increase 3.72 °C for winter and 7.32 °C for summer seasons according to the emissions scenario that stabilises CO_2 concentrations at 750ppm,
- will increase 2.73 °C for winter and 5.48 °C for summer seasons according to the emissions scenario leading to stabilise CO_2 concentrations at 550ppm.

Precipitation by 2070-2099:

- *will decrease by 1 mm/day in average precipitation resulting from the unmitigated emissions scenario,*
- will decrease by 6.55 mm/day and 0.27mm/day in annual precipitation with two stabilisation scenarios of CO_2 concentration at 750ppm and at 550ppm, respectively.

Such a warming of the atmosphere would alter precipitation patterns, change the frequency of droughts and severe storms. Atmospheric GCMs generally show an increase in the proportion of days with heavy rainfall as climate warms, even in places where total number of rainfall days decreases. So there would be an increase in intensity of daily precipitation. On the other hand, warming would cause wide spread reduction of soil moisture and relatively large portion of rainfall would be lost as caused by severe flooding. This is particularly expected in the narrow coastal strip between the shoreline and the lee sides of the eastern Black Sea Mountains.

Both results of the HadCM3 model and our modeling experiments indicate that potential evapotranspiration is likely to increase throughout the Mediterranean (Mitchell *et. al.* 2002). Coupled with increases in temperature this would lead an increase in land degradation, deterioration of water resources, and in long-term, may affect coastal agricultural production as well as aquatic ecosystems. This may increase risk of forest fires in the Aegean and Mediterranean coastal areas. An increase in temperature could also lead to a gradual extension of the tourist season, with concomitant environmental problems and economic benefits.

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GLOBAL WARMING AND CLIMATIC CHANGES IN PAKISTAN

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Global warming is one of the most influencing factors that are having a huge impact on the world's population by affecting the water resources of different countries. Most countries of the world are adapting to this change, but as far as Pakistan is concerned, limited studies have been made to assess the climate and its implications thereof. Global climatic changes and water-resources are deeply inter-related. Precipitation is the largest source of fresh water. Global climatic changes have major effects on precipitation and runoff. The water crisis worldwide resulting from the climatic changes has highlighted the importance of the changing climatic conditions. In this research, it has been studied that whether there is a substantial climatic change occurring in Pakistan or not. Rim stations for the Indus, Kabul, Chenab and Jhelum rivers were selected to see the changes in climatic variables within these areas. Regression analysis was done to investigate whether there is any substantial effect of these climatic changes.

1. Introduction:

It has been seen from various studies that the temperature of earth is increasing with the passage of time because of the increasing emissions of various chemicals especially the carbon dioxide. Global climatic changes will have major effects on precipitation and runoff. In the relatively arid and semi-arid regions, modest changes in precipitation can have proportionally large impacts on water supplies. In mountainous watersheds, higher temperatures will increase the ratio of rain to snow, accelerate the rate of spring snowmelt, and shorten the overall snowfall season, leading to more rapid, earlier, and greater spring runoff. Climate-induced changes in hydrology will affect the magnitude, frequency, and costs of extreme events, which produce the greatest economic and social costs to humans. Flooding could become more common and extreme (FAO, 1996). Recent reports of the Intergovernmental Panel on Climate Change (IPCC, 2001) suggest that a greenhouse warming is likely to increase the number of intense precipitation days as well as flood-frequencies in northern latitudes and snowmelt-driven basins.

According to the global warming scenario presented earlier, the global warming is reflected in the river-flow data of Pakistan, especially in the nineties. From the data available form 1975 to 2000it was seen that in the post-Tarbela era, the water diverted from the rivers to the canal system has remained constant around 104 MAF per year (128 BCM). The fresh-water outflow to the sea may, therefore, be considered to be a good indication of the total river flow for this period. From the year 1975/76-1989/90 the average flow into the sea per year has been 34.13 MAF/year. However from the year 1990/91 to 1999/2000, this flow has been 47.88 MAF/year i.e. about 40 % greater. (UNFCCC, 2002)

For the winter season for the same period, the average flow into the sea from the year 1975/76-1989/90 was 1.86 MAF/year. However from the year 1990/91 to 1999/2000, this flow has been 3.28 MAF/year, i.e. about 76 % greater (UNFCCC, 2002). Although other factors may also be contributing, nevertheless the change visible in this time-frame is quite large. This increased river-flow could be taken as evidence for local effect of global warming. The global warming is expected to initially cause the river-flow to increase as the glaciers melt, then decrease as they recede. Another important point that has emerged from the data is that when there is an excessive amount of water in kharif season, the succeeding rabi season also has more water than usual; this increased water-availability in rabi could be due to increased rains because of local effect.

An overall increase in rainfall of 50-150mm has been observed in the monsoon belt for the period 1931-90 (Imtiaz Ahmad, 2001) However, a decrease in rainfall was seen in the rest of the country. The decrease is 50-100 mm in western and northern mountains, whereas in the southeastern and central parts it is 25-50 mm. These variations are in line with the predictions made on the expected effects of global warming. Global warming is expected to cause drier south and wetter north.

According to a United Nations report (1997) to determine water consumption~water availability ratio, moderate to high water-stress translates to consumption levels that exceed 20 per cent of available supply. This ratio has already exceeded 65 percent as far as Pakistan is concerned. Water-use in agriculture is projected to increase as our food-demand rises. World-wide, agriculture accounts for about 70 per cent of water-consumption; in Pakistan, its share is already 95%. Future projects show a 50- to 100-percent increase in demands for irrigation water by 2020. Better management of water-resources is the key to mitigating water-scarcities in the future in the short-term and avoiding further damage to aquatic ecosystems. Thus we can say that global warming is happening at a much faster rate than was expected, global temperatures are rising nearly twice as fast as previously thought (IPCC, 20001). Their prediction, based on computer models, is that temperatures could rise by as much as 5.8^{o}C by the end of the century. The report stresses that human activity is responsible for this crisis and that industrial pollution, and, in particular, green-house gases emissions are the worst offenders. A lot of research on the impact of the climatic variables on the water resources has been carried out in other parts of the world like Cosgrove & Rijbersman, 2000; Gleick, 1998; Arnell, 1996; Arnell, 1999; WMO, 1997; Vogel *et al*. 1997; Arnell, 1999.

2.0 Methodology:

2.1 Study Area:

The study area consisted of Indus Basin Irrigation system, which is the main source of Irrigation water in Pakistan. Within this system, the following rivers were selected the data of which was then analyzed.

- River Indus at Tarbela in the North West Frontier Province
- River Kabul at Warsak in the North West Frontier Province
- River Chenab at Maralla in Punjab Province
- River Jhelum in Punjab Province

2.2 Research Methodology:

The principal objective of this study was to see whether the climatic variables are changing significantly. The data for the research work was collected from the Pakistan Meteorological Department, Water and Power Development Authority, Pakistan Agricultural Research Council as well as the Irrigation Department

The data consisted of

- Meteorological data for the selected catchments
- Discharge data for the same catchments

After the data collection, the data was analyzed so that the trends in the Climatic changes can be compared. Different statistical parameters were calculated to see whether the climatic variables are changing significantly and also are affecting the discharges significantly or not.

2.2.1 Simple Regression Analysis:

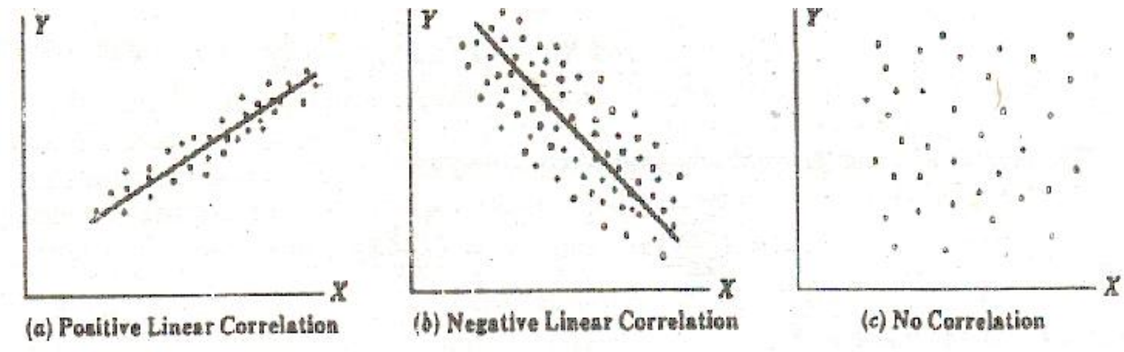
The simple regression analysis of all the data was done. The historic data of Temperature, Rainfall and discharge data for the catchments was used to see the variation and overall trend of these parameters against the time and the following were calculated

- Linear relationship/correlation between the parameter and time
- The Pearson product moment correlation co efficient
- The coefficient of determination
- P-value for 95% confidence limits

***Linear Relationships/Correlation*:**

If X and Y denote the *two* variables under consideration, a *scatter diagram* shows the location points (X, Y) on a rectangular co-ordinate system. If all points in this scatter diagram seem to lie near a line, as in *(a)* and *(b)* of figure, the correlation is called *linear.*

- If Y tends to increase as X increases, as in *(a)*, the correlation is called *positive* or *direct correlation.*
- If Y tends to decrease as X increases, as in *(b),* the correlation is called *negative* or *inverse correlation.*
- If all points seem to lie near some curve, the correlation is called *non-linear* and a non-linear equation is appropriate for regression or estimation.
- It is clear that non-linear correlation can be sometimes positive and sometimes negative. If there is no relationship indicated between the variables, as in Fig.-*(c),* we say that there is *no correlation* between them, i.e. they are *uncorrelated*



(a) Positive Linear Correlation (b) Negative Linear Correlation (c) No Correlation

Figure 2.1: Linear Correlation

So in a similar manner explained above, linear relationships of the selected parameters against time were analyzed to see what kind of relationship/trends exists between the parameters and time.

<u>*Least Square Regression Lines:*</u>

After analyzing the trends, the linear relationships between the parameters and time were established using the concept of least square regression lines. The least square regression line of *Y* on *X* is given by

$$Y = a_o + a_1 X \qquad (1)$$

where

a_o and a_1 are obtained from the normal equations

$$\sum Y = a_o N + a_1 \sum X \qquad (2)$$

$$\sum XY = a_o X + a_1 \sum X^2 \qquad (3)$$

After calculating the values of a_o and a_1, the linear equation for the trend line was obtained to see how the parameters are changing with time which can be useful for future forecasting of these parameters.

Pearson product moment correlation co efficient

After determining a relationship between the parameters and time, the Pearson product moment correlation coefficient "r" was calculated for each of the parameters to see whether the change in the parameters is significant or not using the relation:

$$r = \frac{\sum z_x z_y}{N-1} \qquad (4)$$

“r” is a measure of how well a linear equation describes the relation between two variables *X* and *Y* measured on the same object or organism. It is defined as the sum of the products of the standard scores of the two measures divided by the degrees of freedom. The coefficient ranges from −1 to 1. A value of 1 shows that a linear equation describes the relationship perfectly and positively, with all data points lying on the same line and with *Y* increasing with *X*. A score of −1 shows that all data points lie on a single line but that *Y* increases as *X* decreases. A value of 0 shows that a linear model is inappropriate – that there is no linear relationship between the variables.

The Coefficient of Determination:

The coefficient of determination given by the ratio of explained variation to total variation is given by:

$$r^2 = \frac{\sum(Y' - \overline{Y})^2}{\sum(Y - \overline{Y})^2} \qquad (5)$$

where:

- ***Y*** = a score on a random variable *Y*
- ***Y'*** = corresponding predicted value of *Y*, given the correlation of *X* and *Y* and the value of *X*
- $\overline{Y}$ = **sample** mean of *Y* (i.e., the mean of a finite number of independent observed realizations of *Y*, ***not*** to be confused with the expected value of *Y*)

***P-value for 95% confidence limits*:**

A value of the variate estimated from a probability distribution for a given return period is usually in error due to limited sample size. Therefore, a statement is needed indicating the limits about the estimated value within which the true value is contained with a specific probability. This statement is made by constructing confidence limits, or control curves. Thus the confidence interval indicates the limits about the estimated value and the probability with which the two value will lie between those limits. This statement accounts for sampling errors only.

Let the confidence probability be α.(P-value).Alpha is the significance level used to compute the confidence level. The confidence level equals 100*(1 - alpha) %, or in other words, an alpha of 0.05 indicates a 95 percent confidence level

Normally Z-test is used to calculate the P-value. The z-test generates a standard score for x with respect to the data set (array) and returns the two-tailed probability for the normal distribution. This function can be used to assess the likelihood that a particular observation is drawn from a particular population.

If we take confidence probability as α, the confidence interval of the variate x corresponding to a return period T is bounded by values x_1 and x_2(Nemec, 1973) as

$$x_{1,2} = x \pm G(\alpha)S_e \qquad (6)$$

where G(α) is a function of the confidence probability α and can be determined by using the table of normal variates. S_e is the probable error expressed as:

$$S_e = b\frac{S_{N-1}}{\sqrt{N}} \qquad (7)$$

where

$$b = \left(+1.3K + 1.1K^2\right)^{0.5} \qquad (8)$$

where K is the frequency of the factor of the given distribution under consideration. S_N is the standard deviation of the sample and N is the sample size. By using this method. Confidence limits can be placed above and below the fitted distribution curve.

3.0 Results and Discussions

3.1 Regression Analysis:

Regression Analysis was carried out on the available Temperature, Rainfall and Discharge data for the selected catchments. The details of which are given below.

1. **River Indus:**

Temperature Data:

First of all the overall trend of Temperature was seen by doing the Linear Regression Analysis of the available data.

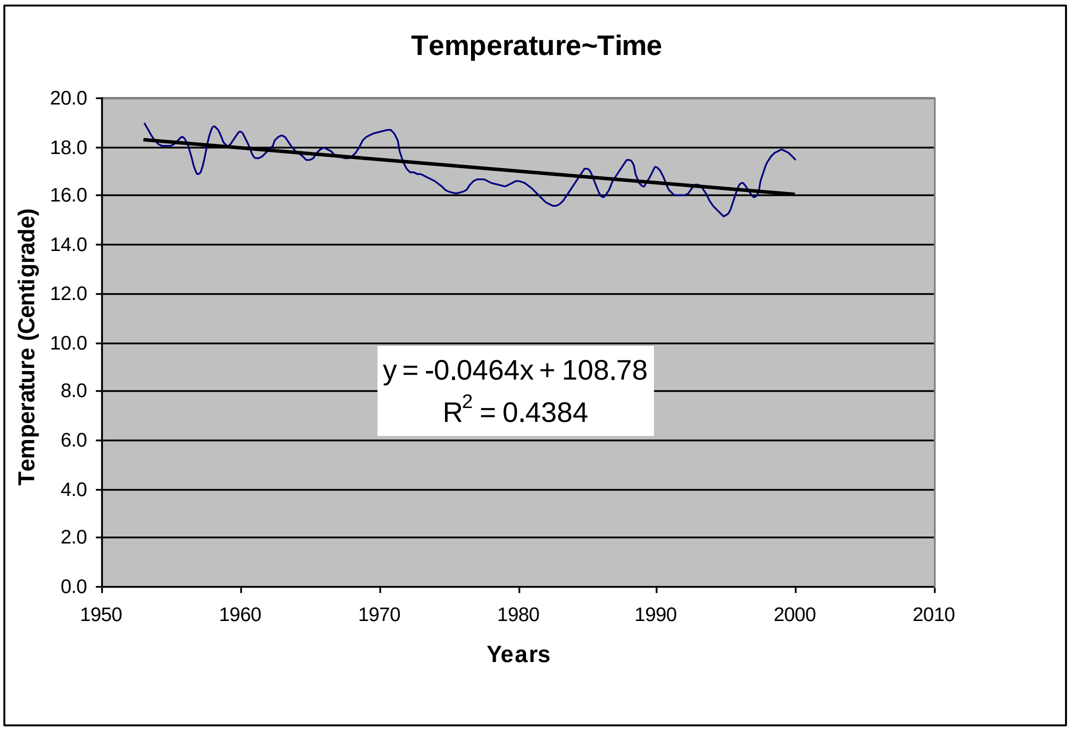


Figure 3.1: Temperature data for River Indus at Tarbela.

From the available Temperature Data (1953-2000) it was seen that as a whole the Temperature trend was decreasing around the area with an overall decrease of about 0.0464°C per year. But since 1990, it was observed that there is a slight increase in the temperature at the rate of 0.1°C per year. Regression analysis was also carried out on the available temperature data and it was found that the change in temperature was quite significant with P value of 6.14×10^{-9} (<0.05), thus we can say that there is appreciable change in Temperature with 95% (Singh, 1992) confidence that the Temperature change is Significant. The value of R-Square (Fig. 3.1) of 0.4384 was also quite significant, giving a value of "r", the correlation co-efficient as 0.66, showing negative correlation, which was significant as well.

Rainfall Data:

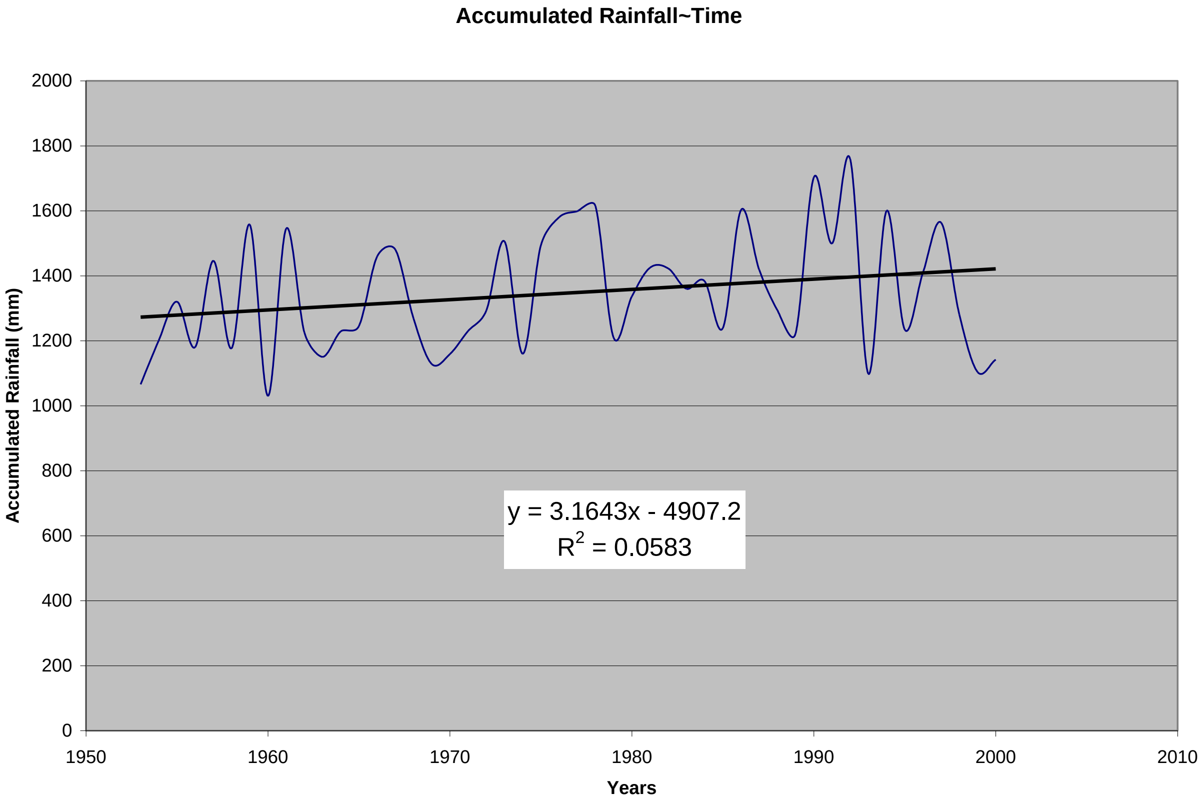


Figure 3.2: Rainfall data for River Indus at Tarbela

The Simple linear Regression analysis was also carried out for the Rainfall data of the area from 1953-2000 (Fig. 3.2) which showed that the value of R-square to be 0.0583 with corresponding value of "r" being 0.24, and the P-value was 0.19. So, there is not that much significant change in the rainfall trend in the past 48 years or so. But from the trend line it has been observed that there is some increase in the annual accumulated precipitation which has increased by 7.16% for the whole duration of 48 years.

Discharge Data:

The Discharge data was also analyzed to see how it is changing with the passage of time. Regression analysis was done to see whether the discharge is increasing / decreasing appreciably and if so, what is its overall trend.

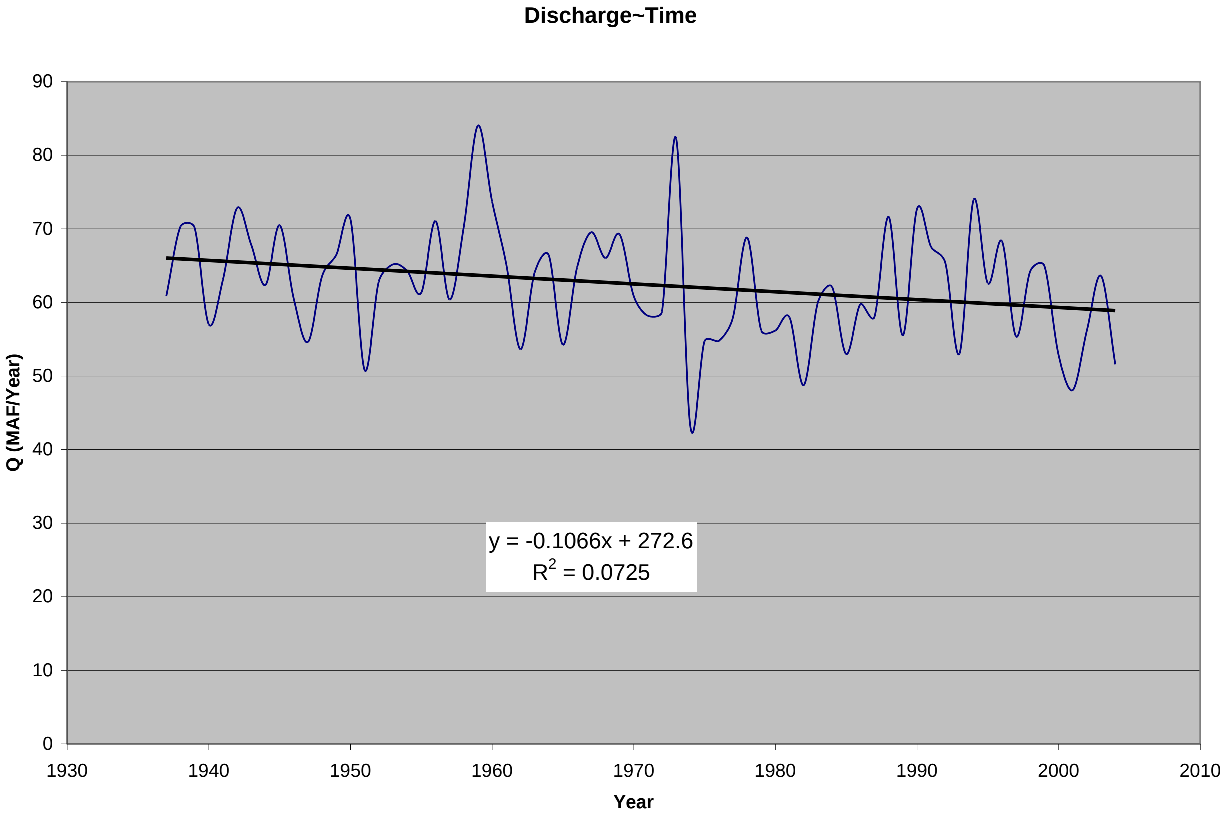


Figure 3.3: Discharge Data for River Indus at Tarbela

The regression analysis of the data from 1937 to 2003 (Fig. 3.3) showed that the overall trend of the discharges is decreasing with time at a rate of 0.1066 MAF per year. Also the R-square value was 0.07 and the corresponding “r” value of 0.27 showed a negative correlation. P-value was estimated to be 0.02(<0.05), therefore we can say that the decrease in the annual discharge is quite significant with 95% confidence.

2. River Kabul

Temperature Data:

Similar to the previous analysis, first of all the available Temperature data (1950-2000) at the Metrological station for the Kabul River at Warsak was analyzed. The graph of the mean annual temperature change is given below

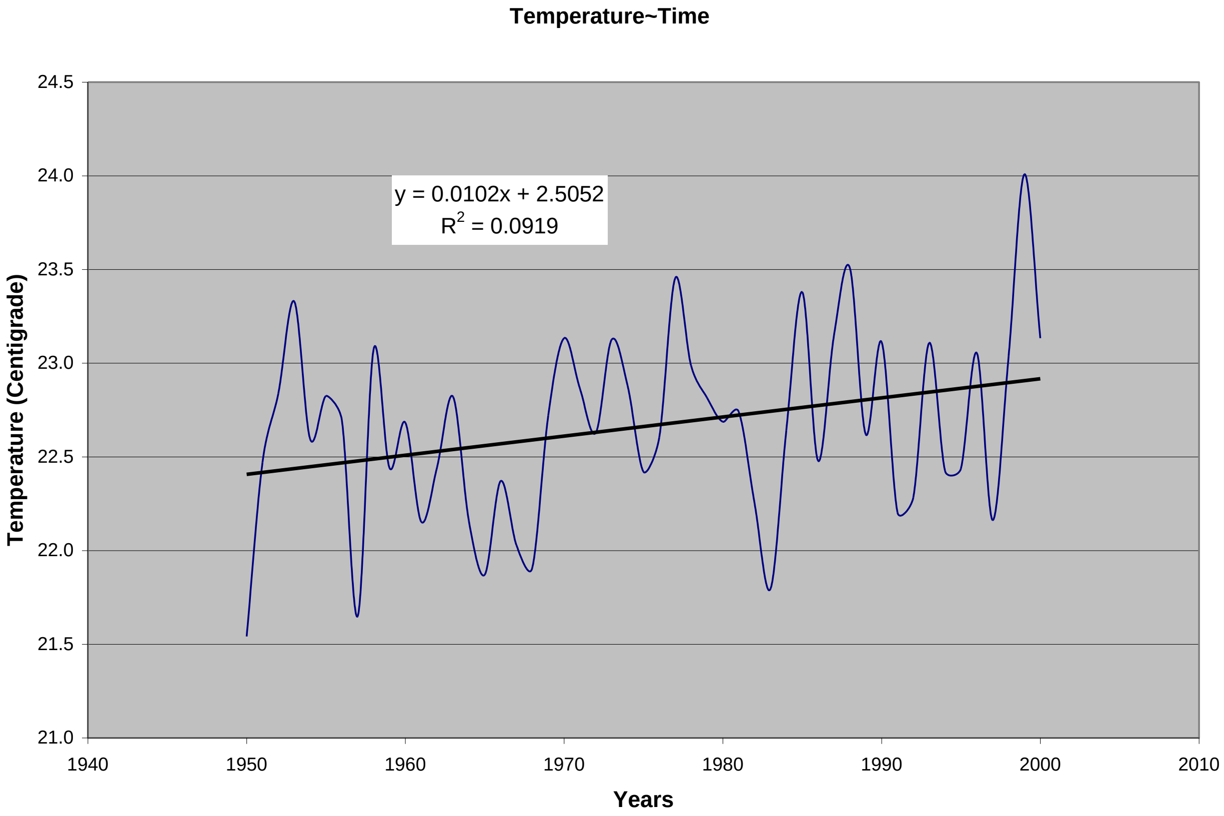


Figure 3.4: Temperature Data for River Kabul at Warsak

From the Fig. 3.4, it can be seen that the overall trend of the Temperature during the past 51 years is increasing at a rate of 0.0102°C per year with an overall increase of about 0.52°C during the same period, which is quite significant. The simple regression analysis gave the correlation co efficient "r" as 0.30, indicating a positive increase.

Rainfall Data:

The rainfall data for the from 1950 to 2000 was analyzed (Fig. 3.5) and it was found that the value of R-square was 0.14 with corresponding "r" value of 0.37, showing a positive increasing trend. The P-value for 95% confidence limits was found to be 0.011, again showing an appreciable increase in rainfall amount which came out to be 39.6% during the last 51 years.

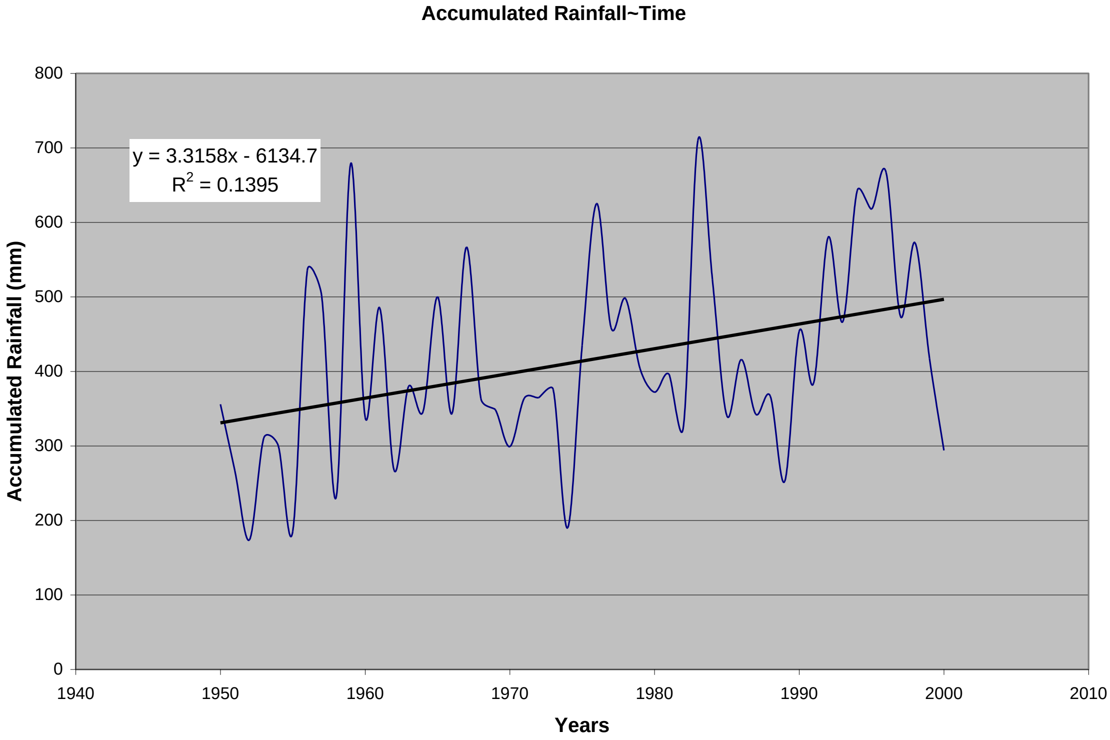


Figure 3.5: Rainfall Data for River Kabul at Warsak

Discharge Data:

The discharge data (1937-2003) for river Kabul was then analyzed to see whether there is appreciable change in the Discharge trends during the past years or not. The analysis showed that the discharges are decreasing at the rate of 0.155 MAF per year, which is a substantial amount of decrease. The regression analysis gave the value of R-square as 0.31 with corresponding value of “r” to be 0.556 and showing a negative correlation i.e the discharges are decreasing with time. Also the P-value for 95%confidence limit was 1.63x10$^{-7.}$ The overall trend of the discharges can be seen from Fig. 3.6.

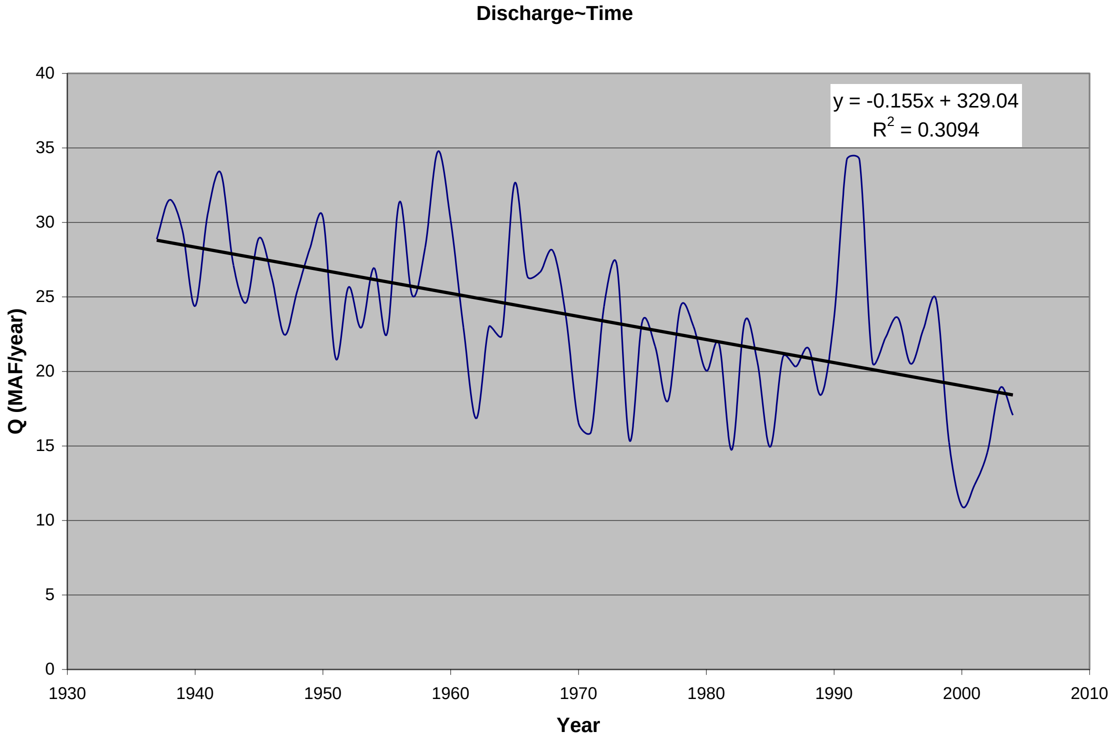


Figure 3.6: Discharge Data for River Kabul at Warsak

3. River Chenab

The third catchment area that was selected was of River Chenab at Maralla. Similar to the previous analysis, the data of Temperature, Precipitation and Discharge was analyzed, first separately, and the through multiple regression to see any significant changes.

Temperature:

The available temperature data for the metrological station close to the catchment area from 1971 to 2000 was analyzed which can be seen from Fig. 3.7.

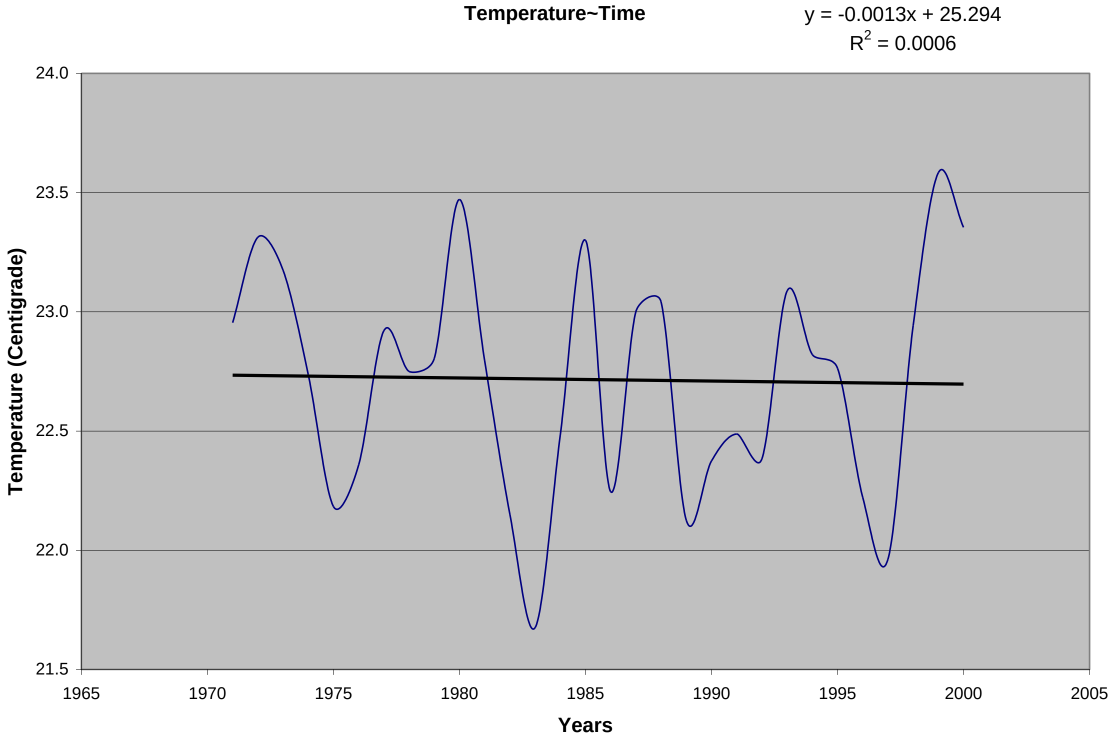


Figure 3.7: Temperature Data for River Chenab at Maralla

From the analysis, it was seen that the annual temperature for the Maralla catchment area has not increase significantly during the past 30 years. This can be seen from the fact that the above graph shows an annual decrease of 0.0013°C per year. Also from the regression analysis, it was seen that the R-square value was 0.0006 and the corresponding co-efficient of correlation "r" came out to be 0.02 and showing a negative trend i.e decreasing trend. The p-value for 95%confidence limits was also not in the significant zone. Thus we can say that there is no significant increase in the Temperature for the catchment area of Maralla, for River Chenab.

Rainfall:

After analyzing the temperature data, rainfall data for the same catchment was analyzed to see whether there is any appreciable change in rainfall during the last 49 years. For this the trend line of the historical data was drawn and also the regression analysis was done.

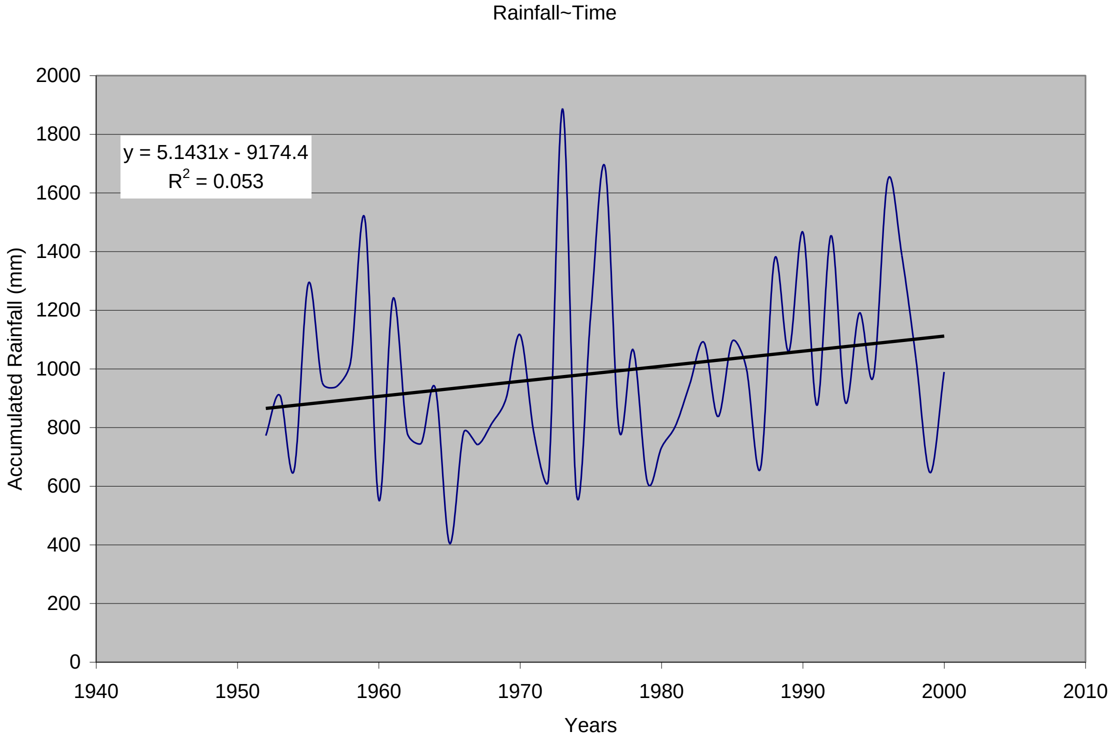


Figure 3.8: Rainfall Data for River Chenab at Maralla

As shown in Fig. 3.8 and from the results of the analysis, it was seen that the annual accumulated rainfall has increased during the last 49 years by 43.92%. The regression analysis showed that the value of R-square was 0.053 and the corresponding value of “r” was 0.23, showing a positive trend. Also the p-value for 95% confidence limits was 0.15.

Discharge Data:

After temperature and rainfall, the discharge dataa(1937-2004) for river Chenab was analyzed. From the trend line it was seen that there is not that much overall change in the discharges for the above mentioned period. The discharge values, though decreasing, were not affected substantially with the passage of time. The R-square value was found to be 0.0032 (Fig. 3.9) and the corresponding value of “r” was 0.056, showing a negative correlation, i. e. the discharges were decreasing with time. The P-value for 95%confidence limits was also not that much significant and came out to be 0.33.

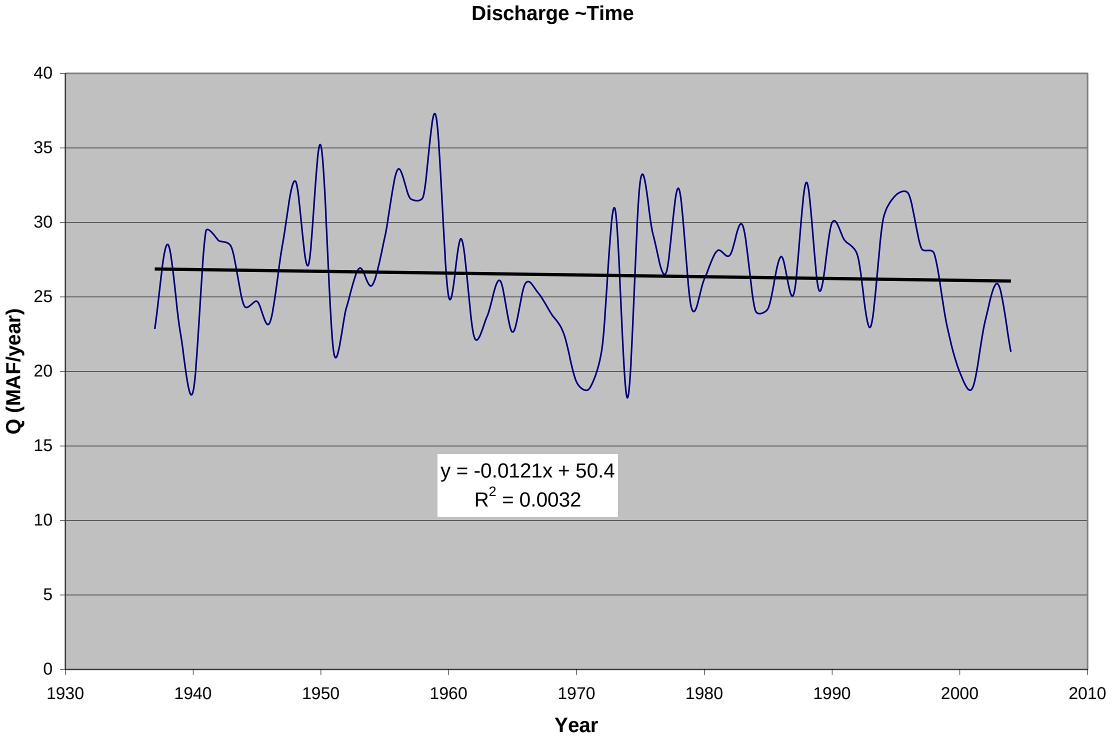


Figure 3.9: Discharge Data for River Chenab at Maralla

4. River Jhelum

River Jhelum was the last river that was analyzed to see whether there are any appreciable effects of the selected climatic variables on its discharges or not. The selected catchment was that of Mangla Dam. Data of Temperature, Precipitation and Discharges was analyzed first separately and then in combination and the statistical terminologies were calculated.

Temperature Data:

First of all the temperature data (1950-2000) for the area was analyzed. From these analysis it was seen that the value of R-square came out to be 0.0115 and the corresponding value of “r” the correlation coefficient was 0.11, indicating a positive trend in the temperature over the past 51 years, i. e. the temperature is increasing at a rate of 0.0035^{o}Cper year and has increased by 0.18^{o}C over the last 51 years. Also the P-value for 95%confidence limits was found to be 0.07. The plot of the temperature record versus time is given in Fig. 3.10 below.

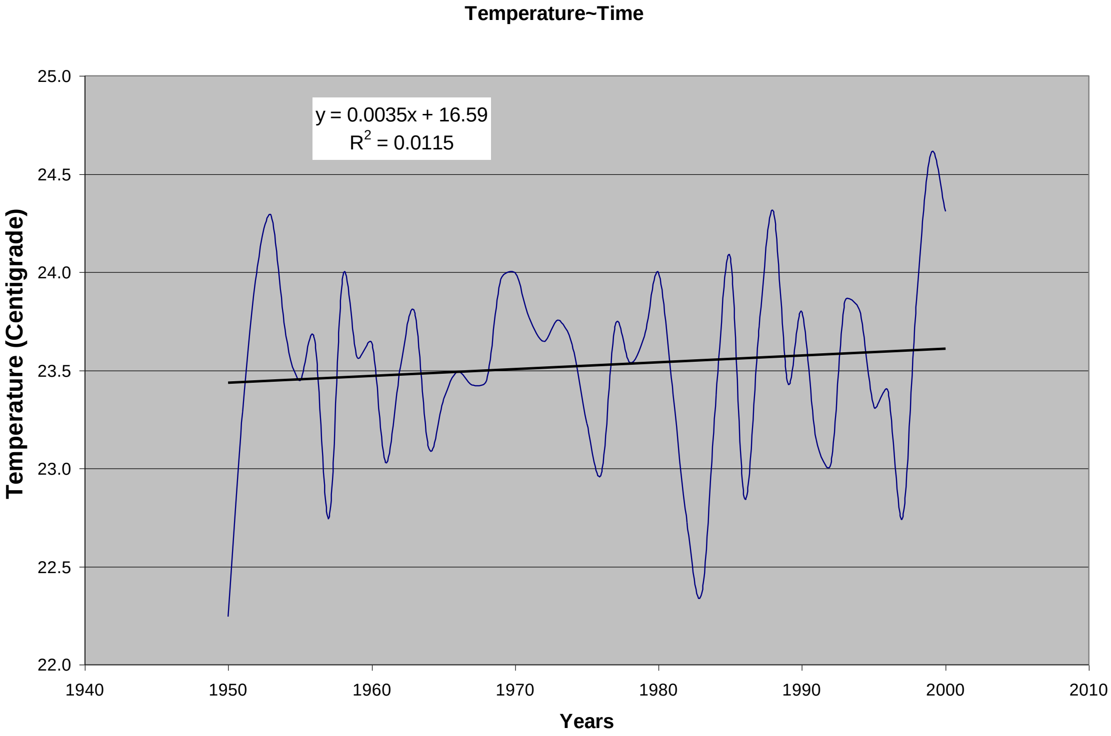


Figure 3.10: Temperature Data for River Jhelum at Mangla

Rainfall Data:

After analyzing the Temperature data, the rainfall data (1949-2000) for the area was also analyzed (Fig. 3.11). The results of the analysis showed that the R-square value came out to be 0.0959 and the corresponding value of correlation coefficient "r" came out to be 0.31, indicating a positive correlation, again showing that the annual rainfall is increasing wit time, which was of the order of 27.18%. The analysis also showed that P-value for 95%confidence limits was 0.045.

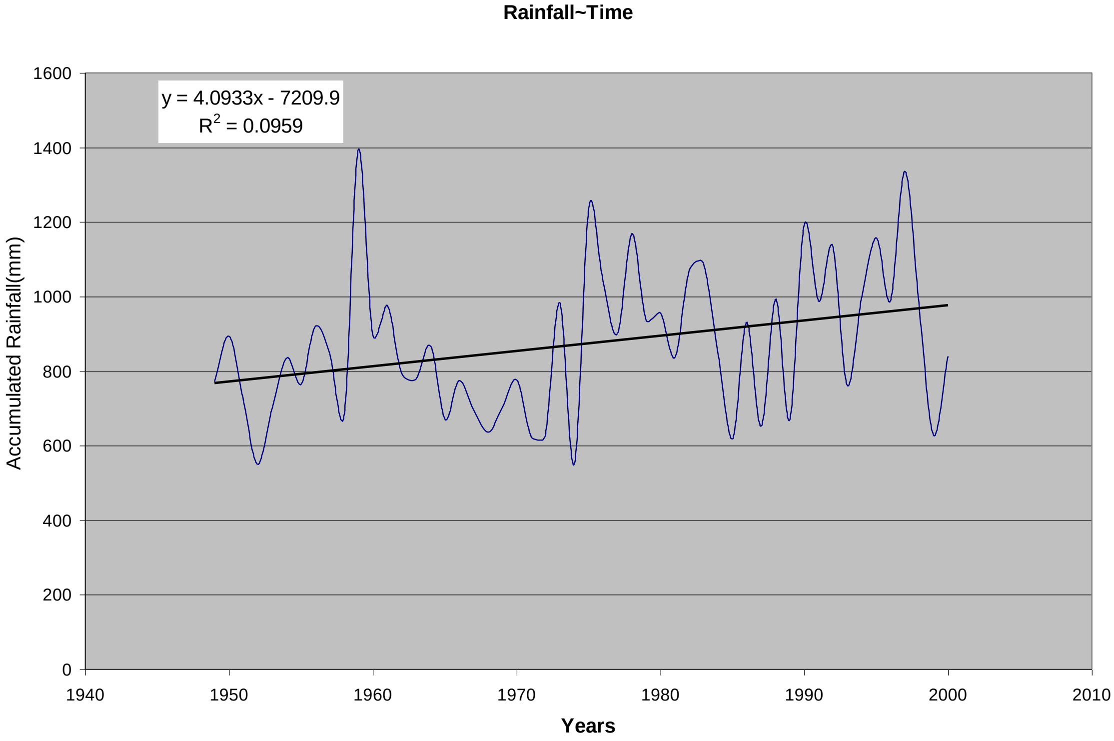


Figure 3.11: Rainfall Data for River Jhelum at Mangla

Discharge Data:

Next in line for the analysis was the discharge data. The data for Mangla from 1937-2004 was analyzed and it was seen that the value of R-Square was 0.0001 (Fig. 3.12) and the corresponding value of "r" was 0.0109, indicating a positive, though not that much significant change. But from 1996 to 2004, the discharge has decreased considerable at a rate of 1.332MAF per year which is not a good indication. Also the P-value for 95% confidence limits was found to be 0.77, again not that much significant.

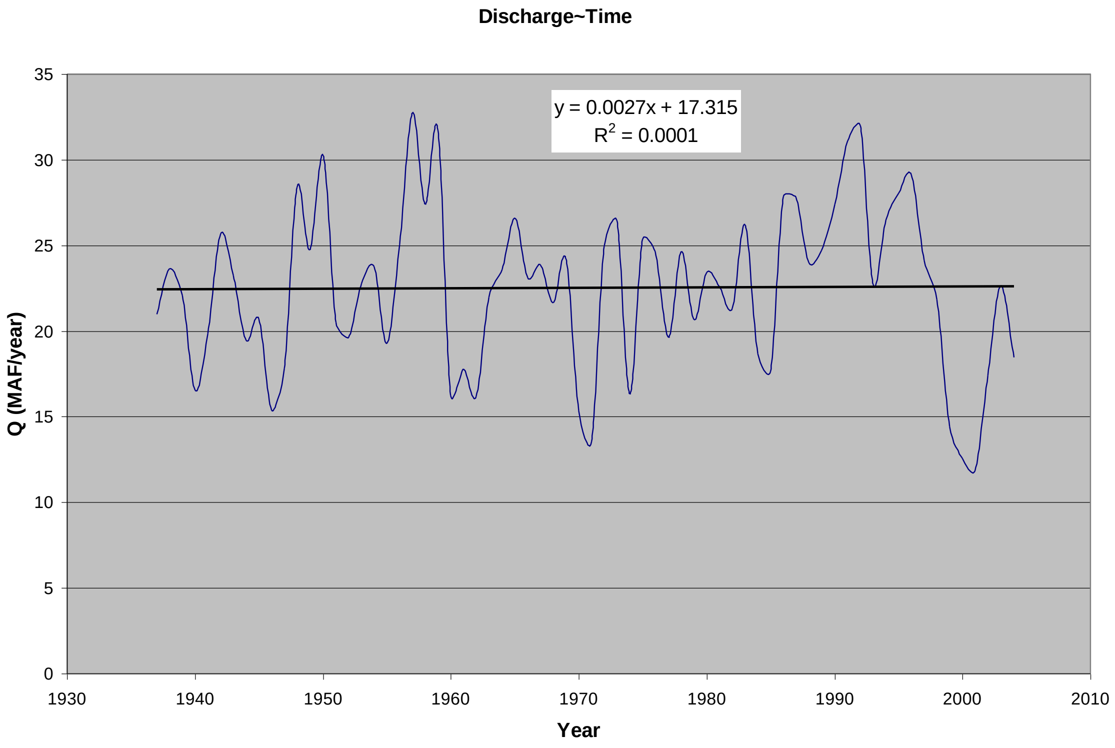


Figure 3.12: Discharge Data for River Jhelum at Mangla

4.0 Conclusions:

The summarized result of the individual regression analysis of the parameters are given below in Table 4.1.

Sr. No.	**Statistical Terminologies/Rivers**	**R-Square**	**Correlation Co-efficient "r"**	**P-value for 95% Confidence Limits**
1.	***River Indus***			
A	Temperature	0.4384	-0.66	6.14x10^{-9}
B	Rainfall	0.0583	0.24	0.19
C	Discharge	0.07	-0.27	0.02
2.	***River Kabul***			
A	Temperature	0.092	0.30	0.783
B	Rainfall	0.14	0.37	0.011
C	Discharge	0.31	-0.556	1.63x10^{-7}
3.	***River Chenab***			
A	Temperature	0.0006	-0.02	0.226
B	Rainfall	0.053	0.23	0.15
C	Discharge	0.0032	-0.056	0.33
4.	***River Jhelum***			
A	Temperature	0.0115	0.11	0.07
B	Rainfall	0.959	0.31	0.045
C	Discharge	0.0001	0.0109	0.77

Table 4.1: Summarized Results for Linear Regression Analysis

From the above results it can be seen that for River Indus, the Temperature was decreasing *(r = -0.66)*, the rainfall is increasing *(r = 0.24)* and again the discharges are decreasing as well *(r = -0.27)*.

For River Kabul, the temperature is increasing *(r = 0.30)*, the rainfall is increasing as well *(r = 0.37)* and the discharges are decreasing *(r = -0.556)*.

For River Chenab, the temperature is decreasing *(r = -0.02)*, rainfall increasing *(r = 0.23)* and Discharge is decreasing as well *(r = -0.056)*, although it is not that much significant.

For River Jhelum, all the parameters i. e. Temperature, rainfall and discharges are increasing with *(r = 0.11 for temperature), (r = 0.31 for rainfall) and (r = 0.0109 for discharge).*

4.1 Floods:

Due to the correlation between the climatic variables and discharges, it is obvious that the climatic changes definitely result in floods in the way that with the increase in temperature, the huge volumes of snow that have accumulated over the northern areas of Pakistan, definitely melt down, which results in increased discharges during summer months. There is a growing consensus that the impact of climate change may well lead to an increase in both the frequency and magnitude of floods. Mankind has to live with floods and devise measures to minimize their damages and optimize their benefits.

Floods in Pakistan:

During the last fifty years, Pakistan has suffered a cumulative financial loss of more than Rs. 380 billion and the loss of more than 6000 people as a result of major flood events in the Indus Basin Irrigation System. Heaviest direct flood damages in Pakistan occur to infrastructure, agricultural crops, damage to urban and rural property and public utilities. Historical flood damages in Pakistan are given in the table 4.2.

Year	**Value of Property Damaged (million rupees)**	**Lives lost (nos.)**	**Villages affected (Nos.)**
1950	11’282	2190	10000
1956	7356	160	11609
1957	6958	83	4498
1973	118684	474	9719
1976	80504	425	18390
1978	51489	393	9199
1988	25630	508	1000
1992	69580	1008	13208
1995	8698	591	6852
2001	450	219	50
Total	**380631**	**6051**	**84525**

Table 4.2: Floods in Pakistan Source (Federal Flood Commision, 2002)

5.0 Recommendations:

- More studies in developing the linkages between the climatic variables and discharges should be done in order to more careful understand the phenomenon by considering different climatic seasons and developing the co relations between climatic variables and discharges in these seasons.
- Also, variable of green house emission may also be taken into consideration for future analysis.
- The extent of snowmelt, the main cause of flow in rivers of Pakistan may also be related with the discharges, so that a most accurate relationship between the climatic variables and discharges can be obtained.
- Since the discharges in most of the rivers are decreasing, it is about time that we start building more water reservoirs for the storage of water so that increased demands for water can be met in future.

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WHO PAYS THE BILL? – THE IMPACT OF CLIMATE CHANGE ON REAL ESTATE MARKETS

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Purpose – This paper seeks to critically review the existing literature and models on climate change with regard to the effects on real estate markets. With the aid of selected parts of the Tyrolean real estate market as an example the costs and loss of value which are due to the change of climate already today are analyzed.

Design/methodology/approach – The research is based on hedonic pricing models as well as the results of the general research on climate change in order to find an improved method for the real estate industry.

Findings – The author identified that research activity concerning the impact of climate change on real estate markets has to be improved, since climate change has a very strong impact on property markets and until today this field of research is just about untouched.

Practical implications – The impact of climate change on real estate is very strong. Still practitioners do not react proactively since the effects have not been researched in detail. Especially very fragile regions like the Alps seem to be very intensely affected.

Originality/value – This Paper indicates one first step towards a new research field which deals with the quantifications of the impact of climate change on real estate markets.

Keywords – Climate Change, Real Estate, Market Value, Multiple-Regression, Welfare loss, Hedonic-Pricing

Introduction & Background

Due to the changes of the global climate, our civilization is confronted with profound transformation which will affect all areas of our lives. In scientific circles it is now generally accepted that a significant portion of the climatic changes is due to human activity. While climate change is better understood we also find a wider range of activities concerning the profound quantitative assessment of risks by ecologists and other research groups. The link between financial markets, the general economy and climate change is very important since climate change can be seen as the biggest "Market Failure" (Stern, 2006, pp. 24 ff) ever – climate change is a result of the negative external effects associated with emissions. Those who created the emissions did not pay for all the costs associated with the usage of the good. The "remaining costs" must be paid by the whole population or maybe even future generations. Therefore all activities to quantify the impact are a strong guidance to economists as well as politicians for decision making. The Stern Report (Stern, 2006) concludes that without further activity against climate change the average temperature change will be similar to the temperature difference between the last ice age and the present. Such a serious change of the physical geography of the earth will inevitably lead to a change of the human geography, i.e. where people live and how they live.

The costs of extreme weather conditions are already rising due to the increase of natural disasters such as floods, droughts, storms/ hurricanes, hail, mudslides etc. From 1995 to 2005 three times as many natural disasters occurred as in the 1960s. (Source: Münchner Rück). But also the gradual change due to changes in the rainfall patterns and the rising of the global mean surface temperature, as well as water pollution and acid rain are affecting our lives to a great extend.

A high quality of the environment and especially also of the soil, its sustainable usability for agricultural and economic purposes, its bearing capacity etc. are vital location factors. An impairment of the real estate markets is contra-productive for the entire economy. If you take into account that real estate valuation is based on the premise that real estate is valued according to its "highest and best use", it becomes clear that a loss of the utilization method which determines the highest-and-best-use-value leads to welfare loss. This is also true for losses which are due to climate change. Based on this it is surprising that real estate related research has not dealt with this field yet. In general the economic follow-up costs of pollution clearly exceed the annual costs for the protection of the environment (see Brügenmeier, 2006). The follow-up costs of this pollution have not yet been quantified for the real estate market. Very often the quantification of the costs caused has only been carried out insufficiently and/or has not been carried out at all as it is the case for the ground rent and the resulting land value. This is very surprising as land together with labor and capital represents one of the three major production factors according to the production functions of Gutenberg.

Present State of Research

Climate change has a number of characteristics which are unique (see in detail Stern, 2006):

- “It is global in its causes and consequences;
- The impacts of climate change are long-term and persistent;
- Uncertainties and risks in the economic impacts are pervasive.

- There is a serious risk of major, irreversible change with non-marginal economic effects."
- Originator and persons concerned are usually not identical;
- Negative external effects caused climate change;
- Climate Change is a very complex field and until today not very well understood;
- There is an interaction with other aspects of market-failure;
- Aspects concerning ethics, justice and freedom are also relevant;
- The problem of climate change is inter-generational.

The challenges that arise out of this situation are manifold and turn it into a challenge to convert climate change into a financial figure. In future, there will be a focus on aspects like cause/effect relationships, temporal components of the changes, questions about regional consternation as well as strategies to internalize negative external effects or neutralize developments that are already (possibly) irreversible. Of equal importance is the answer to the question of how every individual can adapt to the changes. All around the world thousands of biologists, meteorologists, statisticians and other experts from various disciplines are working on the above mentioned research questions. For an economic analysis aspects like the special restriction of effects, the definition of adequately long time horizons, the implementation of the uncertainty in terms of the input variables and the model structure itself, the consideration of ethics in economic-models etc. must carefully be looked at. It is obvious that a lot of the analytical tools and models used in economics today are likely to fail when it comes to the quantification of the welfare loss and general economic impact of climate change (for further details see Stern, 2006). For example a main reason why probabilities based on historical results must fail is because due to climate change the developed models are constantly changing. Therefore it is not possible to derive probabilities by using statistical data series since these results can be used as an estimator for future volatility of the distribution. All present approaches have in common that the analysis does not focus on the individual economic subject or land but rather on the entire economic costs and welfare loss.

Especially since 2005 a lot of publications and research work have focused on the financial implications and costs of climate change driven by the rising damages, which had to be covered to a great extend by insurance companies like Swiss Re and Munich Re. Since the companies focus on their profit and the needed premiums of the insured climate change has eventually become a more financial figure. The German Max-Planck-Institute expects rising costs of 27 billion € annually in Germany until 2050. Major investors and insurance companies therefore legitimately ask companies to develop climate strategies in order to secure their assets in the long run (see Bergius, 2006).

Stern, 2006, was the first economist who in depth started to quantify the impact and cost of climate change on a global basis. But also geo-engineering experts like Crutzen (see Schürmann, 2006) start to quantify the costs of climate change or more exactly the costs of reversing the development to more than 50 billion € p.a. worldwide.[1]

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[1] see Stern, 2006 for further discussion of a more detailed framework concerning intertemporal appraisal, uncertainty, changing population, inequality within generations, market imperfections , etc.

Research Structure and Objectives for Real Estate

Land is one of the three elementary production factors and the most significant subject in real estate economics. A large part of the capital in the economy is tied up in real estate, which is why both the function of its pricing processes and the forecasts for pricing trends have always been the most intensively studied fields. The objective of this paper and of the real estate industry in general must be to clarify the relationship between climatic transformations and the resulting changes in land values. For this reason it is necessary to first isolate the effect of the climate on land values and the yield rate generated by the use of land. In order to determine the price changes for real estate, concrete points have to be found that can be transferred into an impact on the prices or indirectly on the expected yield rates generated by the use of land and other input variables for the appraisal process.

Until today climate change has not been a field of research in real estate

The "market value“ of any real estate is the "the estimated amount for which a property should exchange on the date of valuation between a willing buyer and a willing seller in an arm’s length transaction after proper marketing wherein the parties had each acted knowledgeably, prudently and without compulsion.” (RICS, 2003). In the end today's value of land is always the current value of future profit potentials which can result thereof. If this future profit is restricted due to climate change, it has to be considered in today's value. Investment or income methods for real estate appraisal show this relation most clearly since these methods discount future cash-flows to calculate their net-present-value which represents the market value.

Looking at the discount rates which should be used reveals another challenge. A long-lasting, healthy environment has its pay-off in the future instead of the consumption of all the benefits of nature, climate and the entire environment today. Therefore a relatively high discount rate of the future cash-flows will more likely lead to a capital value of the benefits which is smaller than the costs today to achieve the course of events which is in favor from the standpoint of future generations. In other words: if you do not care about your children choose a high discount rate. On the other hand every real estate appraiser knows that choosing a relatively high discount rate expresses also that the investment cash-flows are somehow uncertain, especially when the horizon is very long like in the case of climate change. So even finding the “right” discount rate is difficult but at the same time crucial for the results (see also Stern, 2006).

Until now, researchers (e.g. Christaller and von Thünen) have mainly published studies illuminating the influence of demographic and socio-economic aspects on values. Two spheres that have not yet been analyzed scientifically are the influence of climatic conditions on the value of land in depth and the effects of climate change on future real estate values. More exactly, the essential research field that deals with the issue of the effects of climate change on land values has been left almost completely untouched. Neither real estate economists nor climate researchers have drawn definitive conclusions for this particular field.

First the available results of the general climatic research must be scrutinized to determine their relevance for the real estate economy from a qualitative perspective. Hereby one must distinguish between natural disasters caused by climate change (such as storms, hail, flooding, droughts, acid rain, and water pollution) and creeping transformations (such as global temperature increases). Using the comparison method a lot of the value drivers used in this method are directly related to the climate and therefore also exposed to climate change:

- **Defined macro and micro location:** climatic conditions, especially illumination, sun, wind, immissions (noise, smoke, dust);
- **Soil conditions of the location:** surface formation, natural cover, bearing capacity, ground water conditions, mud slide areas, exposure to dangerous areas (flooding, avalanches, torrents).

Even a very superficial review reveals that the impact on the use of land and the connected yields generated is very powerful:

- **Migration:** E.g. about 200 million people of coastal regions will not be able to enjoy their familiar quality of living and will therefore move inland.
- **Destruction:** Vast regions of Africa and the Mediterranean will be destroyed by decreasing precipitation and will not be economically usable anymore.
- **Decreasing crop yields:** Certain regions will have to face decreasing crop yields
- **Melting of the glaciers:** As mountain glaciers disappear the potential threat to water supplies in several areas rises and during the transformation mud slides are likely to happen.
- **Change of water distribution worldwide**: Significant changes in water availability will lead to increasing expenses for the distribution and/or migration will be encouraged
- **Rising sea level:** Reduces the habitat which can be used by human beings and leads to flooding etc.
- **Fragile ecosystems collapse:** A large fraction of (especially more fragile) ecosystems will be unable to continue at existing forms (rainforests, Alps, Coral reef etc.)
- **Protection costs** for extreme weather events will rise (like for storms, forest fires, droughts, flooding and heat waves etc.)
- **Change of construction methods and operating costs:** Rising operating costs e.g. for cooling. For example the unequal distribution of precipitation will more frequently lead to torrential rain with its respective requirements on infrastructure.

Specific examples of places that have already experienced irreversible changes concerning the environment and therefore also land value include the following: Austria in areas where high-risk zones because of floods or other climate change related risks were extended after the deluges; in Portugal in the regions afflicted by forest fires; and in Florida where there has been an increase in the damage caused by hurricanes.

Approach I: Using multiple regression and hedonic pricing models?

Hedonic pricing models attempt to decompose the given housing prices into their value drivers by using multiple regression models. However, until now these analyses have focused on the influences of infrastructure, population density and other socio-economic aspects within the framework of hedonic pricing models. Some environmental factors like crime, neighborhood, earthquake risk, air pollution and climate where also analyzed (see Gyourko, Kahn and Tracy (1999)). Leaving other variables constant, how much lower would the market values be in a city with a mild climate compared to hot climate? Hedonic pricing models are useful to disclose the marginal consumer's preference for different value drivers which together are the market value. Levitt (2004), Costa and Kahn (2003) and others estimated how the hedonic price of a non-market good like "climate" can be estimated and how it has evolved as well as how hedonic valuation might be affected by shocks like new laws. This field of research can be called "cross-city hedonic quality of life literature". It has existed for approx. 25 years and its results and hypotheses are a very useful foundation for further research on climate change and its impact on real estate markets.

There are some reasons why the use of hedonic pricing models to estimate the cost and the impact of climate change have been an untouched research field until today. This is mainly because (1) hedonic pricing models analyze historical data and climate change is a dynamical process with a lot of the results only visible in the future and (2) because climate change is a complex topic with a lot of variables interacting and (3) because uncertainty is inherent when talking about climate change. Still hedonic pricing models can help a lot. Since they can disclose the value of "clean air" in one city and "dirty air" in another, there are possibilities to come up with a price for an aspect of climate. Given the models for climate change with the projection of future events both aspects together enable to calculate the impact of further air pollution on the housing market in the location being appraised today. However the problems of interaction, uncertainty, time-preference and changing consumer preference still need to be addressed. The uncertainty of floods for example could be captured by using existing concepts like the *probability of occurrence* and the *expected amount of loss* to evaluate the results.

Approach II: Using experts' views and proxies to calculate the impact on real estate related variables?

Expert interviews and surveys provide information on how the input variables for the valuation of real estate (markets) will change. It is worth considering the functional chains, i.e. responding to the question of how the climate will influence e.g. macroeconomic values and how they are linked with the real estate industry. However, it is problematic that the functional chains have not been researched in depth. As the first results concerning the expected revolution (see Stern, 2006) already exist on the macroeconomic level, it is possible to make rough estimates already now. We will come back to this aspect when dealing with a simple case study for Tyrol.

It is also helpful to continually observe various variables prior to real estate values as they are exposed to visible changes already now due to climate change. Among these points are the prices of renewable resources (e.g. oranges or nutmeg), price quotes for climate certificates, the development of insurance premiums, changes in the GDP dynamics of affected regions, increasing preventative costs related to construction measures and other measures for containing forest fires.

Questions beyond today's research activities

Concerning real estate markets the quantification of the impact of climate change has just reached its starting point. A lot of research questions that have not been discussed in detail until present have to be addressed:

- What can the real estate industry contribute to the internalization of negative externalities and to what extent can irreversible damages be avoided?
- What is the advice real estate researchers can communicate to real estate investors in order to build up their (long-term) investment plans and strategies which incorporate climate related aspects?
- Are there also opportunities for the real estate industry or do we just face threats? Is it possible to reveal real estate markets that present themselves as "windows of opportunity" which could profit from environmental change and would otherwise have escaped the focus of investors?
- Is there a possibility to come up with a more detailed quantification of the costs and maybe benefits of climate change for different regions?
- How do decision makers process information with regard to real estate investments and what is the influence of uncertain future events like climate change? Is the information processing of the players sufficient or is climate change not yet considered sufficiently in the current land values?[2]

In this respect, it would be exemplary to answer the question of why the real estate prices in Spain have risen exorbitantly in the past few years, even if the market participants must be fully aware of the long-term forecasts for the Iberian peninsula (here it will be important to separate climate from the other components in the pricing processes).

Based on these results, an "Ecological Change Impact Index on Real Estate Markets (ECIREM)" should be developed in the middle term. This index must include a feature that makes it possible to continuously enter and update data automatically collected from the various existing climate models. It would probably be sensible to differentiate the index, so that the impact within different timeframes (e.g. 10, 20, 50 yeas) would become more transparent. The Index would cover a global database, whereby Europe will be studied more closely.

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[2] Remark: There is strong evidence that the relevance of the climate change is still underestimated – in fact also by professional participants of the market like e.g. property insurers (Lansch, 2006).

Quantification of the climate impact on Tyrol's real estate markets

General overview

In this first step the paper only focuses on areas which require further and more intense analysis. Therefore the first step does not yet try to fully connect the econometrics of the real estate markets with the current climate models or to show an entire presentation of the monetary effects of the real estate markets based on the occurrence probability of climate scenarios.

In this first analysis we focus only on negative market impacts that can already be “measured”. We use a ceteris paribus model and also leave out the possibility that positive changes might occur (like an increase in the corps production at higher altitudes, higher price for clean power production etc.). In this example we derive the climate change from expert statements and empirical studies representing the current doctrine as well as the state-of-the-art of climate experts. So based on these scenarios of climate change the current real estate values have to be transferred into their expected value in order to quantify the effects of climate change. In this context it is of major importance that the current real estate values did not yet consider the effects of climate change because in this case redundancies would jeopardize the significance of the result. At this point two alternatives can be chosen. The first alternative are hedonic pricing models. Value drivers which are calculated within multiple regressions are the link between the situation for climate A and the situation for a new climate B. For this purpose it has to be proven empirically how much more a piece of land at location C with the feature "180 days of complete snow cover p.a." costs compared to a similar piece of land with the feature "170 days of complete snow cover p.a.". Of course, the expected difference in value has to be discounted in order to represent the current value of welfare loss. However, it is easier – and this is our choice for this example – to use e.g. an average investment value of the past x-years which means largely without climatic elements. Based on the climate models certain real estate input parameters are again changed. However in this case the change only relies on expert assumptions which are supported by climate data and conclusions about chains of cause and effect. Even if the latter method can be questioned concerning the chains of cause and effect which are only verbally substantiated, a first impression of the quantitative welfare loss for the purpose of an awareness analysis can be gained.

This study seeks to examine an especially fragile ecosystem like the Alpine region, taking Tyrol as an example. In Tyrol the following effects relating to land value relevant aspects of climate change can be observed:

- **Melting glaciers and shorter winters:** As mountain glaciers disappear the potential threat to water supplies in several areas rises and during this transformation mud slides are likely to happen.
- **Change of water distribution:** Significant changes in water availability will lead to increasing expenses for the distribution and/or migration is encouraged.
- **Fragile eco systems collapse:** A large fraction of (especially more fragile) ecosystems will be unable to continue at existing forms (rainforests, Alps, Coral reef etc.)
- **Protections costs increase** for extreme weather events will rise (like for storms, forest fire droughts, flooding and heat waves etc.). In Tyrol especially high costs for protective measures concerning avalanches, mud slides, early warning systems, flooding etc. have to be taken into account.
- **Expansion of the security zones:** The non-constructible areas due to increasing natural hazards have lately been expanded considerably in Alpine regions. These areas are not at all (red zones) or only partly constructible (yellow zones). Compared to land without these restrictions significant value losses can be stated due to the expansion of these areas.
- **Change of construction and operating costs:** Rising operating costs e.g. for cooling. Or for example the unequal distribution of precipitation will more frequently lead to torrential rain with its respective requirements on infrastructure.
- **Decreasing income potentials:** Due to shorter winters and rising snow lines Tyrol's most important source of income – winter tourism – will be impaired in a sustainable way. Cable car owners currently have a turnover of approx. 40 million € and the accommodation industry of approximately 1.1-1.2 billion € in the winter season only.

For Tyrol the year 2006 was the hottest period in 1.300 years (ZAMAK, 2006). The effects of climate change are more severe in the Alps than in less fragile regions.

Example: Impact on the lodging market
We are only focusing on winter tourism which represents 60% of all overnight stays. The turnover share of the winter tourism amounts to approx. 70%, especially because per-capita expenses and occupancy rates are higher in winter than in summer. Tyrol is the province with the biggest share of Austria's winter tourism with 42.4% of overnight stays (Source: Landesstatistik Tirol).

Different research projects show that winter tourism in the Alps will be severely affected by the forthcoming changes that are already irrevocable. It is already accepted that the closing of ski resorts which are at an altitude of less than 2.000m is a probable scenario since the snow line will rise by approx. 400m. Tyrol offers approximately 7,200 hectares of ski slopes with approx. 1,200 lifts and cable cars which achieve an annual turnover of approx. 400 billion € (2001). The annual investment amounts to approx. 180 million €, 23 million € of which are used for the production of snow in 2001 – an upward trend (Chamber of Commerce Tyrol). While the share of artificially snowed slopes was 45% in 2001, it has risen to 80% in 2006 (Gasser).

In 2001 86 Tyrolean lifts were closed due to inefficiency, but the construction of new lifts at higher reaches compensated for this again (Ludescher, 2001). About a third of the 70 Tyrolean ski resorts are below an altitude of 2,000m and will therefore be concerned most by the effects of climate change. During the winter season 2006/2007 ski resorts which are situated at lower altitudes have experienced a reduction of turnover and frequency of up to 80% due to lack of snow (Chamber of Commerce Tyrol, Section Cable Cars). A considerable move towards ski resorts at higher reaches with slopes that are well maintained and up to now in perfect snow condition can be observed. As the current climate predictions assume also the melting of very high glaciers it is disputable whether intensified investment in these areas is really profitable. Already today the winter season starts approx. 3 days later and stops again 3 days earlier which means that it is gradually becoming shorter. And so far the operators of ski facilities are all reacting the same way: they buy more snow machines, e.g. SkiWelt, one of the biggest ski resorts with an annual turnover of 43 million €, operates 400 snow machines.

During the past 10 years the average overnight stays amounted to 23,120,000 p.a. in winter. For this period the average number of beds was approx. 307,000. The winter season starts on 1 November of the previous year and ends on 30 April of the indicated year and thus comprises 181 days. This leads to an average occupancy rate of beds for all types of accommodation of approx. 42%. The turnover per overnight stay in a bed and breakfast in Tyrol amounts to approx. 50,- €. If you deduct the costs of the breakfast of approx. 5,- €, the share of accommodation (without taxes) amounts to approx. 45,- € per overnight stay (Source: Landesstatistik Tirol).

Gross Revenue (Turnover)
-Gross Expenditures
=Gross Profit
-Tenant's Expenditures
-Tenant's Share
=Ratable Value (Rental Revenue)
-Other Operating Expenses
=Net Operating Income to Owner

It is assumed that approx. 25% of the turnover remains with the owner of the real estate as ratable value or rental revenue. After deducting the approx. 15 % of the operating expenses the remaining cash flow must be discounted to appraise the property. The capitalization rate for hotel valuations is approx. 6,75 %. In agreement with the theories according to international approaches of valuation this revenue is considered to be perpetual rent.

Example Part I.: Direct capitalization of one stabilized year	
Scenario I.: Average Capital Stock based on historical data	
Number of Beds	307.000
Stabilized Occupancy in %	0,4158
Stabilized Revenue per Night (incl. Breakfast) in €	50
Breakfast portion in €	5
Stabilized Revenue per Night (excl. Breakfast) in €	45
Days of Operation in the Winter Season	181
Stabilized Total Revenue in the Winter Season in €	1.039.714.137
Rental Revenue in %	0,25
Rental Revenue in €	259.928.534
Operation Expenses in %	0,15
Net Operating Income to Owner in the Winter Season in €	220.939.254
All Risk Yield (Discount Rate)	0,0675
YP in perpetuity (Year's Purchase)	14,81
Net Income × Year's Purchase = **Capital Value Contribution of the Winter Season** in €	**3.273.174.135**
Value contribution per Bed	10.662
Value contribution per Room (with two Beds per Room)	21.324

Table 1: Using *Direct capitalization* to appraise the Capital Value Contribution (this strongly simplified example illustrates the issue)

This results in a capital stock contribution based on the NOI-Contribution of the average winter season of approx. 3.3 billion € based on the above mentioned theories and without influence of climate change.

Against the background of climate change the input data for the valuation of the capital stock are changed accordingly. This first, simple example is primarily used to show how the change of climatic variables influences the input parameters of the real estate market. The changing variables are the operation days, the occupancy rate, the average revenues as well as the risk of the investment. All aspects can be quantified. It is a realistic scenario that e.g. the operation days are shortened due to the late start and early end of the winter season. The chosen duration of a total of 5 days represents the lower end of the predicted future development.

Example Part II.: Direct capitalization of one stabilized year	
Scenario II.: Increasing Average Temperature of 2 °C	
Number of Beds	307.000
Negative Impact on Occupancy in %	-0,05
Adjusted Stabilized Occupancy in %	0,39501
Negative Impact on Revenue in %	-0,05
Adjusted Stabilized Revenue per Night (incl. Breakfast) in €	47,5
Breakfast portion in €	5
Stabilized Revenue per Night (excl. Breakfast) in €	42,5
Negative Impact on Days of Operation	-5
Adjusted Days of Operation in the Winter Season	176
Stabilized Total Revenue in the Winter Season in €	907.085.164
Rental Revenue in %	0,25
Rental Revenue in €	226.771.291
Operation Expenses in %	0,15
Net Operating Income to Owner in the Winter Season in €	192.755.597
Negative Impact on Discount Rate	0,0025
Adjusted All Risk Yield (Discount Rate)	0,07
YP in perpetuity (Year's Purchase)	14,29
Net Income × Year's Purchase = **Capital Value Contribution of the Winter Season** in €	**2.753.651.390**
Value contribution per Bed	8.970
Value contribution per Room (with two Beds per Room)	17.939

Net Capital Loss in %	0,16
Net Capital Loss in €	**519.522.746**

Table 2: Appraising the Loss of Capital Value due to Climate Change (this strongly simplified example illustrates the issue)

Of course this calculation is far from being perfect. On the one hand one could argue that e.g. the winter season is shortened, but that the problem can be solved with the aid of snow machines. However, this leads to enormous costs which would have to be taken into account in in-depth analyses. On the other hand it is legitimate to ask why the risk of investment – represented by the increase of the discount rate – is increased in this way.

Indeed this field has to be analyzed critically and furthermore the actual increase must be examined scientifically and empirically. Income effects which concern the 33,000 employees of the tourism industry as well as the approx. 6,000 employees of the cable car operators are not yet taken into account either although they have a (negative) influence on the real estate market and lead to an aggravation of the mentioned changes. Revenues resulting from the clothing industry (winter sports goods) and gastronomy are not considered etc.

Nevertheless the first interpretation of the result is of major interest. Obviously the effect on the real estate capital stock of society with its 500 million € is highly remarkable. This welfare loss becomes reality already when the above mentioned minor changes of the input parameters provable by realistic climate scenarios occur. As only a minor fraction of the concerned areas of the entire Tyrolean real estate market could be dealt with in this analysis, there is a serious need for further research in this field.

Resume

With this paper a contribution has been made to opening the climate discussion also to a larger audience in the real estate economy, and to showing a number of ways how to approach the calculation of the forthcoming changes.

So far neither national nor international researchers have succeeded in uncoupling the economic growth from the use of non-regenerative resources. The quantification of all follow-up costs and value losses which are due to climate change is a fundamental prerequisite for the long-term enforcement of resource prices taking into account also the negative external effects. It is recommended that the real estate industry more actively focuses also on the long-term development of assets in their investment appraisal methods. This also includes the signals – considered to be weak by some real estate experts – of the climate scientists. It is problematic that currently the structural change due to climate change is not sufficiently perceived as a sustainable change yet. Fahrholz (2006) showed that many winter sports resorts meet this change rather passively and with obsolete strategies instead of facing the issue proactively. For this reason the negative effects of climate change will hit these regions especially hard.

The real estate industry can obviously contribute a reasonable as well as considerable part to the current "climate debate". Especially when considering the big share of real estate bound assets of the national economy this aspect is highly important. In order to solve the challenges due to negative external effects only an internationally coordinated approach makes sense. Results of the real estate research may provide decision makers with the necessary input in this context.

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SIGNAL AND TREND ANALYSIS OF TEMPERATURE SERIES: A TURKISH CASE

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With an aim of estimating climate change and its urban-induced bias in selected Turkish cities we have used very recently quality controlled temperature and precipitation data of Turkish stations in the period of 1950-2004, with 55 years long series, adequate to talk about the recent half century climatic changes. These stations are classified into two groups according to their populations; S1, including rural and suburban stations and S2, including large urban stations. Mann-Kendall test statistics are calculated for maximum, minimum, mean temperatures and precipitation to determine the spatial trend patterns. Our results show that 29 stations produced significant warming trends in one or more of their maximum, minimum or mean temperatures. These stations are mainly located on western, southern and southeastern parts of Turkey. On the other hand, significant cooling trends are mostly experienced in the northern parts of the country with 6 stations leading to significant cooling in one or more of their temperature profiles. Regional analysis show that the Mann-Kendall statistics for the minimum temperatures, which is a signal of urbanization, in almost all of the regions are in an increasing trend except for the northeastern parts. Maximum temperatures have significantly increased in south and southeastern regions and some areas in western coastal zone. The mean temperature profiles have shown almost the same behavior as maximum temperatures. The signal analysis of the available daily climate data is performed in various forms. 365 day moving averages are calculated for each day to observe annual temporal patterns of temperature. To eliminate the short term fluctuations and examine the possible trends, a digital low pass filtering is applied. Thus the long term variations, like an apparent increase in the average temperatures of 1990s is detected.

INTRODUCTION

An increasing body of observations and analysis gives a collective picture of a warming world and other changes in the climate system. The global average surface temperature has increased over the 20th century by about 0.6°C. Climate change is threatening the food production, drinking water supplies and sustainable development throughout the world. Rising sea level, extreme weather events and desertification is just a few of the effects, especially threatening the millions of people living in less developed countries. Intergovernmental Panel on Climate Change report (IPCC, 2001) expresses that global warming mainly caused by human activities is a reality and there are growing fears of feedbacks that will accelerate this warming.

Within the last several decades, the increasing efforts to gain insight into the man-made climatic changes have resulted in much work on temperature records, mainly in the developed countries. Previously, much work had focused on North American and European countries owing to the ready availability of abundant data. With the expansion of the global climatic datasets, a worldwide increase in the number of studies on climate variability has taken place, leading to a better understanding of climate system (Jones and Mann, 2004; Charlson and Wigley, 1994; Karaca et al., 1995, 2000; Karl et al., 1993; Kiehl et al., 2000; Nasrallah and Balling, 1993; Tayanç and Toros, 1997; Tayanç et al., 1997, 1998a, 1998b; Wigley, 2005; Ezber et al., 2006; WMO, 1992).

This study is aiming to conduct a research on climate variability in Turkey via historical observation data extending back to 1950s, determine the time and place of significant changes in temperature and precipitation, and comment on the possible effects of the climate variability. In this respect, this work proposes to compile up-to-date and historical meteorological data, carry out nonparametric statistical tests and signal analysis, determine any climatic changes in Turkey, find the threatened regions, and look to the future for any climate change dangers.

In the following section we first classify the 53 meteorological stations having data in the period of 1950-2004 and explain the methods used in this study. In the Results section we look forward to find any climatic changes in the min, mean, max temperature and precipitation series via trend and signal analysis, and comment on the findings and urbanization problems in Turkey.

STUDY AREA AND METHODS

The population of Turkey has grown almost 3.24 times between 1950 and 2000, from 20.947.188 to 67.803.927 [(State Institute of Statistics), 2000]. As can be seen in Figure 1, there is a sharp increase in early 1980’s in urban share of this population. This increase of population in the favor of cities, has dramatic effects in the structure of land-use, convert the green areas to concrete buildings and this in turn may produce significant changes in the micro and meso-scale climatic conditions.

To investigate the changes in climatic variability in Turkey, maximum, minimum and average daily temperature and daily precipitation data, provided by the National Meteorology Service, from 53 meteorological stations in Turkey are analyzed for a 55-years time period, between 1950 and 2004 in the study. The spatial distribution of stations used in the study is presented in Figure 2. The stations are classified into two groups according to the populations they represent; S1 for stations with a population below 100000 and S2 for stations with a population higher than 100000. Detailed information of these stations is provided in Table 1.

A computer code, which synchronizes the data by checking the missing dates or values, calculating the daily average for each day of a month throughout the whole available study period, and replacing the missing values with the calculated climatic averages, is developed for this purpose. The months having more than 15 missing days and the years having no data available are excluded from the datasets in order to obtain more reliable bases for the trend analysis. The homogeneity of each station for each parameter is checked by producing difference series with their neighboring stations. The stations that have one jump in the whole study period are corrected by either adding or subtracting a value, which is obtained by taking the difference between the averages before and after the jump. The program then calculates the monthly, seasonal and yearly averages for each station and for each temperature and precipitation series.

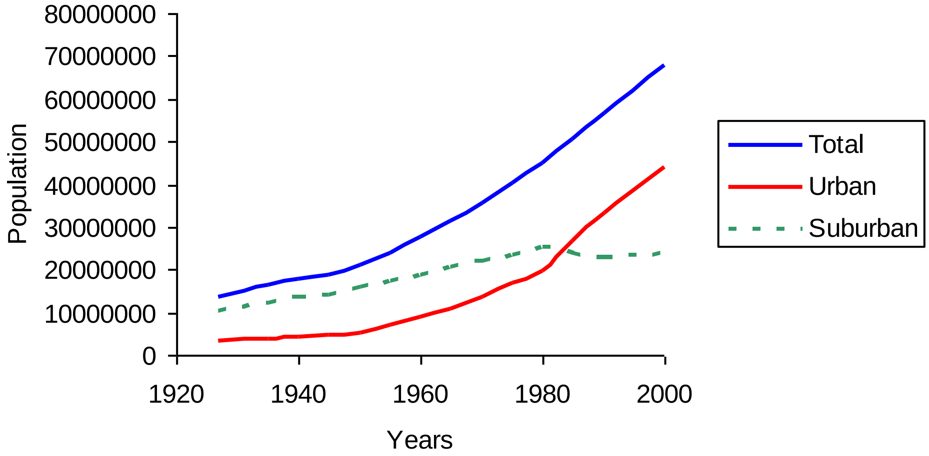


Figure 1. Population variability in Turkey between 1927 and 2000.

Mann-Kendall Trend Test

A non-parametric trend test, Mann-Kendall, is applied to temperature and precipitation series of all stations. If a Mann-Kendall statistic of a time series is higher than 1.96, there is a 95% significant increase in that particular time series. If the result is just the reverse, i.e. lower than -1.96, there is a 95% significantly decreasing trend in the series. The Mann-Kendall statistics are then plotted on a map in order to show the spatial distribution of both the significant and non-significant temperature and precipitation trends in Turkey. These plots are produced on monthly, seasonal and yearly basis to determine any significant climatic changes that might took place during the 55 years time period and to determine the critical months that were mostly affected by the climate change. To prevent unrealistic spatial prediction, the boundaries of the domain are set to 25 – 48° E and 34.5 – 44° N.

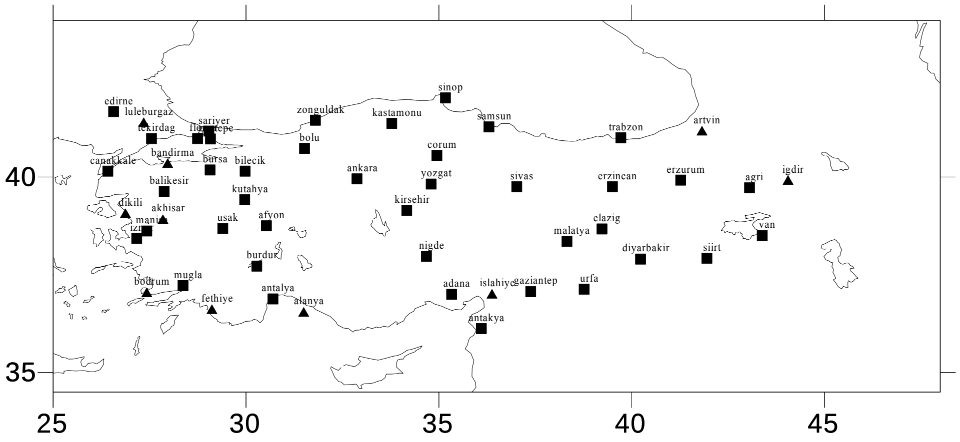


Figure 2. The spatial distribution of the meteorological stations (▲represents the stations characterized by populations up to 100 000, and ■ above 100 000).

Table 1. WMO numbers, Classifications, Coordinates and 2000 populations of 53 stations.

WMO NO	STATION NAME	LAT	LONG	ALT(m)	2000 URBAN POP	CLASS
17022	Zonguldak	41.45	31.80	137	250282	S2
17026	Sinop	42.02	35.17	32	101285	S2
17030	Samsun	41.28	36.30	4	635254	S2
17037	Trabzon	41.00	39.72	30	478954	S2
17045	Artvin	41.18	41.82	628	84198	S1
17050	Edirne	41.67	26.57	51	230908	S2
17056	Tekirdağ	40.98	27.55	4	395377	S2
17059	Kumköy (Kilyos - İstanbul)	41.25	29.03	30	1852	S1
17061	Sarıyer (Kireçburnu)	41.17	29.04	58	219032	S2
17062	Göztepe (Kadıköy)	40.97	29.08	33	663299	S2
17070	Bolu	40.73	31.52	742	142685	S2
17074	Kastamonu	41.37	33.78	800	174020	S2
17084	Çorum	40.55	34.95	776	311897	S2
17090	Sivas	39.75	37.02	1285	421804	S2
17094	Erzincan	39.75	39.50	1218	172206	S2
17096	Erzurum	39.92	41.27	1869	560551	S2
17099	Ağrı	39.72	43.05	1631	252309	S2
17100	Iğdır	39.92	44.05	858	81582	S1
17112	Çanakkale	40.15	26.42	6	215571	S2
17114	Bandırma	40.35	27.97	58	97419	S1
17116	Bursa	40.18	29.07	100	1630940	S2
17120	Bilecik	40.15	29.98	539	124380	S2
17130	Ankara	39.95	32.88	891	3540522	S2
17140	Yozgat	39.82	34.80	1298	315156	S2
17152	Balıkesir	39.63	27.88	102	577595	S2

Table 1. Cont.

17155	Kütahya	39.42	29.97	969	318869	S2
17160	Kırşehir	39.15	34.17	1007	147412	S2
17172	Van	38.50	43.38	1671	446976	S2
17180	Dikili (İzmir)	39.07	26.88	3	12552	S1
17184	Akhisar (İzmir)	38.92	27.85	93	81510	S1
17186	Manisa (İzmir)	38.62	27.43	71	714760	S2
17188	Uşak	38.68	29.40	919	182040	S2
17190	Afyon	38.75	30.53	1034	371868	S2
17199	Malatya	38.35	38.32	898	499713	S2
17201	Elazığ	38.67	39.23	991	364274	S2
17210	Siirt	37.92	41.95	896	153522	S2
17220	İzmir	38.43	27.17	25	2732669	S2
17238	Burdur	37.72	30.28	967	139897	S2
17250	Niğde	37.97	34.68	1211	126812	S2
17261	Gaziantep	37.07	37.38	855	1009126	S2
17270	Urfa	37.13	38.77	547	842129	S2
17280	Diyarbakır	37.90	40.23	677	817692	S2
17290	Bodrum	37.05	27.43	27	32227	S1
17292	Muğla	37.22	28.37	646	268341	S2
17296	Fethiye	36.62	29.12	3	50689	S1
17300	Antalya	36.88	30.70	51	936240	S2
17310	Alanya	36.55	32.50	7	88346	S1
17351	Adana	37.00	35.33	20	1397853	S2
17600	Lüleburgaz	41.40	27.35	46	79002	S1
17636	Florya (Bakırköy)	40.98	28.75	36	208398	S2
17964	Islahiye (Urfa)	37.01	36.38	513	38770	S1
17984	Antakya (Hatay)	36.12	36.10	100	581341	S2

Moving Averaging and Filtering the Climate Data

Let $s[n]$ show the signal representing one of the measured daily climate data considered. The day number, n, is determined by counting respectively for each day from an earlier reference day. Here the data represented by $s[n]$ may be minimum, average, or maximum temperatures, as well as precipitation series.

The 365-day running moving average (MA), $S[n]$, of the original data can be calculated as,

$$S[n]=\frac{1}{365}\sum_{k=n-364}^{n}s[k].$$

This moving average signal, in idealized conditions, is expected to be as steady as possible because of the completion of the world's yearly cycle around the sun. The changes like increases, decreases, or oscillations in this average signal may clearly indicate the long term variances in the climate. The main difference in the definition given above is to calculate the last 365 day average value for *each day* in the working period. That is, $S[n]$ is found for each n in the range. Therefore the signal obtained this way carries much more resolution than, for example, a yearly based moving average signals.

As an example, the daily average temperatures of Bolu and the corresponding 365-day moving average (MA) signal is shown in Figure 3a. The daily average temperature signal oscillates in larger amounts between the winter and the summer values, whereas the MA signal shows a relatively stable behavior as expected. In Figure 3b, on the other hand, only the moving average signal is depicted to show the MA variations in detail.

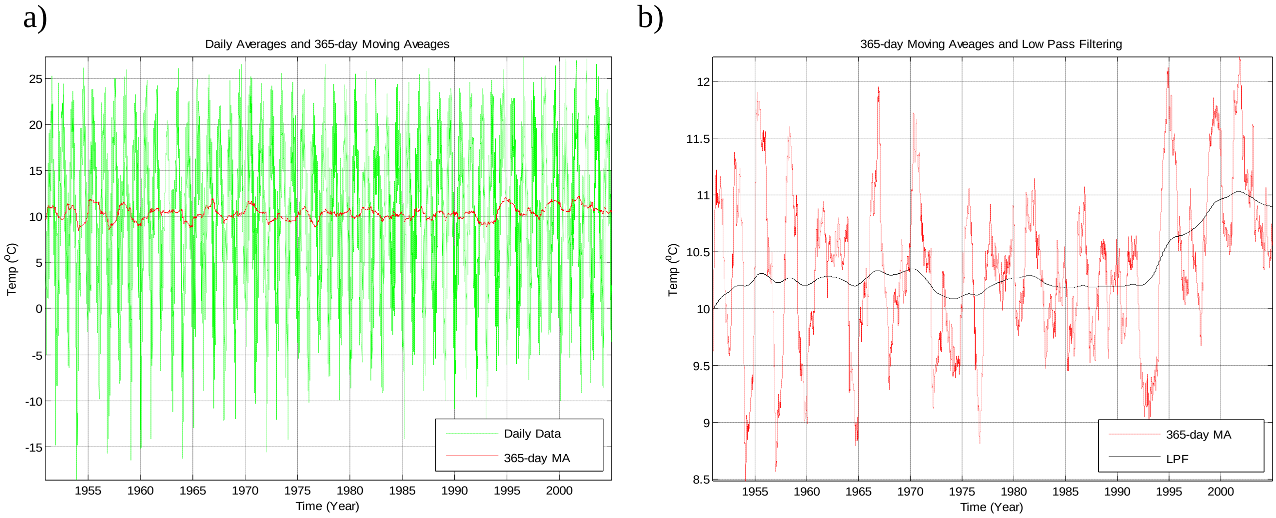


Figure 3. a) Daily average temperature variability of Bolu City and b)its 365-day moving average and the low pass filtered signal.

To remove the shorter term fluctuations from the MA signal, and therefore to observe and detect the presence of longer term variations for trend analysis, a further smoothing can be performed by utilizing a digital low pass filter (LPF). For this, we consider a first order LPF with the following z-transform:

$$H(z)=\frac{1-a}{1-az^{-1}}.$$

To eliminate the short term effects and exhibit the long term trends in the daily data, the parameter *a* is chosen to be 0.999, which produces a proper LPF with the time constant of approximately 3 years. To eliminate the phase shift errors, the data is processed by the filter above both forward and reverse directions. The start-up and ending transients are also minimized by matching initial conditions. The resulting filtered MA signal is also depicted in Figure 3b. Here, an apparent rise in the temperature during the 1990s can be clearly observed, on the other hand, in the original daily data this rise is not very clearly detectable.

RESULTS

Signal Analysis

Low pass filtered moving average (LPFMA) curves for the daily mean temperatures of various cities are produced and presented in Figure 4. In the natural variability of temperature series in the figure, several periodic trends are detected. The northwestern and southwestern stations Edirne, Çanakkale, Bolu, Antalya and Ankara show cooling in the period of 1971-1993, where Antalya has the largest cooling trend. Siirt is located on East Anatolia and this cooling trend cannot be clearly seen in its curve. The 1992-93 years are just after the Mt. Pinatubo eruption in Philippines, when significant amount of particles are forced into the stratosphere, acting as anti-greenhouse agents. Owing to this fact, a majority of Turkish stations show temperatures lower than the normal during this period. One important conclusion that can be deduced is the obvious temperature increase after 1993 valid in all series presented here. This increase in temperature in the last decade together with a maximum in 2001-2002 and a small decrease afterwards is very closely correlated with the findings of global temperature series analysis (IPCC, 2001).

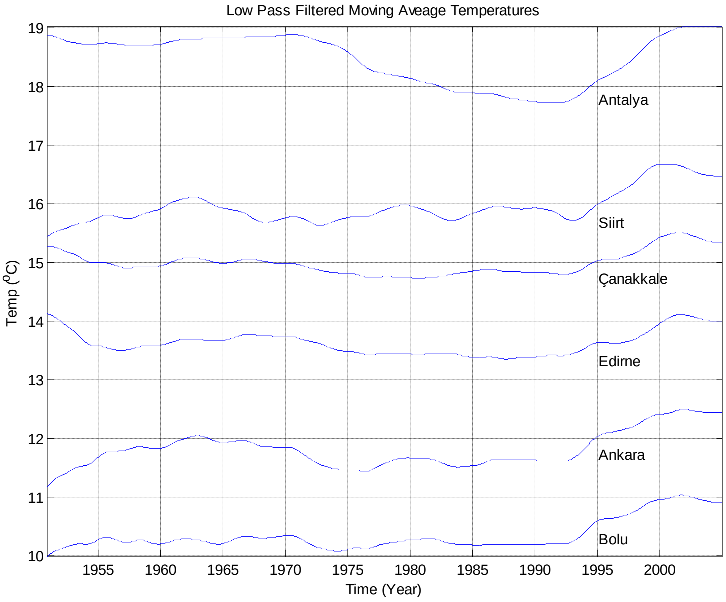


Figure 4. Low pass filtered moving averages of daily mean temperatures for various selected cities in Turkey.

The 365-day moving averages (MA) and their low pass filtered signals (LPFMA) can also be obtained for a group of selected stations together. For this purpose, the average of the daily mean temperatures is calculated from the total group of stations. Then, MA and LPFMA methods are applied to the group average as described. These group averages are calculated for S1 and S2 groups in order to see climatic changes in urban and rural areas separately. The resulting graphs are shown in Figure 5. Furthermore, i) to eliminate the effects of larger scale climatic changes, ii) reduce the problem to a micro-scale level and iii) determine the effects of urbanization, the difference temperature series of S2 and S1 averages are obtained and illustrated as Figure 5b.

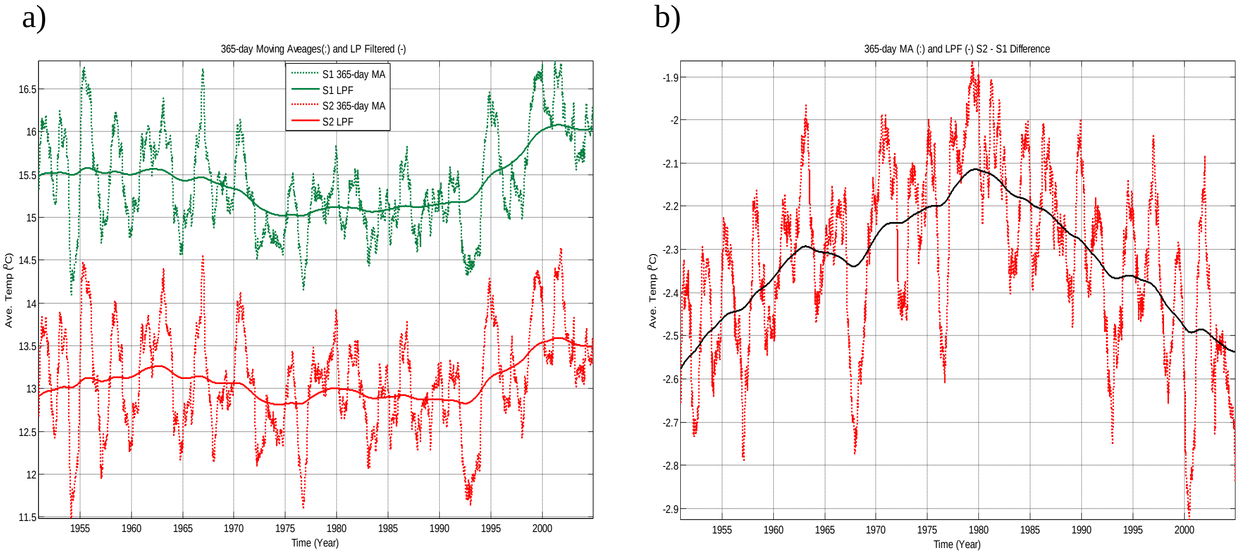


Figure 5. a) Moving averages and low pass filtered signals of S1 and S2 mean temperature series, b) same of (a) except for the difference temperature series of S2 and S1 series.

In Figure 5a both series show a cool period starting in early 1960s and ending in 1993, somehow longer than the cool period seen in the individual series of the previous figure. Since this figure carries the signal of many stations together, it is much more reliable and intuitive than the signal of individual series. Similar to the individual series, a last decade significant warming trend is observed in both of the series, leading to maximum temperatures in this half century analysis period.

Since Figure 5b is eliminating the effects of global climate change, it is possible to say that the urbanization forced temperature increase in urban stations is closing the temperature gap till 1980. However, a sudden decrease in the mean temperature difference curve takes place after that critical date. Possibly the main reasons of this can be i) the stabilization of the urban induced temperature change in urban areas after a certain growth period and ii) the rural and suburban stations also started to be effected by urban problems such as concrete structures and air pollution.

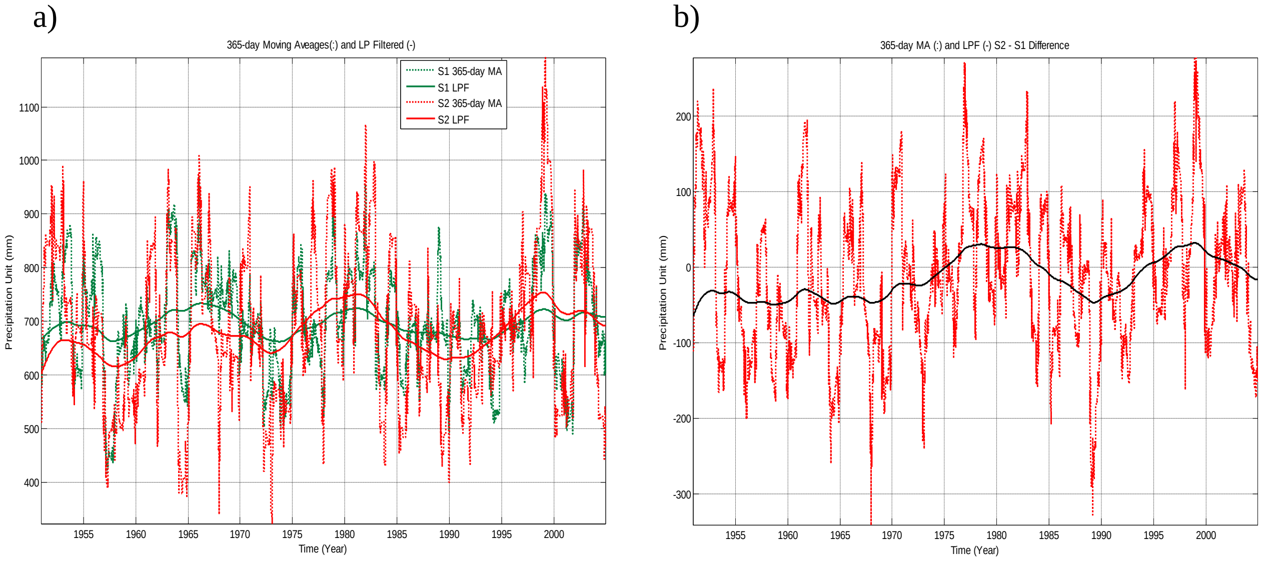
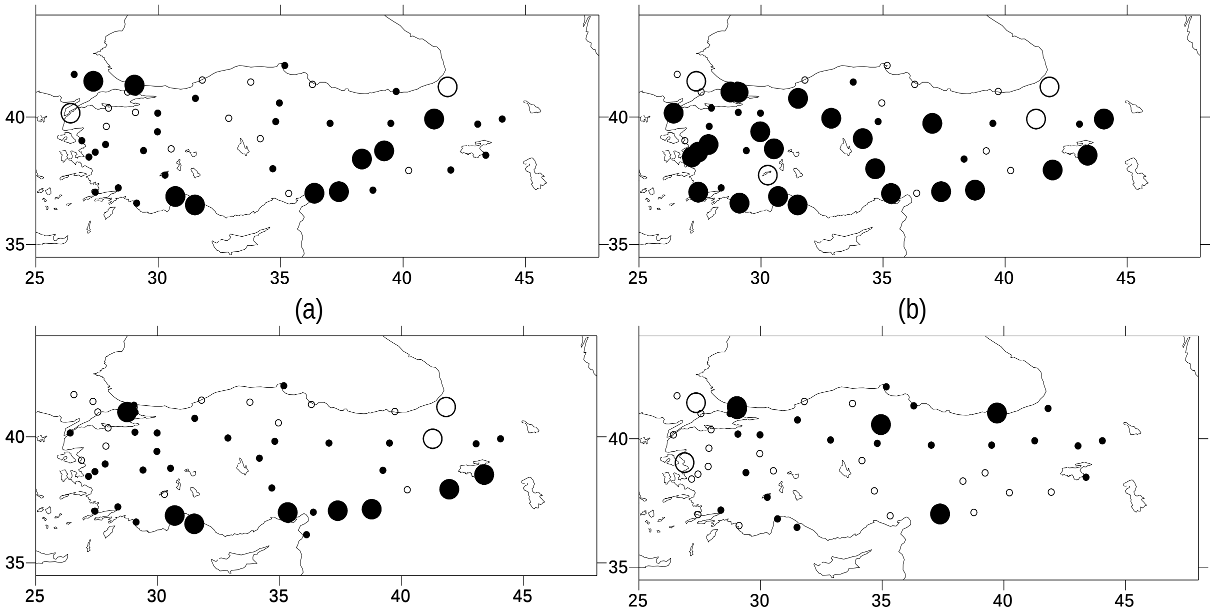


Figure 6. a) Moving averages and low pass filtered signals of S1 and S2 precipitation series, b) same of (a) except for the difference precipitation series of S2 and S1 series.

Spatial Analysis of Mann-Kendall Statistics

The yearly averages calculated for all temperature series show significant warming in southern and southeastern parts and significant cooling in northeastern parts of Turkey. Figure 7 illustrates the spatial distribution of Mann-Kendall statistics as circles. As can be seen from Figure 7a, there is a significant warming trend in the majority of the Mediterranean Region stations, some eastern Anatolia stations and in Lüleburgaz and in some Istanbul stations in the northwest. Looking at the big picture, one can conclude that almost all parts of Turkey are under a warming trend - mostly not significant - except for the northern parts. On the other hand, there is certainly a much more widespread significant warming trend in the minimum temperatures (Figure 7b). Almost all southern parts, western parts and continental regions of the country experienced a warming in minimum temperatures during the last half century. The increase in minimum temperatures can be easily attributed to urbanization and urban heat island effect. The increase in population, thus the increase in residential and industrial areas causes the heat to be absorbed by the buildings and air pollutants, and during the nighttime, when the minimum temperatures are observed, produces an artificial heating source that is called heat islands, increasing the minimum temperatures as well as leading to air pollution episodes.



(a) (b)

(c) (d)

Figure 7. Spatial distribution of annual (a) maximum (b) minimum, (c) average temperatures and (d) precipitation series Mann-Kendall statistics in Turkey (● represents 95% significant warming, • represents warming but not significant, ◯ represent 95% significant cooling and ○ represents cooling that is not significant).

Figure 7c presents the trends in mean temperatures. Again the increase can be seen in most of the regions of Turkey, with the exception of northern regions. The southeastern regions experience significant warming. The significant increases the temperatures of the southern parts of the country is believed to be a result of desertification and the increasing frequency of the Africa and Middle East originated heat waves for the last half century. Another interesting result that can be seen in the figures is the stations in certain regions of the country that show cooling trend in average temperatures but show a warming trend in maximum temperatures (e.g. Artvin, Tekirdağ, Edirne, Antalya). This is a result coming from the calculation of average daily temperatures. The formulation includes 0700, 1400 and 2100 LST observations but 2100 LST observation is included twice in the calculation. Thus, the daily average temperatures are more likely affected by a cooling trend observed in minimum temperatures.

Figure 7d represents the spatial distribution of precipitation throughout the study period. As can be seen from the figure, especially the trend in the southeastern, western and northern parts of the country agrees with the temperature changes discussed above. In the countrywide, there is not a significant change in precipitation series but on the northern parts, there is a significant increase in amount of precipitation received yearly. In the Aegean part of the country, though not significant, there is an opposite decreasing trend which is well correlated with the increasing temperatures in that region. Similarly, in the southeastern regions, generally there is a decreasing trend in the amounts of yearly rainfall agreeing well with the idea of desertification in that region.

The decreasing precipitation rates in the Aegean part of Turkey can be related to the positive values of the North Atlantic Oscillation (NAO) in the recent years. The traditional definition of the NAO is the difference in sea level pressure between a station in Iceland (generally Stykkisholmur, and one in Azores (generally Ponta Delgada). The positive NAO mode has a well developed Icelandic Low and Azores High, associated with stronger westerlies over the eastern Atlantic and Northwest Europe with weaker westerlies over the Mediterranean Basin, while the negative mode has weakened Icelandic Low and Azores High, resulting in a reduction in westerlies over the Northwest Europe but increase in the Mediterranean Basin low pressure systems. Since about 1985, the NAO has tended to remain in a strong positive phase, though with substantial interannual variability. This recent upward trend in the NAO accounts for much of the regional precipitation increase in northern Europe and precipitation decrease in the Mediterranean Basin. Western part of Turkey, especially Aegean Region is the most effected area, where the mountains are perpendicular to the sea shore and precipitation generally is associated with westerlies. Reduction in the number and strength of westerlies in the East Mediterranean is expected to decrease the precipitation in the Aegean.

Regarding the seasonal variations in the temperature and precipitation trends, it is found that there is not much significant change in *winter* in either way, and that maximum temperatures did increase in the southwestern parts and decrease in the continental parts; minimum temperatures increased in almost all regions but decreased in northern parts; mean temperatures increased in eastern parts and decreased in western parts; and there was decrease in the amount of yearly precipitation in southeastern parts and increase in the central regions of Turkey. For the *spring* period, an increase in all temperature series and precipitation series is found, especially in the minimum temperatures. Significant increases in maximum temperatures in southern and northwestern regions and significant increases in average temperatures in southeastern and northwestern parts of the country are found. In the *summer* season, significant warming in almost all of the regions of Turkey, especially in the minimum temperatures, including the northern regions, are detected. On the other hand, decreases in the precipitation of eastern, western and central parts; and increases in northern and southern parts are found. In *autumn*, increase in temperature in most of the country is experienced, being especially significant in the minimum temperatures. Additionally, significant increases in the precipitation are obtained for central and northwestern parts of the country.

CONCLUSIONS

In this study, annual and seasonal temperature and precipitation series from 53 stations are analyzed. Significant warming in southern and southeastern parts of the country is found. Cooling has also been detected in northern parts of the country that is not significant. Particularly, minimum temperature series show significant warming in almost all regions indicating the effect of urbanization. Significant warming in maximum and average temperature series as well as the significant decrease in precipitation, point to desertification in southeastern parts of Turkey. The decreasing precipitation rates in the Aegean part of Turkey can be related to the positive values of the North Atlantic Oscillation (NAO) in the recent years. Minimum temperatures in spring, summer and autumn shows significant warming trends. On the other hand, central and northwestern parts of Turkey experiences significant increase in precipitation in the autumn.

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INTERNATIONAL CLIMATE CHANGE POLICIES AND TURKEY

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The most important results of the studies in international scales on climate change are United Nations Framework Convention on Climate Change that sets an ultimate objective of stabilizing atmospheric concentrations of greenhouse gases at levels of the year 1990 until the year 2000 and its Kyoto Protocol that strengthens the convention by committing Annex I Parties for individually, legally-binding targets to limit or reduce their greenhouse gas emissions.

Turkey has approved the United Nations Framework Convention on Climate Change in May, 24th 2004, and undertaken the legal obligations. Currently, Turkey has initiated the studies for implementing the obligations under discussion.

In this paper, the international efforts on climate change have been generally studied. Also, current and future activities of Turkey, currently non-ratified country of the Kyoto Protocol have been examined in both national and international levels.

1. INTRODUCTION

Although the developed countries have much more contribution to the formation of the climate change, the sphere of influence of the matter is not limited with these countries. Especially in this century, the climate change affects all the countries yet in different ways. Therefore, considering the fact that the climate change is a global matter and it only could be resolved with global efforts, the countries have initiated the international studies with I. World Climate Conference organized in Geneva between the dates of 12-13th of February 1979 under the pioneering of World Meteorology Organization (WMO) (Grubb, Vrolijk and Brack, 2001).

In the time period from I. World Climate Conference to United Nations Conference on Environment and Development realized in 1992, there have been many widely-participated meetings and conferences organized under the pioneering of WMO and United Nations (UN) in order to decrease the negative influence and domination of human being over climate system. These studies eventuated in Framework Convention on Climate Change which was opened for signature in United Nations Conference on Environment and Development organized in the capital of Brazil, Rio de Janerio between the dates of 3-14th of June 1992.

Framework Convention on Climate Change which aims at preventing the negative influence of human-sourced greenhouse gas emissions which reach dangerous levels over climate system and maintain the total CO_2 emissions at the level in the year of 1990 until the year of 2000, have come into force on 21st of March 1994 after 90 days following the approval of the 50th country. 189 countries and European Union (EU) have become a party to the agreement as of the year 2006, August (UNFCCC, 2006).

In the conference of the parties held after the agreement's coming into force, the countries declared that emission reduction commitment which forms the basis of the agreement was not effective and fair for the solution of the matter and emphasized that a kind of protocol or a legal regulation which aims at binding emission reduction objectives for developed countries was a need (IISD, 1996).

As a result of the studies for two years, Kyoto protocol was opened for signature in the 3. Conference of the Parties held in the city of Kyoto of Japan between the dates of 1-11th December, 1997. The protocol brings the commitment of reducing the determined greenhouse gas (CO_2, CH_4, N_2O, HFCs, PFCs, SF_6) emissions. As well as this reduction amounts changes from country to country, it has been a goal to reduce the emissions in total under the %5.2 of 1990 levels for the initial commitment period of the protocol including the years of 2008-2012 (Brack, Grubb and Windram, 2000).

Kyoto protocol could come into force after 90 days following the approval of at least 50 countries who are party to the agreement and in where there are developed countries, who are responsible for at least %55 of total greenhouse gas emission of the year 1990. After Russia approved the protocol as the 136th country on 22nd of October 2004, the total greenhouse emissions of the countries approving the protocol have reached %61.6 of total greenhouse emissions of the year 1990 and thus the protocol has come into force in the date of 16th February, 2005. A number of 159 countries have become a party to the protocol as of the year 2005, February (UNFCCC, 2005).

2. THE INTERNATIONAL APPROACHES OF TURKEY

As a result of the 2nd part talks of 5th meeting held in May, 2002 by Intergovernmental Negotiating Committee charged for the preparation of the agreement, Turkey has been evaluated as a developed country within the context of the agreement by reason of being a member country of Organization for Economic Co-operation and Development (OECD) in 1992. Therefore, it has been included into Annex-I list of the agreement and Annex-II list with both OECD member countries, the countries whose economy is in transition process and OECD countries respectively. It has been obliged to reduce the greenhouse emissions to 1990 levels until the year 2000 for taking place in the Annex-I list and afford assistance to developing countries economically and technologically for taking place in Annex-II list. Turkey did not sign the agreement in 1992 by reason of not being able to fulfill these commitments (Türkeş, 1995).

Furthermore, the situation of Turkey on the basis of the Annexes of the agreement does not comply with common but discriminated principle (Türkeş, 2003). Because, as seen from the Table 1, the energy generation and consumption of Turkey has not been able to reach to even a self-sufficient level as well as being below both OECD and EU averages although it indicates a rapid increase.

Table 1. Total Final Consumption of Energy Per Unit of GDP And Per Capita Compared to the Other Countries (Anonim, 1997).

	TFC/capita (TOE/capita)			
	1980	**1985**	**1990**	**1995**
Turkey	0.61	0.63	0.73	0.79
OECD/Europe	2.38	2.30	2.34	2.35
EU	2.55	2.48	2.60	2.67
OECD	3.13	2.98	3.07	3.14

Note: a) GDP at 1991 price levels and purchasing power parties.
b) TOE values per unit of GDP include Westwern Germany only until 1990. Korea Czech Republic, Hungary and Poland are not included before 1995.

Furthermore, it is seen that Turkey is pretty below both OECD and world averages in per capita energy supply, electricity consumption and total CO_2 emissions from fuel combustion in the year 2000 as seen from Table 2 despite an increasing energy demand year by year (Türkeş, 1995). In addition to all these points, Turkey necessitate economical and technological support so as to realize the studies for providing the transition to sources releasing less CO_2 and more efficient combustion technologies, increasing the energy-savings and research and development.

Table 2. Selected Figures About Turkey and CO_2 Emissions (Anonim, 2006).

Parameters (2000)	**Turkey**	**World Average**	**OECD Average**
Per capita energy supply (Toe/cap-yr)	1,2	1,68	4,74
Per capita electricity consumption (kWh/cap-yr)	1.817	2.343	8.089
Total CO_2 emissions from fuel combustion (Mt CO_2/yr)	204	~120	416
Per capita CO_2 emissions from fuel combustion (tCO_2/cap-yr)	3,1	3,9	11,1

As a result of international evaluations, it has come to the conclusion that Turkey should take place within the context of Framework Convention on Climate Change as developing country. Thereby, Turkey have tried to become a party to the agreement with the different proposals given in Figure 1 in the Conference of the Parties of the agreement which was started to be realized after Intergovernmental Negotiating Committee and then the agreement's coming into force in the period including the years 1992-2000.

The efforts of resigning from the Annexes of Turkey started with the revision proposals submitted by Azerbaijan and Pakistan in 3rd Conference of the Parties held in Kyoto. As stated by Türkeş (2003), the attitude of Turkey on the basis of the agreement can be evaluated at three stages in this period of time. Turkey advanced a proposal to resign from both Annexes of the agreement from 1992 to 1998. In addition to resigning proposal from both Annexes of the agreement in the 4th Conference of the Parties held in 1998, it suggested the target to be below the OECD average in per capita CO_2 emissions. Because the developed proposals until 2000 were not accepted by various countries on account of various reasons, Turkey joined the 6th Conference of the Parties with a new proposal.

3RD Conference of the Parties

-Turkey published the policy paper entitled **"Turkey and Greenhouse Gas Emissions"**

-Azerbaijan, speaking on behalf of Turkmenistan, Georgia and Uzbekistan, made a speech in a supporting way of Turkey's request.

-Except USA and EU, Pakistan, Iran and Australia supported Turkey's request.

- The request of Turkey was decided to be discussed at minister-level of 3rd Conference of the Parties

Minister-Level of 3rd Conference of the Parties

-EU and USA wanted that Turkey should assume the obligations of not exceeding the half of the OECD average in per capita CO_2 emissions in 2010.

-Turkey was required to prepare a national report for submitting in 4th Conference of the Parties.

-The request of Turkey was delayed for the next 4th Conference of the Parties on condition of being discussed again.

2. PROPOSAL: The determination of the target to stay below **the OECD average in per capita CO_2 emissions** in addition to request of resigning from Annex-I and II of UNFCCC (1998-2000)

2-12 June 1998 Auxiliary Bodies Meeting

Turkey stated the target to stay below **the OECD average in per capita CO_2 emissions** in addition to request of resigning from Annexes of UNFCCC

4th Conference of the Parties

-Turkey submitted the national report required in 3rd Conference of the Parties.

-Except EU, G77, China, Australia and Small Island Countries supported Turkey's request.

-The decision could not be determined and the issue was delayed again on condition of being discussed later.

5th Conference of the Parties

-Unanimity could not be reached concerning the issue and it was delayed for the next 6th Conference of the parties on condition of being discussed again.

3. PROPOSAL: Resigning from Annex-II of UNFCCC and staying in Annex-I with the approval of special conditions distinguish itself from parties in Annex-I (2000-2001)

6th Conference of the Parties

-Turkey joined 6th Conference of the Parties with the condition of **resigning from** Annex-**II** of UNFCCC and **approval of special conditions distinguish itself from parties in** Annex -**I**.

-This proposal was not accepted again and delayed for the next 7th Conference of the Parties.

7th Conference of the Parties

-The request of Turkey for becoming a Annex-I country was accepted with the approval of resigning from Annex-II of UNFCCC and approval of special conditions distinguish itself from parties in Annex -I.

Figure 1. The Efforts of Turkey For Joining the International Studies (Babuş, 2005).

By having its name stroke off from Annex-II list and having the special conditions which distinguishes itself from Annex-I countries accepted, Turkey had its proposal of staying in Annex-I list accepted in 7th Conference of the Parties. After this progress, as Kadıoglu and Dokumacı (2005) stated, "The law no 25266 and of 21st October, 2003 no 4990 in official journal- concerning the approval of joining the United Nations Framework Convention on Climate Change" have come into force by being published in no 25266 Official Journal of 18th December, 2003. Thereby, Turkey has been a party to the agreement as the 189th party country on 24th May, 2004.

Turkey had the right to join the Conference of the Parties of the agreement with the role of party country after becoming a party to the agreement. Thus, Turkey joined 11th Conference of the Parties held in the city of Montreal, Canada between the dates of 28th November- 9th December, 2005 with a committee consisting of the authorities from Ministry of Environment and Forests, Ministry of Energy and Natural Resources, General Directorate of Energy Affairs, General Directorate of State Meteorology and Global Environment Facility (GEF) first national communication project team. Furthermore, Regional Environmental Center for Central and Eastern Europe (REC) joined 11th Conference of the Parties in Turkey within the context of REC international delegation. In addition to this, The Foundation of Eurasia Strategic Researches was the first civil community foundation who joined the meeting (REC, 2006).

Turkey, stating the progresses within the context of the agreement and its national situation with the committee who joined in a successful way, declared the progresses concerning the first national communication report preparations within the context of the meeting and received positive feedbacks.

3. THE NATIONAL APPROACHES THAT TURKEY HAVE DEVELOPED

The studies designated in Figure 2 concerning the climate change in Turkey have been realized by relevant association and foundations which are formed in coordination with General Directorate of State Meteorology in 1991-1996 and Ministry of Environment after 1997 (TTGV, 2002).

National Climate Coordination Group (NCCG) was established in coordination with General Directorate of State Meteorology so as to realize the studies on how Turkey can act about climate change in UN Conference of Environment and Development held in 1992. NCCG concluded its studies with two reports entitled “The Protection of Atmosphere and Climate Change” and Energy and Technology”. After the agreement was opened for signature, it formed the **National Climate Program** so as to realize the studies of national and international scientific and political preparations of Turkey (Türkeş, et. al., 1992).

Within the context of the issue, one of the most important progresses is the formation of a **“Specialized Commission on Climate Change”** which is executed by State Planning Organization in 1991 within the context of the preparations of Eighth Five-Year Development Plan in 2001-2005. With this development, the issue of climate change has firstly come to an arguable level within the context of Turkey’s development plans. In the coming development period, **“Specialized Commission on Climate Change Report”** which was prepared as a result of the commission’s studies includes the scientific and technical evaluation of climate change in addition to the policies, preventions and technologies and the difficulties in this field, needed sectoral, legal and institutional accommodations in which the climate change would be paid attention in all kinds of sectoral investments and all kinds of fields in life (Anonim, 2000).

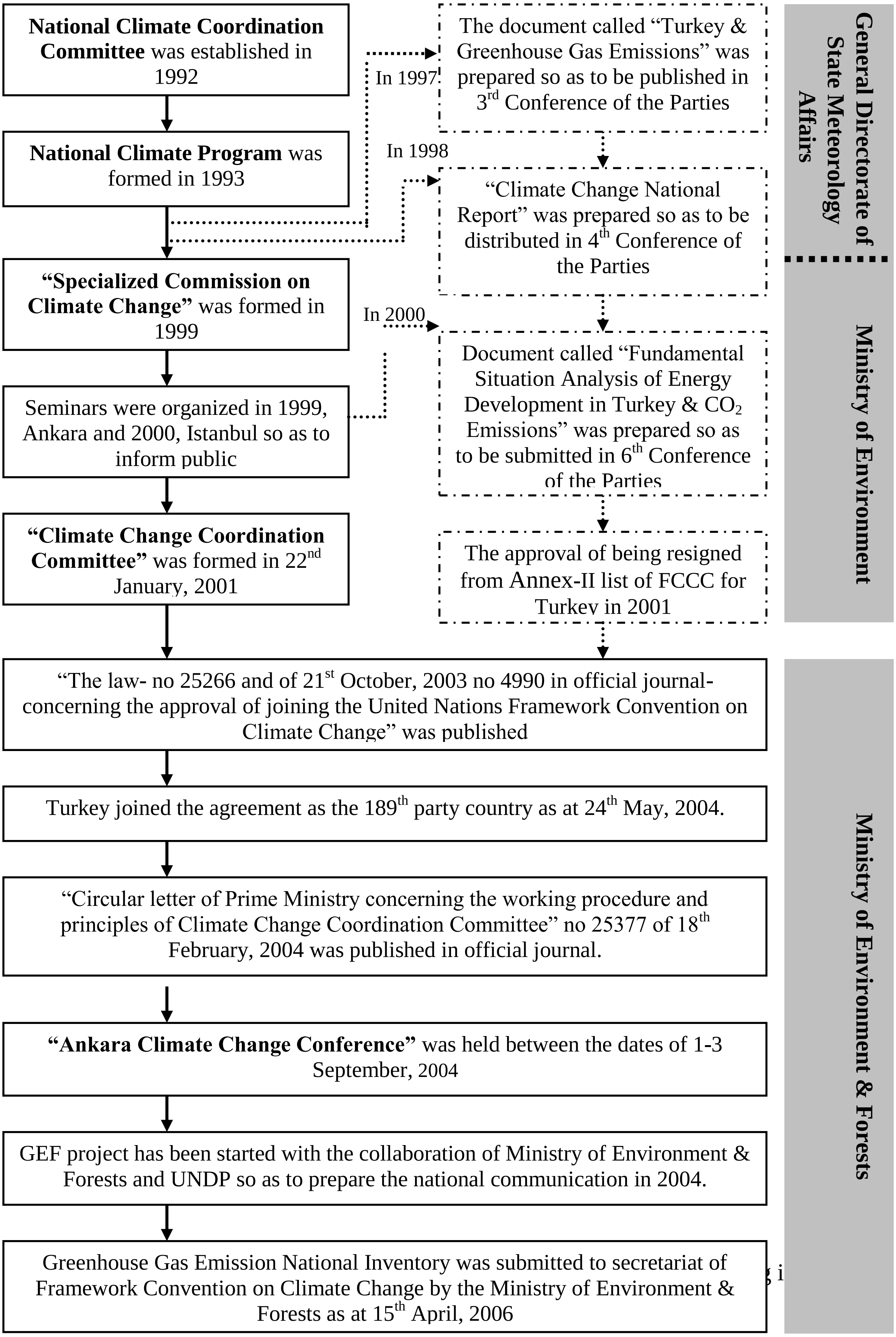

Figure 2. National and International Studies of Turkey in the Process of UNFCCC (Babuş, 2005).

Process by resigning from the agreement Annexes internationally. In accordance with this aim, a document called “Turkey and Greenhouse Gas Emissions” was prepared for submission to 3rd Conference of the Parties held in 1997 within the context of national studies realized.

Turkey who could not get a positive answer for request of resigning from the agreement’s Annexes in 3rd Conference of the Parties prepared “National Report on Climate Change” for being distributed in 4th Conference of the Parties so as to prove that its national situation and conditions could not enable to take place in agreement’s Annexes. Turkey who did not get the expected result submitted the document called “The Fundamental Situation Analysis of Energy Development in Turkey” to the 6th Conference of the Parties where it joined with a different proposal this time in order to become a party to the agreement.

Turkey took the impression that the proposal submitted in 6th Conference of the Parties would be accepted. Therefore, **Climate Change Coordination Committee** was formed by Ministry of Environment in 22nd January, 2001 with the circular letter of Prime Ministry no 2001/2 so as to optimize the studies about climate change issues (TTGV, 2002).

The functions and powers of Climate Change Coordination Committee have been revised after Turkey has become a party to the agreement. In accordance with the circular letter published in 2004, the new function of Climate Change Coordination Committee is to realize the studies about taking necessary precautions, maintaining the task distribution and coordination between public and private sector, foundations and associations and determining the domestic and foreign policies which are convenient for the conditions of our country so as to prevent the hazardous influences of climate change.

8 studying group of which the secretariat has been executed by General Directorate of Environment Management of Ministry of Environment and Forests have been determined with the coordination of Ministry of Environment and Forests within the context of Climate Change Coordination Committee consisting of secretaries from relevant public foundations and associations (Kadıoglu and Dokumacı, 2005).

1. Studying Group on Researching Influences of Climate Change
2. Studying Group on Greenhouse Gases Emission Inventory
3. Studying Group on Reduction of Greenhouse Gas in Industry, Residence, Waste Management and Service Sector
4. Studying Group on Reduction of Greenhouse Gas in Energy Sector
5. Studying Group on Reduction of Greenhouse Gas in Transport Sector
6. Studying Group on Land Use, Land Use Change and Forestry
7. Studying Group on Developing Policy and Strategy
8. Studying Group on Education and Awareness-Raising of Public

The reports prepared as a result of studies that the study groups of Climate Change Coordination Committee realized makes a contribution to the studies of preparations of “National Communication” which Turkey should submit to secretariat of Framework Convention on Climate Change. With the said groups, “National Communication” preparation project was started within the context of the agreement with the United Nations Development Program by courtesy of pecuniary assistance from Global Environment Fund (Kadıoğlu and Dokumacı, 2005). It is expected that Turkey shall submit its first national communication to agreement secretariat by the end of 2006.

In addition to the national communication, another document, Greenhouse Gas Emission National Inventory, which Turkey is obliged to submit because of being a party to the agreement, was submitted to the secretariat of Framework Convention on Climate Change as at 15th April, 2005 by the Ministry of Environment and Forests after prepared with the coordination of Statistical Institute.

Turkey had the right to join Kyoto Protocol because of becoming a party to the agreement in 2004. The completion of national communication which will determine the attitude and policy of Turkey on struggling against climate change shall also determine the approach to Kyoto Protocol. Dr. Hasan Zahuri Sarıkaya, the secretary of Ministry of Environment and Forests, stated that becoming a party to Kyoto Protocol for Turkey could only be realized by considering the fundamental year which would be taken up references, the position concerning the reduction rates, special conditions and economic development. In this context, Sarıkaya declared that Kyoto Protocol could not be signed before 2015 (Yılmaz, 2005).

4. CONCLUSION AND SUGGESTIONS

Turkey spent the 9-year period from 1992 when Framework Convention on Climate Change was opened for signature to 2001 when 7th Conference of the Parties held in with the efforts of partaking in the process. After becoming a party to the agreement in 2004, Turkey entered into a new term and assumed obligations which it should fulfill. In the present case, the studies have been started so as to both provide the necessary conditions nationally and determine its position in international process.

After Turkey has become a party to the agreement, it can join Conference of the Parties as a party country and vote for the decisions anymore. Therefore, the presence of the committee who joined the 11th Conference of the Parties held in Montreal, Canada in 2005 in other Conferences of the Parties is pretty important for the continuousness and efficiency of the studies.

Another important issue is the necessity of partaking in country groups who are congruent with its national situation and targets in international talks. This situation can provide Turkey to both be stronger and more effective in talks and take part in the solution of the matters more actively.

The next target of Turkey for providing efficient participation in the studies realized internationally should be becoming a party to Kyoto Protocol as soon as possible after maintaining the national conditions. However, it shall not be easy for Turkey to join Kyoto Protocol in a short period. The primary reason of this is that there are no program, policy and legal arrangement up to now at national level about climate change issue. So this obstructed the formation of capacity concerning the issue in our country. Renewable Energy Law accepted in 2005 and Energy Efficiency bill which is still being discussed are the important developments realized about this issue.

Furthermore, the reports of study groups prepared within the context of the Climate Change Coordination Committee can be evaluated as an important step for making up a shortage. National Climate Change Operation Plan for guiding the issues in which observable and possible effects of climate change for Turkey are evaluated, the strategies are developed, the precautions are designated, the policies for reducing greenhouse gas emissions at the most convenient level are determined and what kind of attitude can be shown in struggling against climate change should be prepared.

In accordance with the anticipations which show that energy demand and use of Turkey will continue in the coming years ahead, the policies which Turkey can implement for struggling against climate change should be to constitute forests used as carbon absorbent in greenhouse gas emissions, energy saving and energy efficiency. The main reason of increase in greenhouse gas emissions in Turkey is caused by execution of economic policies and environmental policies separately (TTGV, 2002). Therefore, Turkey should determine and execute the environmental and economic policies with a view of completing each other and consider the climate change in the development plans in future and all kinds of sectoral investments.

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EVALUATIONS ON FOREST RESOURCES MANAGEMENT OF NORTHERN CYPRUS AND NEW PLANNING APPROACH IN ACCORDANCE WITH SUSTAINABILITY AND CLIMATE CHANGE RISK

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Natural ecosystems including forest resources are particularly sensitive to the modifications caused by human beings. To enable those woodland areas enjoying a positive evolution and being used in favour of the society in an effective way in the planning term and so on forest management plans should be reevaluated.

Forest inventories and forest management plans of Northern Cyprus prepared by the planning experts of Forest Management and Planning Chairmanship of General Directorate of Forestry of Turkiye are still in practice for the second 10 year interval. The plans put into practice are named as Alevkaya (14 399 ha), Güzelyurt (12 018.4 ha), Lefkoşa (2 176.3 ha), Kantara (26 174 ha) and Girne (8 939.4 ha only having forested lands).

Discussions and evaluations in the paper raised from these five management plans` short term and long term objectives. In addition for the stability and multiple use of the Northern Cyprus forest resources some recommendations put into agenda for designing new quality policies for forest management approaches in those mostly state-owned resources.
In order for the forest management plans of Northern Cyprus to be more effective and successful in terms of productivity, sustainability, carbon storage, and multi-functional usages, the most important factor is redesigning and implementing them with more participation and involvement of related stakeholders in those valuable resources in the country.

Management objectives of the plans should be beared in mind during the redesigning process according to the future conditions anticipating the climatic changes, including forest fires risks and the changes in the society.

Key Words: *Turkish State of Northern Cyprus, Forest Management Plans, Sustainability, Climate Change Risk.*

1- INTRODUCTION

Land of high preservation value is frequently associated with low-intensive farming system, and intensification of agricultural production is thought to influence biodiversity and lanscape in unwanted ways. Increases in the use of inorganic fertilisers and pesticides, farm mechanization, conversion of wetland and semi-natural lands (such as lakes and some rangelands) to cropland, increases in livestock densities, overgrazing and shifts in cropping patterns towards monocultures have caused major change to wildlife, biodiversity, landscapes (ANONYMOUS, 1998, p. 74) and natural ecosystems.

In addition agriculture accounts for an estimated 65 percent of global water withdrawals. In the United States, around 42 per cent of freshwater withdrawals are for farming. In Europe agriculture practices have the largest shares in Mediterranean countries. For instance total water withdrawals for agriculture are of 72 per cent in Spain, 60 per cent in Italy, 63 per cent in Greece, and 71 per cent in Turkiye (ANONYMOUS, 1998, p. 86, 87). Total water withdrawals for agriculture in Northern Cyprus is probably much higher than Turkiye since the climate is drier than Turkiye’s climatic conditions.

Sustainable development is closely linked to the biodiversity protection. But the risks emerging from the global homogenisation of the socio-ecological practices found in the increasing expantion of monoculture agriculture.

Forest ecosystems have indispensable effects on the natural and economic life of countries. This is so important if the country has only limited natural ecosystems having very long and dry seasons throughout the year such as Turkiye and Northern Cyprus. In addition ecological/natural and economical values of forested lands depend on significantly on forest types in natural stands or the types of forests established in afforestation projects as mixed or even-aged high forests.

The ecological/natural value of afforested lands is higher if they are formed as mixed forests than fast-growing energy forests formed with only one or a few forest species under the same family.

Sustainable development policies of a country indicate also the necessity for watershed planning and management (UYSAL and BÖLEN, 2006, p. 189) inside forest ecosystems in which the cooperation and coordination needed among the relevant sectors/agents for the conservation of natural resources.

Unfortunately predicted global climate change will greatly alter natural and agricultural ecological processes in the future. So protection of natural values of our countries is of indispensable responsibility of mankind since environmental problems have been causing unpredictable threats to our globe.

2- THE FORESTS OF NORTHERN CYPRUS and THEIR CONTRIBUTION TO THE ECONOMY

Northern Cyprus has nearly 65 426,0 hectares of forests but only 40 percent of them (25 712 ha) is productive. There is no coppice forests in the Republic of Northern Cyprus.
According to the data obtained in 1999, 1 703 ha have been afforested in order to increase productive forest lands and utilise these resources more efficiently (ANONYMOUS, 2001 c, p. 56).

In general the forests are contributing greatly to the socio-economic development of the Republic of Northern Cyprus. But in recent years this contribution was decreased significantly. For instance the percentage of forestry sector among agricultural components has decreased from 8,1 % to 1,5 % in between 1995-2000 under the agricultural production. On the other hand animal production increased to nearly half of the whole agricultural production (50,4 %) from 37,3 % in between 1995-2000 (ANONYMOUS, 2001 b, p. 43).

Distribution of land use in Northern Cyprus is given in Table 1 below.

Table 1: Distribution of lands according to the land classification (ANONYMOUS, 2001 b, p. 7; ANONYMOUS, 2001 c, p. 55, 56).

Land Use Type	**Area (doenum)**	**Area (decar)**	**Distribution percentage (%)**
Agricultural lands	1 398 123	1 870 689	56,71
Forest lands	480 740	643 230	19,50
Pastures	122 157	163 446	4,95
Settlements	263 471	352 524	10,69
Non-used lands	201 061	269 019	8,15
Total Lands	**2 465 552**	**3 298 908**	**100,00**

Source: Northern Cyprus Ministry of Agriculture and Forestry

1- PLANNING HISTORY of FOREST RESOURCES in CYPRUS

The first forest planning approach was initialized during the Ottoman era in 1873 and 1875 by French forest planners MONTRICITARD and MADON in Cyprus. After completing the studies the two foresters unfortunetly submitted their report to the English management instead of Ottoman officials because of management changing in Cyprus.
First afforestation activities using especially native ones such as Pinus brutia, and the other forest tree species originated from Australia. .

First afforestation activities in this period using especially native forest species such as Pinus brutia, Cupressus sempervirens, Cedrus brevifolia, Pinus nigra A., and the other forest tree species introduced to the island Pinus halepensis, especially Acacia cyanophylla L., Eucalyptus ssp. originated from Australia (ANONYMOUS, 2003 a).

After introduction trials of some foreign species the most existing one is Acacia cyanophylla. This introduced shrub is widely being used in throughout the island especially for sand dune fixation since it has been naturalized easily. This species is also widely used in Southern Turkiye originated from Cyprus because of its own distinctive introduction capability to fixing sand dunes. Then its Turkish name in the mainland Turkiye and in the Turkish forestry literature is being commonly used as Kıbrıs akasyası "*Acacia cyprian".*

But its Turkish name in the island is widely common as Altıntop "*Golden ball*" since it has yellow flowers similar to ball in the spring. (quoted from Şevki Malyalı, forest engineer in Girne). Altıntop has been widely used not only for fixing sand dunes but also used for to improve the appearance of the road sides of highways (Ercan Airport to Lefkoşa) and erosion control shrub in afforestations namely in Dargeçit Afforestation Project in between Girne-Lefkoşa highway by planting as a succession species.

Cadastral borders of forest lands were firstly done after the year in 1886 and finished in 1899. Official registration and ownership of forests was reevaluated in between 1907 to 1929. The last official registration still valid up until now was conducted in between 1940-1950 period. In British era forest resources of Cyprus managed dividing the island to the different three forest regions as Karlıdağ (Trodos), Baf, and Northern Cyprus today Turkish Republic of Northern Cyprus (ANONYMOUS, 2003 a).

In between 1960 to 1974 small scale afforestations carried out in Kantara, Alevkaya, and Tepebaşı Akdeniz Forests. Mostly eucalyptus plantations using *Eucalyptus sargenti, E. occidentalis, E. astringes, E. brotwayi*, true cypress (cemetery cypress), and Aleppo Pine (*Pinus halepensis*), by means of mechanized site preparations done in Değirmenlik Afforestation Project totally in 81 ha, and regeneration works done in Salamis. Most of Aleppo Pines died, growth rates of true cypresses are very low, and eucalyptus trees were only introduced to very limited areas in this plantation (ANONYMOUS, 2003 a).

In general true cypress is commonly used in nearby houses, in the cemeteries and along the agricultural lands as windbreaks. Since its growth form and the kinds of habitats it occupies and its durability and natural resistance to pests and diseases make it an attractive farm forestry species in the annual rainfall zone of Cyprus appr. 413 mm in addition to its high tolerance to drought.

After Turkish intervention as a guarantor country in 1974 "forestry department" established. Then reforestation projects was started in nearly 5 000 ha of degraded forests by forest fires on the slope of Girne (Kyrenia) – Dargeçit locality. Until 1981 2352 ha burnt area reforested. For the need of seedlings forest nurseries established in Alevkaya and Kantara respectively in 1975 (ANONYMOUS, 2003 a).

In between 1974-2002 20 062 ha degraded lands reforested (nearly 1/3 of the whole forest lands today) using nearly 25 136 833 seedlings according to the data of Forest Department (ANONYMOUS, 2003 a).

For plannning and inventory procedures regulation used for in Turkish forestry named as "Regulation of Arrangement, Implementation, Auditing and Replanning of Forest Management Plans"-"Orman Amenajman Planlarının Düzenlenmesi, Uygulanması, Denetlenmesi ve Yenilenmesi Hakkındaki Yönetmelik" (ANONYMOUS, 1991) was taken into consideration.

Northern Cyprus forest resources have been firstly planned in 1981 and all silvicultural treatments made according to these plans.
After ten years in 1991 inventory works repeated and plan preparation finalized for the next planning period (1992-2002) in the country.

After completing this management period successfully new inventory and planning studies conducted in 2002 and forest management plans prepared have been put into effect for the second 10 year period of 2003-2012 still valid. Plan preparations are based on "functional planning approach" and protection of these resources is one of the most essential criteria while planning.

Functional distribution of forest lands planned for the second period of 2003-2012 is given in Table 2.

Table 2: Functional distribution of forest lands according to the *Forest Subdistricts in Northern Cyprus* (ANONYMOUS, 2003a,b,c,d,e)

Number	**Forest Sub-district**	**High Forest**		**Coppice**		**Forest Lands (ha)**	**Non-Forest Lands (ha)**	**Total Forested Area (ha)**
		Productive (ha)	**Non-Productive (ha)**	**Productive ha)**	**Non-Productive (ha)**			
1	Alevkaya	6944,4	7454,6	-	-	14399,0	20223,5	34622,5
2	Girne	4321,9	4617,5	-	-	8939,4	13161,9	22101,3
3	Güzelyurt	6528,7	5489,7	-	-	12018,4	47246,6	59265,0
4	Kantara	5746,9	22146,0	-	-	27892,9	102631,2	130524,1
5	Lefkoşa	2169,8	6,5	-	-	2176,3	83571,7	85748,0
Total		**25711,7**	**39714,3**			**65426,0**	**266834,9**	**332260,9**

In addition as stated in 8th Five-Year Development Plan of Turkiye, "*The Eastern Mediterranean Development Project*" related all sectors of both countries including forestry was initiated jointly by the State Planning Organisation of Turkiye and the Northern Cyprus State Planning Organisation (ANONYMOUS, 2001, p. 72) but still there isn't any improvement achieved yet.

2- FUNCTIONS of THE FOREST COVER and ITS IMPORTANCE for NORTHERN CYPRUS

Functional distribution of forest resources in management plans of Cyprus are given in Table 3 below:

Tablo 3: Distribution and classification of forest lands according to the *Forest* Management Classes *in Northern Cyprus* (ANONYMOUS, 2003 a, b, c, d, e)

No.:	**Forest Management Class**	**Number of Class**	**Forest Land (ha)**	**Non-forest land (ha)**	**Total area (ha)**
1	Production	8	26352,7	21998,1	48350,8
2	Recreation	2	2252,9	83577,4	85788,3
3	Nature Protection	6	15133,7	16719,1	31852,8
4	Soil Protection (Erosion Control)	6	19794,6	141349,1	161143,7
5	Water Protection	2	1892,1	3191,2	5083,3
Total		**25**	**65426,0**	**266834,9**	**332260,9**

The Forest Services in Cyprus and Turkiye are committed to the management of the National Forests in an environmentally sound manner.

Top priority is to maintain and improve the health, diversity, and productivity of forest ecosystems sustaining enjoying the needs of current and future generations.

3- CONTRIBUTION TO CARBON STORAGE

The contribution of forests to carbon storage is beyond the scope of this article and can only be touched on briefly here.

As an example carbon storage in Wallonia's forests (Belgium) in 2003, estimated from data of the region's forest inventory, is about 52 million tonnes of carbon (solely in biomass), while the uptake of carbon by net photosynthesis is about 2.38 million tonnes or nearly 2.1 percent of the region's annual emissions (cited from LAITAT *et al*., 2003 LAURENT, 2003).

The net annual increase in biomass after harvest in Wallonia's forests is almost 500 000 tonnes. This figure is likely to decrease in the future because of the silvicultural methods recommended, which tend to reduce the timber capital per hectare. Given the significant pressure on land, the contribution of afforestation, reforestation and deforestation to Wallonia's carbon stocks may be deemed negligible.

The greatest contribution of forest management to the reduction of carbon dioxide emissions is likely to be indirect, through an increased share of products suitable for long-term use which might replace more energy-expensive materials (cited from ROTH, 2002, LAURENT, 2003).

Contribution to carbon storage of forests calculated and total amount of carbon storage in Northern Cyprus's natural resources is given in Table 4.

Tablo 4: Carbon storage and the total amount of it in Northern Cyprus's Forest Resources (ANONYMOUS, 2003 a, b, c, d, e)

Forest Type	**Amount of biomass** (Ton)	**Carbon Storage** (Ton)		
		Total Amount inside Biomass	Total Amount in the Forest Soil	Total Amount in the Forest Ecosystem
Broadleaved	0	0	0	0
Conifer	574510	258530	149946	218476
TOTAL	**574510**	**258530**	**149946**	**218476**

4- CONCLUSION AND SUGGESTIONS

5.1. Suggestions for Forestry Sector

Forest resources and related natural ecosystems shall be managed, operated and protected within the framework of economic, social, and environmental criteria, in line with the needs of the Northern Cpyrus society and tourists and tourism sector which is dominated one on the island. These objectives shall be reached not only for forestry products and services but also the principles of today's sustainable forestry, biological diversity and protection and multi-purpose use of these resources.

It could not be possible to conserve the strategic water resources in the watersheds / the forest ecosystems if the conflicts among decision makers and actors could not be solved.

In addition underground and surface water resources shall be protected against pollution, and use of treated wastewater in agriculture and industry encouraged as indicated in the 8th Year Development Plan of Turkiye (ANONYMOUS, 2001 a, p. 197). Similar measures are necessary in TRNC as well in Northern Cyprus.

Annual usable drinking water per head (m^3) in Turkiye is about 1.735 m^3 but below the world average of 7.600 m^3. But the average usable drinking water in Asia is about 3.000 m^3 and 5.000 m^3 in Western Europe. In neighbouring countries of TRNC the average is smaller than the average amount of Turkiye and 1.200 m^3 in Syria and 1.300 m^3 in Lebanon (ANONYMOUS, 2001 d, p. 28). The amount depends on mostly Euphrates in Syria and Antitaurus Mountains in Lebanon but in TRNC water resources are very limited. Water shortage of TRNC as an island is a serious problem for years. Manavgat Municipal water project prepared by Turkish officials enables exports of water and supply of water to the TRNC.

New management plans of forests, pastures and water resources shall be arranged together in line with sustainable forest management principles by taking into account management objectives designed according to the changed social requirements, global climate change, various functions of these ecosystems, site inventory including wood and non-wood products and services, plantations by fast-growing and drought resistant species adapted to the island, protected areas, endangered wild life and flora.

Cooperation between Turkish and Northern Cpyrus Forestry sectors should be focused on protection of forests against forest fires and afforestation facilities via adapted provenances of the main species to the ecological conditions of the country.

5.2. Suggestions for Solving the Problems of Rural Development

Essential aim of rural development in general is to improve and ensure sustainability of living and job conditions of rural communities in their surroundings based on utilization of local resources with the aim of protection of environmental assets.

Public services shall be planned and provided for the benefit of the rural community in a comprehensive, coherent, and appropriate manner in the framework of essential aim and priorities.

With respect to controlling natural resources degradation the challenge is to:

- realize the economic benefits of sustainable forest management and
- realize the benefits of rural communities living in the forests or near the forests with efforts to promote sustainable management of the lands which they too drow their living such as private afforestrations.

Relatively less developed rural areas in the country shall be given priority in order to accelerate rural development and diminish development disparities between the rural and urban areas.

5.3. Measures taken for Structural Cohesion to the EU

a) Particular attention has to be given to projects concerning the environment and natural resources protection. Dublication with previous and ongoing activities under programmes at national level funded by the Northern Cyprus Turkish State or by bi-lateral (Turkiye or EU funds) or multi-lateral donors have to avoided.

b) Government and governance are two elements can together create a process of governing which can promote and sustain real policiy progress. In the case of sustainable development policy the intensity of tangible policy achievement is almost always linked to high level of dialogue between local government and civil society (EVANS et al., p. 865, 866).

c) Development Agencies shall be established in the main cities of the selected regions in the country taken into consideration the latest approaches on Development Agencies. These agencies should be aimed at

- to provide technical support to the planning studies of local authorities,
- to support the activities and projects ensuring the implementation of regional plan and programmes;
- to contribute into the improvement of the capacity of the region concerning the rural and local development,
- to monitor other projects implemented by public sector, private sector and non-governmental organizations,
- to improve cooperation among public and private sector, and non-governmental organizations to achieve regional development objectives in the region,
- to carry out researches, or to have them carried out, promote, or have them promoted, business and investment facilities of the region at national and international level,
- to follow and coordinate centrally the permission and licence transactions and other administrative transactions of the investors in the region,
- to support small and medium-size enterprises and new entrepreneurs in different fields,
- to promote activities related to bilateral or multilateral international programmes to which the country has /will have participated, (extracted from ANONYMOUS, 2006)...

d) For sustainable use and management of natural resources EU criteria should be applicable for ensuring the consumption of renewable and non-renewable resources and their associated impacts not exceed the carrying capacity of the environment.

e) Atmospheric concentration of greenhouse gases should be released to a level that will not cause unnatural variations of the earth's climate (ANONYMOUS, 2007 b).

Forests can contribute substantially to, and be affected by the policies on the environment, in particular climate change and biodiversity, as well as on rural development, renewable energy, water policy, and others. One of them is biodiversity for instance includes diversity within species (genetic diversity), between species (species diversity), and between ecosystems (ecosystem diversity). Natural ecosystems especially forests having biodiversity provides mankind with a wide range of benefits, such as important goods (like timber and medicinal products) and essential services (like carbon cycling and storage, clean water, climate and natural hazards mitigation).

The world as a whole is faced with an unprecedented loss of biodiversity, which threatens to undermine environmental, economic and social goals. The European Union has been legislating and taking action since the 1970s to safeguard biodiversity and has set itself the objective of halting the loss of biodiversity on its own territory by 2010 (ANONYMOUS, 2007 b).

The main causes of biodiversity loss are changes in natural habitats due to intensive agricultural production systems, construction and “extractive” industries, over exploitation of forest ecosystems, oceans/seas, rivers, lakes and soils, invasions of alien species, pollution and global climate change.

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GLOBAL WARMING: HOW FAR A PROBLEM

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"**Global warming** refers to the increase in average ground temperatures on earth." A rise in the amount of “greenhouse gasses” has caused higher temperatures across the planet. In the past few years, scientific research has proven without a doubt that global warming is real, and human activity has played a major role in increased greenhouse gases, thus intensifying the greenhouse effect. The greenhouse effect is naturally occurring, however, the burning of fossil fuels which releases greenhouse gases such as carbon dioxide into the atmosphere, increases the greenhouse effect, this making the planet warmer than it would be without human activity. Until recent investigation, the green house effect has simply been described as the process by which the atmosphere traps heat keeping the earth at a livable temperature. Although this trapping of heat is essential to our survival, it has begun to escalate to possibly dangerous levels. Scientists have attributed this to the burning of fossil fuels, chemicals, and other pollutants that wind up in our atmosphere. In the last century alone the levels of carbon dioxide in our atmosphere has risen by 30%. Somewhat obviously, the primary contributors to the greenhouse effect are greenhouse gasses. Greenhouse gasses are vital to our survival. They serve as a sort of blanket to keep the heat in our atmosphere. Without the natural greenhouse effect the temperature of earth would be 15°C lower. But there can be a problem if we get too many greenhouse gases in our atmosphere. When heat enters the earth’s atmosphere, it is in the form of short wave radiation. This is the radiation transmitted from the sun through space to us, and it passes easily through our clear atmosphere. As the short wave radiation warms the earth’s surface, it is then re-radiated back out from the earth’s surface, but now in the form of long wave radiation. The long wave radiation is much less penetrating and therefore it cannot all leave the atmosphere. It is the greenhouse gases that keep the long wave radiation in our atmosphere. The more greenhouse gases there are in our atmosphere, the more the greenhouse effect will affect us.

Global Warming: How far a Problem

Effects of Global Warming : The effects of global warming are very serious and extreme changes in climactic weather have become more common then ever. Some areas of the world have already become as much as 5 degrees Fahrenheit warmer. Effects of global warming for the environment and for human life are numerous and varied. The main effect is an increasing global average temperature. From this flow a variety of resulting effects, namely, rising sea levels, altered patterns of agriculture, increased extreme weather events such as floods, droughts, heat waves, hurricanes , species extinction and the expansion of the range of tropical diseases.

Effects on weather

Increasing temperature is likely to lead to increasing precipitation but the effects on storms are less clear. Extratropical storms partly depend on the temperature gradient, which is predicted to weaken in the northern hemisphere as the polar region warms more than the rest of the hemisphere.

A substantially higher risk of extreme weather does not necessarily mean a noticeably greater risk of slightly-above-average weather . However, the evidence is clear that severe weather and moderate rainfall are also increasing.

Over the course of the 20th century, evaporation rates have reduced worldwide this is thought by many to be explained by global dimming. As the climate grows warmer and the causes of global dimming are reduced, evaporation will increase. This may cause heavier rainfall and more erosion, and in more vulnerable tropical areas (especially in Africa), desertification due to deforestation. Many scientists think that it could result in more extreme weather as global warming progresses. The IPCC Third Annual Report says: "...global average water vapour concentration and precipitation are projected to increase during the 21st century. By the second half of the 21st century, it is likely that precipitation will have increased over northern mid- to high latitudes and Antarctica in winter. At low latitudes there are both regional increases and decreases over land areas. Larger year to year variations in precipitation are very likely over most areas where an increase in mean precipitation is projected"

Effects on ecosystems

Both primary and secondary effects of global warming — such as higher temperatures, lessened snow cover, rising sea levels, and weather changes — may influence not only human activities but also ecosystems. Some species may be forced out of their habitats (possibly to extinction) because of changing conditions, while others may flourish. Similarly, changes in timing of life patterns, such as annual migration dates, may alter regional predator-prey balance. Ocean pH is lowering as a result of increased carbon dioxide levels. Lowering of ocean pH along with changing water temperature and ocean depth will have a direct impact on coral reefs.

Another suggested mechanism whereby a warming trend may be amplified involves the thawing of tundra, which can release significant amounts of the potent greenhouse gas methane that is trapped in permafrost and ice clathrate compounds

Decline of agriculture

For some time it was hoped that a positive effect of global warming would be increased agricultural yields, because of the role of carbon dioxide in photosynthesis, especially in preventing photorespiration, which is responsible for significant destruction of several crops. In Iceland, rising temperatures have made possible the widespread sowing of barley, which was untenable twenty years ago. Some of the warming is due to a local (possibly temporary) effect via ocean currents from the Caribbean, which has also affected fish stocks

While local benefits may be felt in some regions (such as Siberia), recent evidence is that global yields will be negatively affected. Rising atmospheric temperatures, longer droughts and side-effects of both, such as higher levels of ground-level ozone gas, are likely to bring about a substantial reduction in crop yields in the coming decades.

Moreover, the region likely to be worst affected is Africa, both because its geography makes it particularly vulnerable, and because seventy per cent of the population rely on rain-fed agriculture for their livelihoods. Tanzania's official report on climate change suggests that the areas that usually get two rainfalls in the year will probably get more, and those that get only one rainy season will get far less. The net result is expected to be that 33% less maize—the country's staple crop—will be grown

Insurance

An industry very directly affected by the risks is the insurance industry; the number of major natural disasters has trebled since the 1960s, and insured losses increased fifteen-fold in real terms (adjusted for inflation) . According to one study, 35–40% of the worst catastrophes have been climate change related. Over the past three decades, the proportion of the global population affected by weather-related disasters has doubled in linear trend, rising from roughly 2% in 1975 to 4% in 2001 (ERM, 2002).

A June 2004 report by the Association of British Insurers declared "Climate change is not a remote issue for future generations to deal with. It is, in various forms, here already, impacting on insurers' businesses now". It noted that weather risks for households and property were already increasing by 2-4 % per year due to changing weather, and that claims for storm and flood damages in the UK had doubled to over £6 billion over the period 1998–2003, compared to the previous five years. The results are rising insurance premiums, and the risk that in some areas flood risk insurance will become unaffordable for some.

Transport

Roads, airport runways, railway lines and pipelines, (including oil pipelines, sewers, water mains etc) may require increased maintenance and renewal as they become subject to greater temperature variation, and, in areas with permafrost, subject to subsidence .

Development

The combined effects of global warming may impact particularly harshly on people and countries without the resources to mitigate those effects. This may slow economic development and poverty reduction, and make it harder to achieve the Millennium Development Goals .

In October 2004 the Working Group on Climate Change and Development, a coalition of development and environment NGOs, issued a report Up in Smoke on the effects of climate change on development. This report, and the July 2005 report Africa - Up in Smoke? predicted increased hunger and disease due to decreased rainfall and severe weather events, particularly in Africa. These are likely to have severe impacts on development for those affected.

Water scarcity

Eustatic sea level rises threaten to contaminate groundwater, affecting drinking water and agriculture in coastal zones. Increased evaporation will reduce the effectiveness of reservoirs. Increased extreme weather means more water falls on hardened ground unable to absorb it - leading to flash floods instead of a replenishment of soil moisture or groundwater levels. In some areas, shrinking glaciers threaten the water supply .Higher temperatures will also increase the demand for water for cooling purposes.In the Sahel, there has been on average a 25 per cent decrease in annual rainfall over the past 30 years.

Health

Rising temperatures have two opposing direct effects on mortality: higher temperatures in winter reduce deaths from cold; higher temperatures in summer increase heat-related deaths. The European heat wave of 2003 killed 22,000–35,000 people, based on normal mortality rates . It can be said with 90% confidence that past human influence on climate was responsible for at least half the risk of the 2003 European summer heat-wave.The 2006 United States heat wave has killed 139 humans in California as of 29 July 2006.

Global warming is expected to extend the favourable zones for vectors conveying infectious disease such as malaria In poorer countries, this may simply lead to higher incidence of such diseases. In richer countries, where such diseases have been eliminated or kept in check by vaccination, draining swamps and using pesticides, the consequences may be felt more in economic than health terms, if greater spending on preventative measures is required.

Impact on glaciers

Global warming has led to negative glacier mass balance, causing glacier retreat around the world. Oerlemans (2005) showed a net decline in 142 of the 144 mountain glaciers with records from 1900 to 1980. Since 1980 global glacier retreat has increased significantly. Similarly, Dyurgerov and Meier (2005) averaged glacier data across large scale regions (e.g. Europe) and found that every region had a net decline from 1960 to 2002, though a few local regions (e.g. Scandinavia) have shown increases. Some glaciers that are in disequilibrium with present climate have already disappeared and increasing temperatures are expected to cause continued retreat in the majority of alpine glaciers around the world. Upwards of 90% of glaciers reported to the World Glacier Monitoring Service have retreated since 1995

Of particular concern is the potential for failure of the Hindu Kush and Himalayan glacial melts. The melt of these glaciers is a large and reliable source of water for China, India, and much of Asia, and these waters form a principal dry-season water source. Increased melting would cause greater flow for several decades, after which "some areas of the most populated region on Earth are likely to 'run out of water'"

Biomass production

The creation of biomass by plants is influenced by the availability of water, nutrients, and carbon dioxide. Part of this biomass is used (directly or indirectly) as the energy source for nearly all other life forms, including feed-stock for domestic animals, and fruits and grains for human consumption. It also includes timber for construction purposes.A rise in atmospheric carbon dioxide can increase the efficiency of the metabolism of most plants, potentially allowing them to create more biomass. A rising temperature can also increase the growing season in colder regions. It is sometimes argued that these effects can create a greener, richer planet, with more available biomass. However, there are many other factors involved, and it is currently unclear if plants benefiting from global warming is a realistic scenario. Plant growth can be limited by a number of factors, including soil fertility, water, temperature, and carbon dioxide concentration.PCC models currently predict a possible modest increase in plant productivity; however there are several negative impacts: decreases in productivity may occur at above-optimal temperatures; greater variation in temperature is likely to decrease wheat yields; in experiments, grain and forage quality declines if CO_2 and higher temperature are increased; and the reductions in soil moisture in summer, which are likely to occur, would have a negative impact on productivity.

Satellite data shows that the productivity of the northern hemisphere has indeed increased from 1982 to 1991 . However, more recent studies found that from 1991 to 2002, wide-spread droughts had actually caused a decrease in summer photosynthesis in the mid and high latitudes of the northern hemisphe .NOAA projects that by the 2050s, there will only be 54% of the volume of sea ice there was in the 1950s.

Mitigation of global warming

The possibility that global temperatures will continue to significantly increase has led others to propose means to mitigate global warming. Mitigation covers all actions aimed at reducing the negative effects or the likelihood of global warming.There are five categories of actions that can be taken to mitigate global warming:

1. Reduction of energy use (conservation)
2. Shifting from carbon-based fossil fuels to alternative energy sources
3. Carbon capture and storage
4. Carbon sequestration
5. Planetary engineering to cool the earth

Strategies for mitigation of global warming include development of new technologies, wind power, nuclear power, solar power, renewable energy, biodiesel, electric or hybrid automobiles, fuel cells, energy conservation, carbon taxes, enhancing natural carbon dioxide sinks, population control and carbon capture and storage. Some environmentalist groups encourage individual action against global warming, often aimed at the consumer, and there has been business action on climate change.

The world's primary international agreement on combating climate change is the Kyoto Protocol. The Kyoto Protocol is an amendment to the United Nations Framework Convention on Climate Change (UNFCCC). Countries that ratify this protocol commit to reduce their emissions of carbon dioxide and five other greenhouse gases, or engage in emissions trading if they maintain or increase emissions of these gases.

Although global warming has been seen as potentially dangerous for some time, the first international attempt to define what constitutes a 'dangerous' level occurred at the Avoiding Dangerous Climate Change scientific conference in February 2005. This took place in Exeter, United Kingdom under the UK presidency .

At the conference it was said that increasing damage was forecast if the globe warms to about 1 to 3 °Celsius (1.8 to 5.4 °Fahrenheit) above pre-industrial levels. It was concluded that the stabilization of greenhouse gasses at the equivalent of 450 ppmv CO_2 would provide a 50% likelihood of limiting global warming to the average figure of 2 °C (3.6 °F). Stabilization below 400 ppm would give a relatively high certainty of not exceeding 2 °C, while stabilization at 550 ppm would mean it was likely that 2 °C would be exceeded.

It was stated that unless 'urgent and strenuous mitigation actions' were taken in the next 20 years, it was almost certain that by 2050 global temperatures will have risen to between 0.5 and 2 °C (0.9 and 3.6°F) above current levels. With carbon dioxide levels currently around 381 ppm and rising by 2ppm per year, without such action greenhouse gasses are likely to reach to reach 400ppm by 2016, 450ppm by 2041, and 550ppm by around 2091.

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MODELING METHANE EMISSION FROM ÇANAKKALE DUMPSITE AND ITS EFFECT ON GLOBAL WARMING: A LANDGEM USE APPROACH

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Global warming is one of the most important environmental problems at present. Several gases contribute parts to this problem and researches indicated that methane is one of the most important gases. Dumpsites (landfills) are among the major sources of methane emissions to the atmosphere because of the inefficient precautions and operations. Despite the fact that methane is a natural product, its raise in the current global atmosphere could be unfavorable to the climate due to the fact that its excess production by the human activities, e.g. agrarian (such as cattle and rice) output, faulty mining, unsatisfactory industrial processes (such as insufficient burning of natural gas), and improper management of solid waste dumpsites, has led to a yearly increase of approximately one percent. Indeed, methane supplies nearly one-tenth of the global warming caused by atmospheric gases and is much more heat-absorptive than carbon dioxide. In this research, we used a computer modeling program named as Landfill Gas Emissions Model (LandGEM ®) developed by the USEPA to model gas output from the dumpsites. LandGEM ® is a computerized modeling software tool with a Microsoft® Excel interface that can effectively be used to approximate emission rates for total landfill gas, methane, carbon dioxide, nonmethane organic compounds, and other related individual air pollutants from municipal solid waste landfills. By engaging this tool in modeling currently operated dumpsite in Çanakkale, we investigated emissions, especially methane, of landfill gases and their effects on global warming and mitigation techniques at Çanakkale dumpsite.

Key words: *Global warming, methane, dumpsites, landGEM, Çanakkale, Turkey*

1. Introduction

Global warming, caused by ozone, chlorofluorocarbons, water vapor, carbon dioxide and methane, is currently significant environmental problem. Dumpsites are one of the major sources of this problem by means of emitting various gas emissions to the atmosphere. Although the developed countries tried to develop environmentally-efficient technologies and methods to manage their domestic wastes at their origin, such as recycling, composting of yard wastes, reducing their wastes by reusing selected resources, i.e. plastic bags, many open dumpsites are currently operating worldwide. [1]

Landfills contain various types of organic wastes and the course of time organic wastes consume by microorganisms in anaerobic reactions and generate leachate and also various gases called landfill gas (LFG), mainly consist of methane and carbon dioxide with trace amounts of more than a hundred non-methane organic compounds (NMOCs) such as ethane, toluene, and benzene. [2]

Methane (CH_4) and carbon dioxide (CO_2) are the most active greenhouse gases. Methane is more important than carbon dioxide because its global warming potential (GWP). In other words methane's effectiveness of trapping heat in the atmosphere is about 23 times higher than carbon dioxide. [3-4]

Çanakkale dumpsite has been into operation since 1990 occupying approximately 2 hectare of land area and has a distance of approximately 3 km to the city center (Figure 1). When waste acceptance started, the site was outside of the city; yet, now some of the settling areas were constructed near the site distance of approximately 500 meters subsequent to remarkable development of the city specifically after 1992 when a state university was established. Therefore, the site has become a source about environmental and health concern for people living around.

Most of the wastes accepted into the waste dump area consisted on biologically degradable materials as shown in Figure 2. [5] Along with biodegradable matter, package materials and recyclable matter consists remarkably high (summing 36%) of the total materials accepted into the facility.

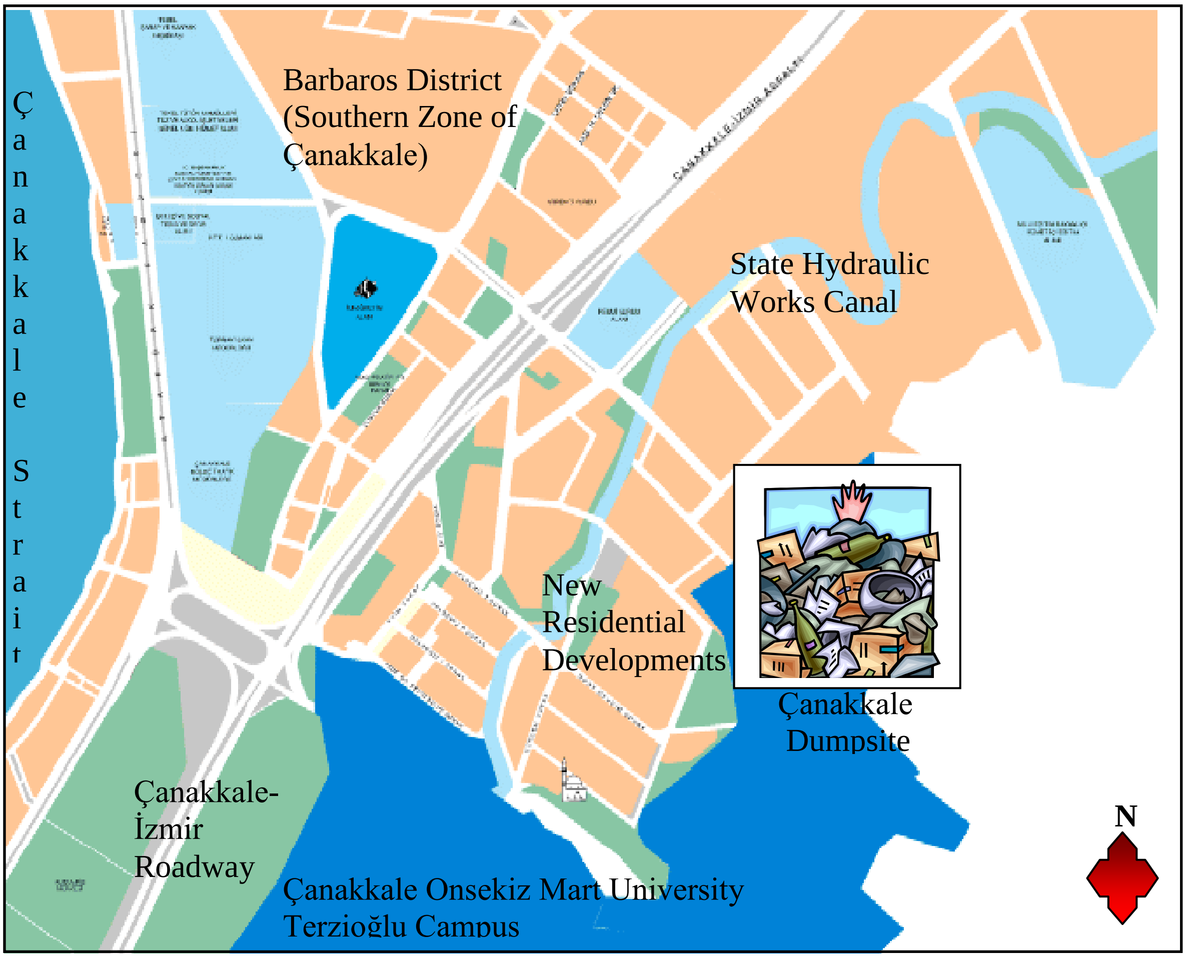

Figure 1. Plan of Çanakkale (southern district) and the location of dumpsite (no scale)

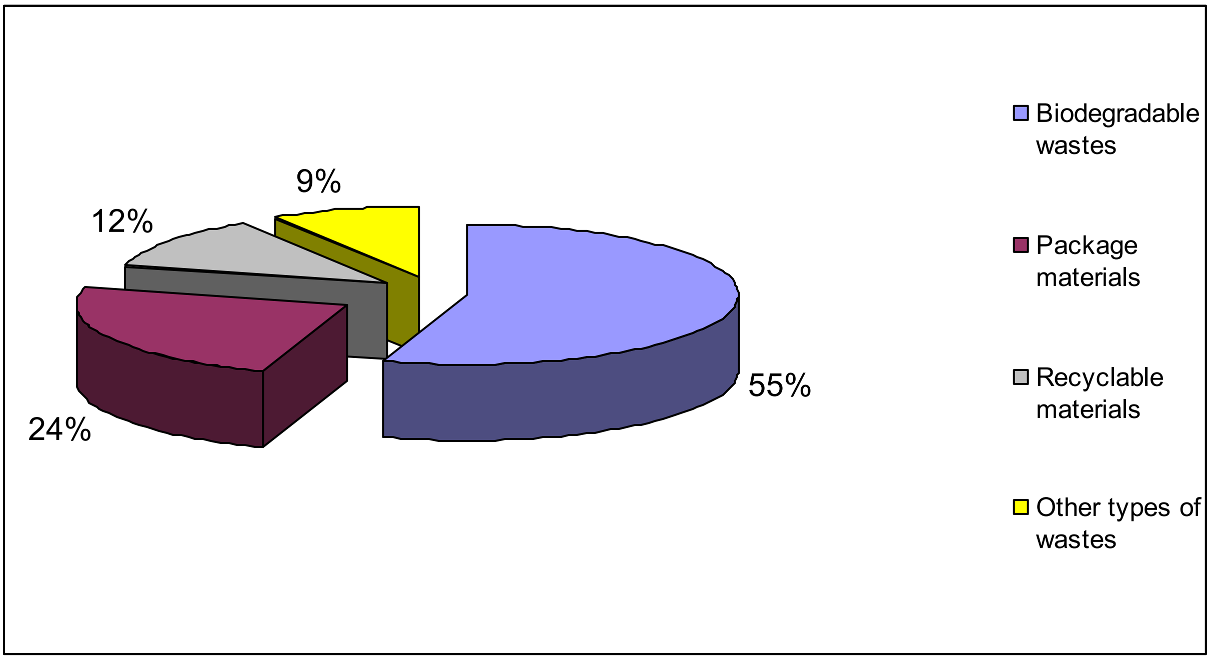

Figure 2. Types and percentages of wastes accepted into the Çanakkale dumpsite.

Biodegradable wastes include kitchen wastes, garden (yard) wastes, household paper and cardboards and easily convertible into heat energy wastes. Recyclable materials include all kind of domestic papers, plastics, glasses and metals. Packing materials include all kinds of cardboards, foam type of packaging materials, non recyclable plastics and metals specifically generated from trade facilities. Other wastes include house hold hazardous waste, non burnable wastes and electrical and electronic wastes. [6]

2. Materials and Method

In this research, we use computer software to estimate approximate mass and volume of the gases emitted from dumpsite of Çanakkale. This software designed by the United States Environmental Protection Agency (EPA) Office of Research and Development and named LandGEM ®. Material inventory, as mentioned previously, was obtained from Çanakkale Municipality.

Landfill Gas Emissions Model (LandGEM ®), a software application with a Microsoft Excel ® interface that estimates air pollutants and other gases emit from municipal solid waste (MSW) landfills. The software mainly consists of four steps listed below

- Enter landfill-specific data,
- Choose between site-specific and default model parameters,
- Estimate emission rates, and
- View and print tabular and graphical results (Alexander et al., 2005)

Enter landfill-specific data step for providing landfill characteristic and include landfill name, landfill open year, landfill closure year, option closure year calculation and waste design capacity data. Second step is about model parameters determination. LandGEM ® program use first order decomposition rate equation to estimate annual emissions and for this calculation some model parameters have to be chosen by user. First one is methane generation rate “k” (year^{-1}). This parameter related with the precipitation or more precisely annual rainfall. Arid area landfills are located in areas that receive less than 25 inches of rainfall per year and this value approximately equal to Çanakkale average annual rainfall. Because of this specification, “k” parameter for arid area value (0.02 year^{-1}) has chosen for calculation. As illustrated in Figure 2, types and amounts of wastes were obtained from the Çanakkale Municipality, Department of Environmental Management in May 2006.

The potential methane generation capacity, Lo, depends only on the type and composition of waste accepted to the landfill. For inventory arid area, this parameter was defined as 100 m^3 Mg^{-1}.

The NMOC Concentration in landfill gas is a function of the types of wastes in the landfill and the extent of the reactions that produce various compounds from the anaerobic decomposition of waste. NMOC Concentration is measured in units of parts per million by volume (ppmv) and is used by LandGEM ® only when NMOC emissions are being estimated. The NMOC concentration where co-disposal of hazardous waste occurred (medical waste deposition which had been accepted to the site until mid-2000s) has to be chosen as 2,400 ppmv.

For LandGEM ®, landfill gas is assumed to be 50 percent methane and 50 percent carbon dioxide, with additional small amounts of other gases. However, using LandGEM ® at landfills that have methane content outside the range of 40 to 60 percent is not recommended. The first-order decomposition rate equation used by LandGEM ® to determine emissions may not be valid outside of this range. Finally, the last step is the waste acceptance rate entrance. Then the program automatically generates the graphical results as a report. [7]

3. Results and Discussion

As noted by the Çanakkale Municipality, the dumpsite is expected to close down by 2009. Therefore, a modern and new sanitary landfill is anticipated to accept wastes generated from Çanakkale. Thus, a total of 19 years of life was assumed for the current dumpsite. Indeed, this life-span is not acceptable for such facilities since most of the environmental projects are designed to serve at least 30 years. Figure 3 shows the waste amounts accepted by the dumpsite with respect to year.

With the expected closure of the dumpsite, the gas flow into the atmosphere is not expected to slow down since gas generation process involves a complex and time taking steps. LandGEM ® generated an exponential growth for methane, carbon dioxide and total landfill gases until 2010. Then reducing trends in these gases' emissions are expected (Figure 4). In 2010, annual a total of approximately 10 million cubic meters of total methane gas and for a 30 year duration annually 6 million cubic meters of methane gas anticipated to be emitted from the open waste dumpsite that can yield nearly $6x10^6$ kW-h (or $2.2x10^{10}$ kilo joule per year) per year as a result of heat of combustion. [8] For a 30-years lifespan, if a modern gas collection and combustion system could be utilized on the existing open waste dump area, nearly 700 kW-h electric energy per hour will possibly be utilized even if the methane collection and combustion system could work 50% for total yield. Combustibility of methane was assumed to be 10% by volume as noted by LaGrega [8]. Indeed, the electric energy generated by the dumpsite examined in this study is not less than 3% of the total domestic energy consumption occurred in Çanakkale under the circumstances on the present day. In Figure 5, predictions on non methane organic gases in the future years are illustrated.

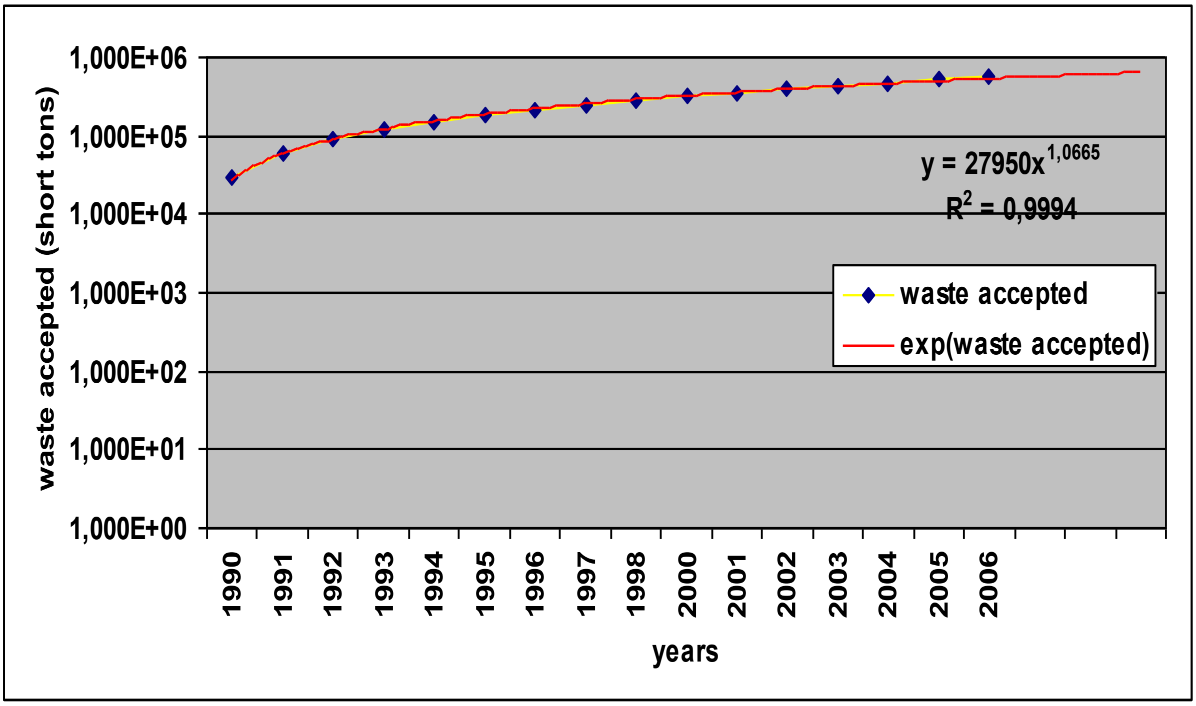

Figure 3. Waste acceptance to the Çanakkale dumpsite(1990-2006).

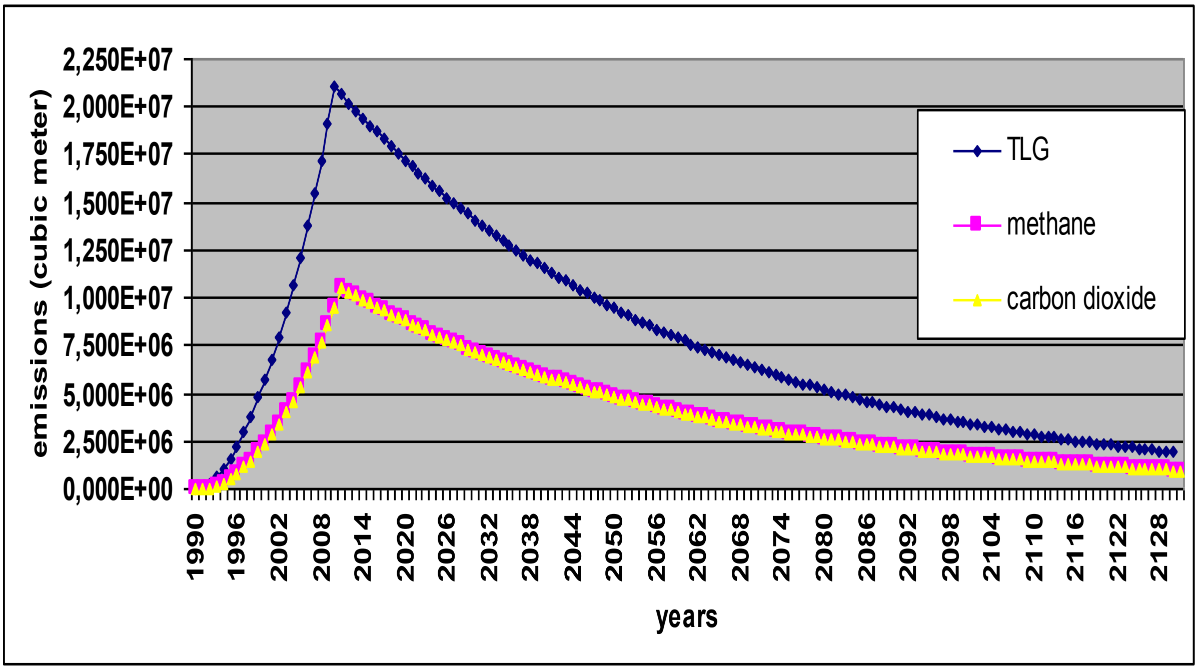

Figure 4. Estimated total landfill gas, methane and carbon dioxide emissions from Çanakkale dumpsite.

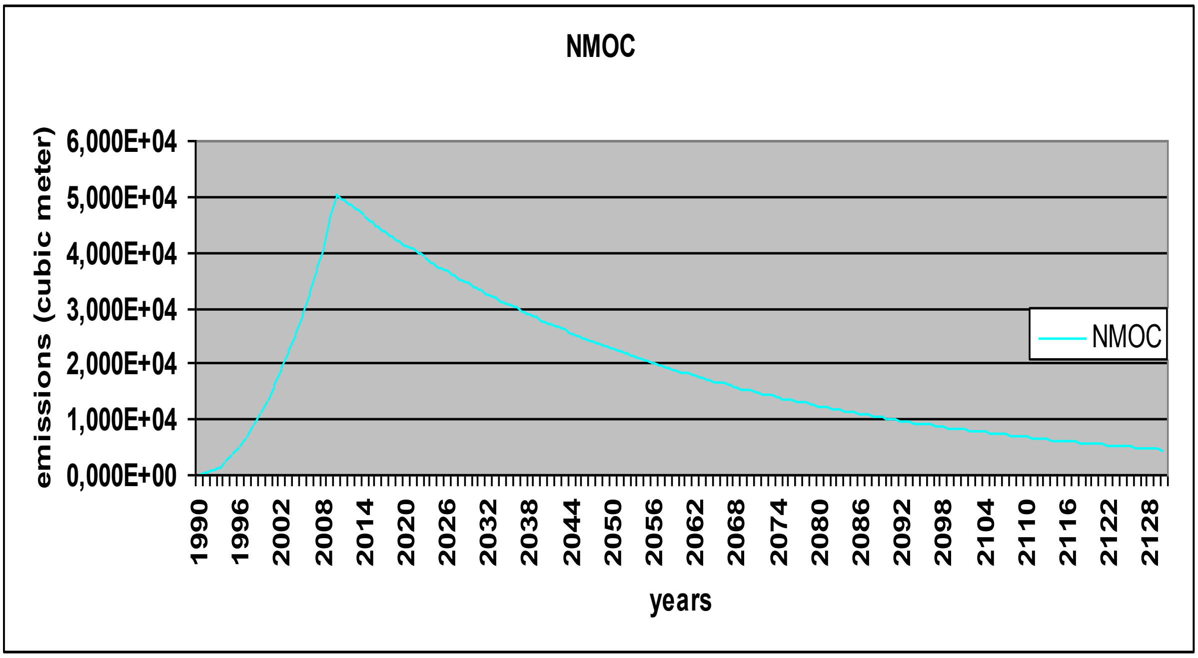

Figure 5. Estimated non-methane organic compounds emissions from the Çanakkale dumpsite.

4. Conclusion and Recommendations

Generally, methane emission can be minimized either by utilizing them as energy source or converting them to carbon dioxide. In small waste disposal sites where the utilization of landfill gas is not economical feasible, the produced gas can be eliminated by using the gas flaring system or biological activity in cover soil referred to as methane oxidation. The occurrence of methane oxidation by methanotrophic bacteria was commonly found in a final cover of landfill under aerobic conditions at which methane is being oxidized to carbon dioxide. [9-10] In this study, a dumpsite was examined to predict future total landfill, methane, carbon dioxide and non-methane organic gas compounds. It was obtained that after a closure of a dumpsite, remarkable amounts of energy can be utilized if available technologies could be adopted. Prior to safely closure of the dumpsite, a successful recycling program should be initiated in the city so that economically reusable materials (such as plastics, glass, and metals) could be removed from the original domestic wastes. A feasible gas production, even after a closure of the dumpsite, was found to occur based on the computations. Both existing and planned for future solid waste management facilities could consider obtaining methane gas from their domestic wastes to safely use in heat production for urban, agricultural (greenhouses' heating), or industrial uses. Public education on recycling and waste minimization shall most probably the most challenging and crucial issue when such plans are considered to be implemented because of the fact that recycling, reusing and waste minimization starts at household level.

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INTEGRATED APPROACH IN SEARCHING SUSTAINABLE DEVELOPMENT OPPORTUNITIES

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Since the Rio UN Conference the developed countries have made great efforts in the exploitation of renewable sources and the development of low environmental impact technologies. These are largely utilised and when are not yet profitable, are subsidized by national or local institutions through economical or financial contributions as, for example, the energy generators from wind and sun. However, the policy to promote a technology in itself encourages, in some instances, solutions which are extraneous to the local cultural and the environmental context, sometimes even with the formal disapproval of the population, and, on the other side, discourages the research of local sustainable development opportunities in keeping with the stringent economic and social problems. Even for the conservation of woodlands the common strategy is to bind over rather than to look for a rational use.

The approach here proposed is based on the principle that any geographical area has to be considered as a field of renewable sources which may become economically exploitable within an integrated project able to positively solve different problems related to water scarcity, drought and desertification, abandoned soils, land use, energy supply, together with local natural and cultural peculiarities and population expectations. That is, a local environment challenge may be convert in an economic development opportunity only with a global approach taking into account also the population's attitude and acceptability.

As a working example of a methodology in searching local sustainable development opportunities, a study on a particular area in a south Italy's province is discussed, which may be considered as a prototype of diffused situations in the Mediterranean region, where the preservation of coppice woodland and the promotion of free time activities and tourism are two more items to consider in the cost-benefit analysis.

This approach today seems workable in that several micro-technologies are available for energy production with micro- or mini-hydro or from biomass, solar radiation, wind, etc.

Foreword

Since the 1992 UN Conference held in Rio de Janeiro the developed countries have made great efforts in exploitation of renewable sources and development of low environmental impact technologies.

Nevertheless the environmental problems seem still critics at any level from climate change to air quality of life in large cities. Furthermore the perspectives appear even worse looking at some growth factors in developing countries as China and India or, for a geographical area of a closing concern for Europe, at some emerging issues and pressures in the Mediterranean area, especially in the southern coast.

A recent UNICE Statement(1) starts declaring that "*climate change is a global challenge that requires a global solution*", but going on into suggestions for actions gives very general and well-known recommendations related, for example, to energy efficiency improvement, greenhouse gas reduction, market-based policies which by themselves may not be effectively prevent long-term climate change. At least those solutions should be coupled with more strategic ones able to match social problems which are at the origin of the climate change.
In fact, social, environmental and economical problems are strongly linked each others in a kind of complex skein which needs to be disentangled in the effort to find one or few heads. In the opinion of the Authors, the migration phenomenon, reported all over the world, from countryside towards urban areas and in particular towards large cities is one of the major heads.

It has been well experienced in the last century so that at the moment in the world around 25 cities have a population higher than ten millions of inhabitants and in the old Europe almost 75% leaves in urban areas(2). In the world, about 60 millions of persons move every year towards large cities. In the Mediterranean basin in few decades around 70% of the population will live in urban areas and a large part along the coast. This process is threatening both environment and social life. From one side the abandonment of agriculture areas is cause of desertification and biodiversity loss, and from the other side the growing urban areas demand more potable water, energy, chemical products, land for urbanization, roads, mobility, which, in a synergetic way, carry with an increasing production of solid wastes, waste water, air pollution, environmental damages.

It is not possible to supply, assure at long-term and manage "rivers" of fresh water to megacities anywhere in the world and much less in the Mediterranean basin where the shortage is already a worrying problem in several areas.
One may dream that future megacities with millions of inhabitants will have only Zero Emission Vehicles using, for example, hydrogen, and will be supplied energy only through Aeolian power generators or solar panels or biomass power plants all around the urban area, but it is still hard to picture a sustainable mobility in large cities being in continuous growth and sprawl with new residential areas, industries, ever larger commercial centres which need to be served by networks of all kind of services.

From the social point of view the migration phenomenon exacerbates both the rural poverty and the degraded life in the outskirts of the large cities. Also on this front it is hard to imagine that solving the climate change life may improve in ever larger cities.

Therefore any strategic policy to match environmental and public health challenges may not ignore the migration phenomenon which seems the main and more urgent problem to face and to cross.

In a recent report(3) which analyses the urban sprawl in Europe some initiatives to counter it are mentioned, but they appear quite unreliable. It is a dream that a new urbanism (‘creative control’) may replace the dominant trend of urbanisation (‘laissez-faire’); it is a dream the hope that what should be locally driven and what should be EU driven may be identified and managed; neither may be in the power of Authorities to select geographical territories for development.

The simple criteria which should be adopted is to help small communities to find and promote any kind of natural local opportunity for a sustainable life.

Which opportunities ?

Several technologies able to exploit renewable energy sources are available and when not yet profitable, are promoted by national or local institutions through economical or financial subsidies. The last are justified when environmental external costs are internalised according to the polluter-pays principle as the key element of the strategic policy.

However, a policy which favours a clean technology in itself could be a contradiction of the mentioned principle. In fact, in some circumstances the favoured use of clean technologies encourages solutions which are extraneous to the local cultural and the environmental context, or discourages the research of alternative local sustainable development opportunities in keeping with the stringent economic and social problems. It is not unusual to find beautiful landscapes disfigured by aeolian power generators to produce energy not for local demand. Even for the conservation of woodlands the common strategy is to bind them over, without any consideration for the local communities, rather than to look for their rational use, so that lastly they are let fall into decay.

A different approach to follow, that the Authors whish to propose, should be based on the assumption that any geographical area is like an opencast mine of *opportunities* for a sustainable development which, even if of apparent marginal interest, have to be systematically considered without prejudices. The aim is to evaluate if some or all those *opportunities* may be exploitable within an integrated project when the external costs of environmental and social implications, normally disregarded, are internalized in the cost-benefit balance. That is, solutions to positively tackle local problems related to water scarcity, drought, land use, energy supply, must be searched with respect to natural and cultural peculiarities and community expectations.

Working example

As a working example of searching local *opportunities,* a particular geographic area in south Italy has been considered, since it offers a kind of a prototype situation which is quite diffused in the Mediterranean basin.
The Murgia's area is a karstic plateau with an average elevation of 400 m on the see level which cover a central part in the Italian region Apulia (Fig. 1). It decreases, sometimes sharply, towards the Adriatic seacoast on the north-east side and the Ionio see on the south-west direction.

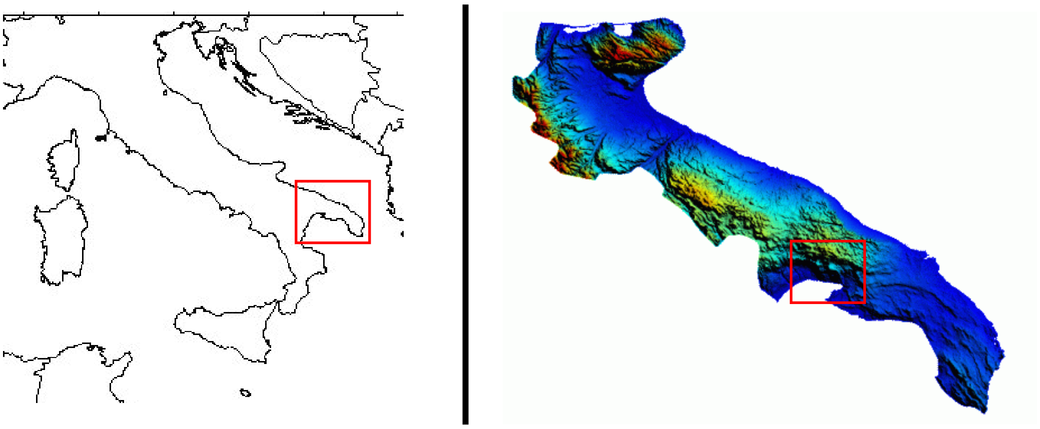

Fig. 1 – The Murgia plateau in Apulia - Italy

Here the attention is focused only on a belt of the south border of that plateau, overlooking on the Taranto Gulf (Fig. 2), which in few hundreds meters decreases very sharply with quite steep scarp to heights of few tenths of meters on the see level.

Fig. 2 – The south-west side of the Murgia plateau overlooking on the Taranto Gulf

The upper green area of the plateau has an altitude varying from 425 to 250 m s.l. and is characterised by limestone. It is largely covered by a coppice wild forest, formally protected and bound by national laws, practically abandoned with the ecosystem dry and easily inflammable.

The yellow-pink areas below, with an altitude from 250 to 100 m s.l. are covered by clayey ground (red clay) which in the past favour the formation of temporary stagnation, protected by shade provided by tall tree all around. Long time ago water storage in Dolines and in wells, was enough to supply the agriculture practices requirements. Nowadays those natural resources vanished due to lack of shade in the wild coppice woodlands and desertification which, on their turn, caused degradation of the karstic environment favouring soil erosion and modification of the water cycle. The area at second level is only partially used for farming since the territories are considered no more fertile in the *industrialised* modern agriculture view.

A larger development of agriculture and farming is localised in the area below at few tenths of meters of elevation on the see, where for many decades groundwater has been using which now is everywhere contaminated by salt due to the seawater intrusion.
The local climate is arid or semi-arid and the rainfall, between 650 and 750 mm per year, is completely lost for the karstic hydrological feature of the area which is permeable through porosity and crevice.

Let search which *opportunities* may be identified in the shortly described situation, considering that the main life prerequisite is the provision of water and energy which on their turn influence agriculture and food supply.

The runoff is normally low and become appreciable only with high intensity rainfall and in winter with saturated field, due to the diffused presence of large canals (*gravine*) up to few hundred meters, karstic rock incisions with overhanging lateral walls and, in some places, a difference in altitude of several tens of meters.

This rainfall rate could be usefully reclaimed channelled to different low-capacity dams taking advantage of some natural depressions in order to preserve the habitat. Furthermore the opened channel network may easily be realised in the bottom of the mentioned karstic rock incisions.

For example, let consider a network of open channels within a belt (between the two green curves put on the top of Fig. 2) of about 3 km wide and 20 km length, corresponding to about 60 km^2, able to collect water in the range of 3 to 5% of the annual rainfall. This water, corresponding to 1,8 to 3 millions of cubic meters, should be storage in ponds distributed at a lower level along the yellow-pink areas in order to supply the agriculture areas at lower level mentioned before.

With a very rough economic estimations, made on Italian base, considering the annual amortisation of the investment for channels, ponds and pipes up to the cultivable fields together with general expenses, maintenance and the profit from the water reclaimed, the Payout Period (PP) has been evaluated in about 15 years. It may be considered profitable, mainly if more benefits are internalised coming from the assurance to afford water for irrigation even in time of shortage, the less drawn salt contaminated groundwater, the less electric energy to draw groundwater, the improvement of the local micro-climate and the return to natural moist habitat.

One more opportunity is to use some of the ponds for the production of electric energy through micro-hydro installations since a quite high head (up to 200 m) could be available even if the flow rate is expected low. A Pelton turbine should be suitable in this case coupled with a three-phase asynchronous generator in order to have an output of few kW. Very roughly, having an output of 5 kW and an annual production of 40.000 kWh the PP in this case could in the order of 5 years. Once again more benefits should be internalised, in terms of cross-media effects, coming from less 8.8 tons of equivalent petroleum (tep) and 50 tons of CO_2.

One more local *opportunity* is the exploitation of the biomass from the coppice woodland as an energy renewable source. This is not economically feasible in that the forest restoring cost is in the order of 2400 €/ha, 90% covering operating labour and 10% equipment rent or depreciation, while the gross revenue from the wood used to recover thermal energy by combustion is in the order of 300 €/ha. However, from a large extension of woodland the recovered biomass may be important in terms of, once again, less tep and CO2 to which more benefits have to be added.

The periodic selective cutting improves the lamination of the water flow in the compluviums of the slopes with an increase of the runoff rainfall rate, the evolution of the coppice woodland towards taller tree forest, the biodiversity preservation, the renovation capacity, the impregnated soil with a reduction of the fire probability, the enrichment of water table, the increase of photosynthesis, the reduction of soil erosion. Furthermore it may be an occasion for the promotion of free time activities and tourism which may be not marginal source of profit.

A deeper and wider analysis of the working example is not important to conclude that similar situations may be found in many regions, with different or more or less *opportunities*, but always worthy to be analysed especially in developing countries where the cost-benefit balance has a different approach.

Conclusions

Despite the great progress made in the last few decades in terms of clean technologies and exploitation of renewable sources, the environmental problems still cause concern. The environmental policy seems to favour solutions which are not really strategic in that they look at some visible or perceptible issues, but not at the core of the problem which could be called *the poverty gradient*.

Poverty and social unease in countryside are the driving force of the migration phenomenon towards large cities which causes a continuous sprawl of the urban areas and, on its turn, causes environmental impact and again social unease, together with poverty in the degraded outskirts.

The migration phenomenon seems to be the main and more urgent challenge to face and to cross.

Nor a global village policy, neither a policy which takes care only of the large city management may solve the climate change or the environment degradation or the poverty.
There is no way to convince people to leave in poor abandoned area unless their lands are turned in human and liveable ones with respect to local natural and cultural peculiarities. Rather, a policy to promote and preserve millions of small towns or villages should be strongly and clearly adopted at global level.

Any geographical area may have some peculiar *opportunities* of apparent marginal interest which, within an integrated project and when the external environmental and social costs are internalizing in the cost-benefit balance may effectively leave up to population's expectations. From the technical point of view this approach today is workable in that several micro-technologies are available for energy production with micro- or mini-hydro or from biomass, solar radiation, wind.

Then, the point is that the developed countries should deserve their greatest and convinced efforts in largely and with priority sustaining integrated projects aimed at preserving the environment and the life of small communities everywhere in the world.
The real pursuance of the "polluter pays" principle is the reduction of the *poverty gradient*.

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INDEX

A

A. A.HAROUN, 3237
A. ABAZI, 2225
A. AKKURT, 3551
A. ALATON, 4015
A. Baran DURAL, 3797
A. BEZZAR, 3157
A. Bülent GÖKSEL, 5453
A. Çinçinoğlu SALICI, 2917
A. Duygu KAÇAR, 903
A. Ekrem YÜCE, 1515
A. ESMAILI, 5421
A. Gökhan YILMAZ, 4280
A. H. ZAKRI, XIII
A. I. OLAYINKA, X
A. JAGADEESH, X
A. K.ONUR, 4007
A. L.SALPYNOVA, 2233
A. MACHINCHIYAN, 5421
A. MELINTESCU, 1953
A. MIKAELYAN, 4791
A. O. AKSOY, 4059
A. PERENDECI, 3019
A. Ph. SAVINKOV, 2233
A. R. DEMIRKIRAN, 3013
A. R. KESHTKAR, 4288
A. R.VAEZI, 4183
A. RAHMANI, 359
A. S. OYEKALE, 5233
A. SALAJEGHEH, 4288
A. SANDIKCIOGLU, 3551
A. SHAKHNOVSKY 4199
A. Suat ATEŞ, 5051
A. ŞEN, 3459
A.T ALEVA, 3465
A. VALACKIENE, 1563
Abdollah Fatollah ZADE, 1737
Abdollah Hassanzadeh GORTTAPEH, 1737, 1925
Abdul KHAKEE, X
Abdul Razzaq GHUMMAN, 3687
Abdulkadir DEVELİ, 111
Abdullah Adil ANSARI, 3003
Abdullahi Elmi MOHAMED, X
Ada KERTUSHA, 1323
Adem BAYRAM, 3541
Adem EREN, 4995, 5095, 5105
Adnan DİLER, 1015
Adrián MENDOZA, 1393
Afig MALIKOV, 2359
Agustin Gonzales Fontes de ALBORNOZ, X
Aharon KLIEMAN, 4517
Ahmad KHAN, 3069
Ahmad MARRAKCHI, XIII
Ahmet ACAR, 5063
Ahmet BALCI, 3187
Ahmet BOZKURT, 3325
Ahmet CELIK, 2099
Ahmet DEMIRAK, 3187
Ahmet DURAN, 621
Ahmet GÖKKUŞ, 557
Ahmet HADROVIĆ, 4326
Ahmet IPEK, 459, 467, 753
Ahmet KOCATAŞ, 5051
Ahmet Nesimi KİŞİOĞLU, 2343
Ahmet SAMSUNLU, 1437
Ahmet SAVAŞAN, IX
Ahmet SERTESER, 277
Ahmet Uğur DEMİR, 2305
Ahmet YÜCEER, 3043,3961
Aiad Ashor ALTAAY, 2615
Ajmal KHAN, X
Akbarinia MOSLEM, 387
Akhmedov Zaur MUSA, 2479
Akiva FLEXER, 4121
Alaaddin YÜKSEL, 1931
Alberto ARENAS, 2395
Aleh RODZKIN, X, 1673
Aleksandra NASTASOVIĆ, 3423
Aleksandra PEJČIĆ, 2559
Alev BAYSAL, 4575
Alev YUCEL, 2187
Alex CHENG, X
Alexander FEHÉR, 313
Alexey Arkady VOINOV, XIII
Ali Abdual Zeahrah ALWAILY, 2615
Ali Emre AKGÜN, 1975
Ali GÜNEY, 1521
Ali İŞMEN, 439
Ali KESKİN, 1817
Ali UNYAYAR, 3509
Alkan ÖZTEKİN, 439
Alp ÖZERK, IX
Alpaslan ATEŞ, 3081
Altıngül Özaslan PARLAK, 557
Altuğ ŞENOL, 2365
Amit KULKARNI, 4481
Ammar RAFIEI EMAM, 2769
André Francisco PILON, 5399
Andrea E. RIZZOLI, XIII
Andrew BROOKES, XIII
Andrew MCKILLOP, 1903, 1911
Anıl SOYUMERT, 353
Aniello Russo SPENA, 3777
Anjum SUHAIL, 4753
Anna RE, 2451
Anne BUTTIMER, XIII
Annelie SJÖLANDER-LINDQVIST, 1793
Anthony J. JAKEMAN XII
Antonije ONJIA, 3423
Antonio PRESTIA, 1043
Anwar NASIM, III, XIII
Archana GODBOLE, 221
Armağan KORKMAZ, 781
Arturo Sousa MARTIN, 4155
Arzuhan Burcu GÜLTEKİN, 1207
Asal ROOHISALARI, 1737
Asım KADIOĞLU, 595
Asım VEHBİ, XXVII
Aslı Sungur ERGENOĞLU, 5189
Aslı TUNÇOL, 889
Aslıhan KABTAN, 339
Atilla ERİŞ, 453, 459, 467, 753
Ayca TELATAR, 2187
Ayda AKKARTAL, 4709
Ayfer AYTUG, 5189
Ayhan AYTAC, 1303
Aykut SAĞLAM, 595
Ayla ARSLAN, 2005, 3291
Ayla ÖZER, 3471
Aylin KAYA, 2793
Ayman Abou HADID, X
Aysel KEKILLIOGLU, 329
Aysel YONTAR, III , IX
Aysu KES, 4417
Aysun SOFUOĞLU, 3393
Aysun TÜRKMEN, 3081
Ayşe Bahar YILMAZ, 3139
Ayşe DÖNMEZER, X
Ayşe EVEREST, 611
Ayşe ÖZDEMİR, 621
Ayşegül KIBAROĞLU, 4507
Ayşegül SAMSUNLU, 121
Ayşen AKSU, 889
Aytaç YILDIRIM, 5429
Aytan HAKAN, 5357
Ayten EROL, 1133
Ayten SURURI, 2471
Aytuğ SIVASLIGIL, 3119
Aytul SOFU, 2091

Azhar ALI, 4689,5009
Aziz ERTUNÇ, X, 4587
Aziz ŞENCAN, 3027
Azra JAGANJAC, 2387

B

B. ARMAGAN, 1859
B. BIZHGA, 4769
B. D. TRIPATHI, 2983
B. ESKIN, 695
B. İNCE, 3227
B. MAVI, 3555
B. MIOVA, 2225
B. TÜTÜNCÜ, 3459
Babagana ABUBAKA, 4477, 5015
Bahar BAYHAN, 5055
Bahar Güçiz DOĞAN, 5365
Bahar TANK, 5063
Bahri AYDIN, 5357
Bahtiyar EROĞLU, 917
Banu ÇAKIR, 2301
Barış GÖRAL, 4709
Barış ÖNOL, 3679
Barry W. WILSON, XIII
Başak İPEKOĞLU, 3393
Başak MESCİ, 3601
Bayram Ali MERT, 3961
Beatriz LORA, 1777
Behzat GÜRKAN, 353
Belay TEGENE, XII
Benoit GUIYESSE, 3415
Beran GÜLÇİÇEK, 1379
Berna Balcı İZGİ, 2869
Berna BARADAN, 4605
Berra Gültekin SINIR, 5105
Beşer Oktay VEHBİ, 977
Beyza AĞCIOĞLU, 5269
Beyza Şat GÜNGÖR, 2461
Beyza ÜSTÜN, 5269
Bhattacharyya APURBA, 4143
Bilsen BELER BAYKAL, 1505
Birutė DARŠKEVIČIŪTĖ, 95
Biserka DIMISKOVSKA, 2213
Bjarne Bruun JENSEN, XIII
Bouazzi NAGIA, 5117
Branimir JOVANCICEVIC, XIII
Burcu ERTEM, 2833
Burhan SAKALLI, 889
Bülent MİRAN, 2163
Bülent TOPKAYA, 3059,4350
Bülent VEREP, 3267

C

C. YALÇIN, 3555
C. YARCI, 695
Cahit Tagi ÇELİK, 3353
Can KARA, 789
Canan CENGİZ, 955
Caner ZANBAK, 1515
Cankut ÖRMECİ, 2657, 2667
Cansu Filik İŞÇEN, 3097
Cantürk CANER, 2907
Carmit LUBANOV, 5309
Carol YÜRÜR, 5453
Celal F. GÖKÇAY, 1365
Celalettin Eren OĞUZ, 1975
Cem BİROL, 2591
Cem HAMİ, 1983
Cem SORUŞBAY, 3669
Cemal BULUTOĞLULARI, XXVI
Cengiz MUTLU, 3267
Cengiz YILMAZ, 1379
Cenk ÖNER, 4935
Ceren KELEŞ, 4987
Ceren PARALİK, 2591
Ceren UYSAL OĞUZ, 3813
Cevdet TINAZCI, 5371
Champika KARIYAWASAM, 3939
Charles MLINGWA, 249
Charles N. ALPERS, XIII
Cheslav ROMANOVSKY, 1673
Christoph J. BLASI, 4037
Costa MARQUES, 37
Coşgül YÜKSEL, 4859
Coşkun BULUT, 4635
Coskun ERUZ, 2275
Cristina FIERA, 255
Cristina MUNTEANU, 255

Ç

Çağatay GÜLER X,1975, 2173, 5357
Çağrı GÖKDEMIR, 5269
Çiğdem ÇİFTÇİ, 4027, 4334
Çiğdem YIĞIN, 439

D

D. GALERIU, 1953
D. GULER, 4007
D. HOVHANNISYAN, 4791
D. K. CHAKRABORTY, 1195
D. KARADAG, 1463
D. KUZNETSOV, 4047
D. M. S. KADYAMPAKENI, 3847
D. MOHAN, 1597, 3279
D. OUAZAR, 2785
D. SUSNIENE, 1563
Dafina NIKOLOVA, 1331
Daiva BERŽINSKIENĖ, 95
Dan C. C. GALERIU, XIII
Dana KOLEVSKA, X
Daniela RADUCU, 255
Daniela ŞINCU, 3197
David A. STAH, XIII
David HUMPHREYS, 3785
Davut AYDÜZ, 5381, 5391
Demet UYGAN, 4255
Deniz Anıl ODABAŞI, 439
Deniz BABUŞ, 3735
Deniz BOZKURT, 4965
Derin ORHON, III , XIII, 4015
Derviş YUKSEL, 1491
Derya B. ÖZKAN, 1821
Derya Çakır AYDIN, 5343
Derya ÇAMUR, 5357
Derya EŞEN, 339
Derya OKTAY, 789
Devrim Yücel BESIM, 2417
DharmPal MALIK, 1179
Dicle AYDIN, 941
Didem EVCİ, 2173
Dilek ASLAN, 2105
Dilek DEHMEN, 5365
Dilek TAYLAN, 4280
Doğan CANIVAR, 5095
Dragana ĐORĐEVIĆ, 3423
Dragica JAKOVLJEVIĆ, 3423
Dudu ÖZKUM, IX , 537
Dunja ANDIC, 2559
Duygu ERDOĞAN, 5365

E

E. DIMCO, 4769
E. DJONOVA, 3465
E. Gülbuğ EROL, 4845
E. M. GURBANOV 749
E.O. SOOLA, 5317
E. OSMA, 695
E. Sibel BEŞLİ, 3267
Ebenezer Adebisi OLAWUYI, 4885
Ebru SAATCI, 345
Ebru Z.BOYACIOĞLU, 5247
Ece TURHAN, 453, 459, 467, 753
Ece Ümmü DEVECİ, 5063
Ed BOLES, X
Edip AVŞAR, 3767
Edwin NJEBA NGANJI, 2435
Egemen ARAS, 3401,3991
Ekmeleddin İHSANOĞLU, XXXV
Ekrem KURUM, 4155
Ekrem Şanver ÇELIK, 439
Ela ATIŞ, 1535,2163
Elchin KHALILOV, III, XIII
Elçin AKDUMAN, 2353
Eliahu ROSENTHAL, 4121
Elif GÜNDÜZ, 931,3915
Elif KARAKURT TOSUN, 2907
Elif KUZU, 3089
Elizabeth GONZALEZ X
Elizabeth THOMAS-HOPE, X
Elsa GEGA, 2123
Emel BADUR, 2833
Emel ÖZKAN, 345
Emel Tozlu ASLAN, IX
Emel YILDIZ, 5247
Emine BUDAK, 5083
Emine Ş. OKUDAN, 439
Emine YALÇIN, 2139
Emine ZAİMOĞLU, 2711
Emrah A. ERKURT, 3509
Emrah YALÇINALP, 393
Emre DURMAZ, 2015
Engin GÜRTEKİN, 3037
Epule Terence EPULE, 2195
Ercan KÖSE, 1817, 2275
Ercan SARIDOĞAN, 1549
Erdinç ŞAHİNÖZ, 287, 305
Eren SARIKAYA, 2505
Ergün TAŞKIN, 295
Eric JOHNSON, XIII
Ersi Abacı KALFOĞLU, X
Ersin KARABACAK, 571
Ersin USKUN, 2343
Ersin YÜCEL, 565, 651,659
Ertan TAŞKAVAK, 5055
Esad BUKALO, 4665
Esra MARTİN, 621
Esra YALDIZ, 917
Esteban G., JOBBAGY, XIII
Eşref CERRAHOĞLU, XXV
Eti Akyüz LEVI, 4899
Eunkyung LEE, 3149
Evelina BAZINI, 1323
Evin ARAS, 2257
Evren ÇALIŞKAN, 3559
Evren KOBAN, 345
Evrim ÇELİK, 3149
Ezel TİLKAN, 3187

F

F. B. ÖZDEMİR, 3551
F. Balık ŞANLI, 2727
F. BALTACI, 4007
F. DEMET, 839, 5343
F. GHOMARI, 3157
F. I. LATIFOV, 3433
F. KULALI, 3555
F. M .SULTANOVA, 3411
F. Nur AKSAKAL, 2257
F. Saadet KARAKULAK, 1481
F. SEVENCAN, 2539
F . Yeşim EKİNCİ, 2091
F.Z. ABDULAEV, 3433
Fabian M. JAKSIC, XIII
Fadim YAVUZ ÖZDEMİR, 3915
Faize SARIŞ, 3657
Faral ARAL, 305
Farhad FARAHVASH, 671
Farhad JAFARİ, 671
Farhat M. ALI, XIII
Farmik Vali MOHAMADI, 1925
Farudin HOXHA, 1725
Faruk ARAL, 287
Faruk TEKBAŞ, 2173
Faško MARTIN, 4081
Fathi ELOSTA, 4243
Fatima BATOOL, 3069
Fatma CESUR, 1303
Fatma KALPAKLI, 4581
Fazıl ÇELİK, 4955
Fehime Yeşim GÜRANİ, 769
Fehminaz TEMEL, 2173
Ferdağ ÇOLAK, 2321
Ferdi SABİT SOYER, XXXIV
Ferid MURAD, XIII
Feriha YILDIRIM, 2517
Ferit YAKAR, 4955
Fernando CASTRO DE ABREU, 1685
Fethiye GODE, 3027
Feyera SENBETA, 475
Feyza CANDAN, 637
Feza GEYİKÇİ, 4362
Fidan AKBAŞ, 1057
Figen Esin KAYHAN, 4797
Fikret ÇAKIR, 439
Fikret ÖZGÜR, 5357
Filiz BULUT, 2105
Filiz DİLEK, X, 1365
Filiz GÜR, 3301, 3585
Filiz SAVAROĞLU, 2321, 2989
Filiz SUNAR, 4709
Fiona J. Y. ROTBERG, 4387
Firdaus Fatima RIZVI, 3951
Florence NANGENDO, 689
Folashade O. OMOKHODION, 2157
Folorunso Sunday AYADI, 4367
Frank BATES, 1527
Frederick I.B. KAYANJA, XIII
Funda ÇETİNDAĞ, 2845
Funda KAHRAMAN, 1817
Funda SEVENCAN, 2173
Funda TIHMINLIOĞLU, 3393
Funda VARNACI, 2603
Furkat KHASSANOV, X
Füsun Erkan YURDABAK, 439

G

G. A. URAZOVA, 2233
G. BOZTAŞ, 2539
G. CİVELEKOĞLU, 3019, 3523
G. M. KULNIYAZOVA, 2233
G. R. MUGHAL, 67
G. S. HASANOV 3433
G. STATYUKHA, 1609, 4199
G. TORUNOĞLU, 4015
G. TOZ, 871

Gabriele VOIGT, XII
Gagik TOROSYAN, 2585, 4237, 4791
Galip AKAY, XIII
Gamze Yücel IŞILDAR, 2517, 2895
Gaudelia A. REYES, X
Gaye TUNCER, 2421
Gazi CONTUK, 4797
G-C. FANG, XIII
Geoff BERTRAM, XIV
George CONSTANTINOU, X
George G. LUNT, XIV
George PETRIDES, X
Gerald J. ZAGURY, 2149
Gerald LALOR, XIV
Germano MWABU, XIV
Gh. ZEHTABIAN, 379
Gh.A. JALALI, 641
Ghasem Ali Dianati TILAKI, 325
Ghorban ELMI, 2879
Giovanni BARROCU, III, XIV
Giovanni QUARANTA, 4109
Girja K. SHUKLA, XIV
Giuseppe FUMAROLA, 3777
Gopal B. THAPA, XIV
Gökçen BİLGE, 5055
Gökçen BOMBAR, 1833
Gökhan KAYADURMUŞ, 4453
Gökhan ÖZDEMİR, 1817
Gökhan SAVAROĞLU, 2989
Gönül Tuğrul İÇEMER, 4987
Gözde AKGÜN, 2687
Grainne GILMORE, 529
Gregory KOFF, 4673
Guido VAN HUYLENBROECK, 1081
Gunnar TELLNES, III
Guntis BRUMELIS, X
Guo JIAN-FENG, 4597
Guor-CHENG FANG, 2943
Gülcan ÖZKAN, 2327, 4801
Gülcan SARP, 2631, 4619
Güler TEPE 2105
Gülerman SÜRÜCÜ, 1365
Gülhayat Gölbaşı ŞIMŞEK, 143
Gülistan ERDAL, 1849
Gülnur Mertoğlu-ELMAS, 1941
Gülriz BAYCU, 3419
Gülsen BOZKURT, 2055
Gülser ÇELEBİ, 1207
Gülsüm TER, 941
Gülşah ELDOĞAN, 5365
Gümüş Funda GÖKÇE, 3443
Günay KOCASOY, X, 2971
Güngör TURAN, 4469
Günseli YAPRAK, 3301, 3585
Gürdal HÜDAOĞLU, IX
Güven GÖRK, 2935

H

H. A. BAHRAMI, 4183
H. A. YALIM, 3551
H. ABGHARI, 4647
H. AHMADI, 4647
H. AKYILDIRIM, 3551, 3555
H. ARZANI, 2747
H. AYDIN, 3595
H. AZARNIVAND, 379
H. BAYHAN, 1463
H. Derya KOL ARSLAN, 4655, 5301
H. Ece SALALI, 1535, 2163,5453
H. EJTEHADI, 487
H. F. MANSOUR, 3237
H. Filiz Alkan MEŞHUR, 2647
H. KESHTKAR, 4288
H. M. MASHALY, 3237
H. MIRDAVODI, 2747
H. Q. WANG, 3157
H. R. NASERI, 379
H. S. TORTOP, 1767, 1947
H. W. RYU, 3533
H. Zahedi POUR, 487
Habib Amir- HALAJİ, 671
Habib SAADOULI, 4264
Hafiz Mogira BADAR, 3069
Haim SHULMAN, 4121
Hakan ACET, 111
Hakan ALLI, 2365
Hakan ALPHAN, 187
Hakan ALTINTAŞ, 2205
Hakan ATAMTÜRK, 2533
Hakan AYGÜN, 5063
Hakan BAHADIR, 2935
Hakan HAKYEMEZ, 557
Hakan OĞUZ, 3819, 5469
Hakan TONGAL, 3981
Hakan TÜRKOĞLU, 2343
Hale ÖZGİT, 5429
Halil ÇAKAN, 187
Halil SEYIDOĞLU, 1155
Halime PAKSOY, X
Halit FİLİZ, 5055
Hallvard ØDEGAARD, X
Hana RUSI - SALIU, 5281
Hanwant B. SINGH, XIV
Haris BRADIĆ, 4326
Hartmut FRANK, XIV
Hasan AKCA, 5197
Hasan BÖKE, 3393
Hasan CESUR, 3495
Hasan ERTEN, XI
Hasan GÖKSEL ÖZDILEK, 3767
Hasan Ş. HAŞTEMOĞLU, 781
Hasan VURDU, 241
Hasan ZOLFAGHARI, 1869
Hassan O. KAYA, 4133
Hatice Ataçağ ERKURT, 3471, 3509
Hatice GÖKÇEKUŞ, IX
Hatice GÜLEN, 459, 467, 753
Havva Alkan BALA, 4027, 4334
Havva ARSLANGAZİ, IX
Havva DINÇ, 345
Hayrünisa BAŞ, 2365
Heila LOTZ-SISITKA, XIV
Helen SCHNEIDER, XIV
He-lin FU 4597
Henning SCHROLL, 4169
Herdem ASLAN, 439
Heval OCAL, 4741
Hillel S. KOREN, XIV
Hilmi ERDAL, 1849
Himmet UMUNÇ, 4557
Hiromi YAMASHITA, XIV
Hj. Dahlan TAHA, 2761
Hj. Kamaruzaman JUSOFF, 2761
Holmes ROLSTON, XIV
Hosin RANJI, 1925
Hruska JAKUB, XIV
Huriye KUBİLAY, 2863
Husnija RESULOVIĆ, 4665
Hussein LAHMAR, 5117
Hülya CICEK, 2099
Hünay EVLIYA, XI
Hüseyin AKYÜZOĞLU, 5381, 5391
Hüseyin GÖKÇEKUŞ, II , III, VII, IX, XVII, VIII, XX, XLI, 2923, 4219
Hüseyin KARACA, 4987
Hüseyin ÖZDEŞER, 1243
Hüsnü Ezber BODUR, 5179
Hüsnü KAPTAN, 889

I

I. AKKURT, 3551, 3555
I. C. OKORO, 5155
I . DZHYGYREY,4199
I. İSKENDER, 4015
I. STOIMENOVA, 3465
Ibrahim Abdel Gelil Said, ABDULA XI
Ioana GOMOIU, 3197
Irena TWARDOWSKA, XIV
Irina CHESNOKOVA, 4673
Isaac RAMPEDI, 1161
Isak IDRIZI, 1725, 4093
Isfaq AHMAD, XIV, 3607
Işık K. ORAY, 1481
Işık Özge YUMURTACI, 1527

İ

İ. ÇOK, 3459
İ. Sevinç KRAVKAZ, 241
İbrahim BEKTAŞ, 1931
İbrahim ORUN, 2311
İbrahim S. ALNAIMI, XI
İclal ALUCLU, 823
İclal Geyikli MERAM, 2099
İdil ALKAYA, 5269
İdil ALTIPARMAKOĞULLARI, 1379
İlhan ALTINOK, 3267
İlhan SAĞSEN, 4507
İlker KILIÇ, 2845
İlknur AK, 439
İlknur ÖZDEMİR, 2311
İlyas TENLİK, 5357
İlyas YILMAZER, 1275, 4635
İnci TOGAN, 345
İncilay YURDAKUL, 4867
İpek İMAMOĞLU, 1365
İpek YILMAZ, 3059, 4350
İrfan GÜNEY, XI
İrfan GÜNSEL, IX
İrfan SAYAN, 5063
İsmail GÜNDÜZ, 4677
İsmet ÇOK, 2015
İsmet UYSAL, 571
İsmühan Potoğlu ERKARA, 2333

J

J. ABDOLLAH, 2747
J. ABESHI, 4769
J. F. Santos OLIVEIRA, XIV
J. H. EPHRAIM, 3863
J. J. BEZUIDENHOUT, 2701
J. NAJI, 4302
Jaco VANGRONSVELD, XI
Jaeweon CHO, 3149
Jalali Seyed GHOLAMALI, 387
James DEVILLERS, XIV
James SEGGANE, 689
Jane GOLD, 1071
Janki ANDHARIA, 4695
Jaroslav BOHAC, XIV
Jean BALOUGA, 4367
Jeffery J. SMITH, 1125
Jennifer BROWN XIV
Jianping WU, XIV
Jim C. BRIDEN, XIV
Jim LAMEROX, III
Joe LEWIS, XI
John A. HOSKINS, 1965
John DAISH, XIV
John GREGORY, XIV
John HOSKINS, XIV
John SAKA, XI
Joseph S. PAIMPILLIL, 4927
Josephine Phillip MSANGI, 5257
Juan GUZMÁN, 1393, 4975
Judith T. ZELIKOFF, XIV
Julian Scott YEOMANS, 11
Jurgis Kazimieras STANISKIS, 1
Jurka Lepicnik-VODOPIVEC, 2575
Jyrki LIESIVUORI, XIV

K

K. A. IBAYEVA, 749
K. ANKUR, 3279
K. OBIRI-DANSO, 3863
K. S. CHO, 3533
K. SWATHI, 4809
K. Tuluhan YILMAZ, 187
Kadriye Deniz TOPÇU, 1411
Kai-Uwe KRAUSE, 3887
Kaku NOKOE, XIV
Kamran ZENDEHDEL, 1081
Karen OCEGUERA, 4975
Katerina BISEVA, 2213
Kemal BİRDİR, 1339
Kemal ESENGÜN, 5197, 1849
Kenan ERDOĞAN, 2311
Kenan OK, 3875
Kengo SUNADA, 4067
Kenneth N. TIMMIS, XIV
Khalid S. AL-SHALLASH, 1989
Konstantin V. SUDAKOV, III
Kou IKEJIMA, 4067
Kriš JOZEF, 4081
Kristine WALRAEVENS, XV
Kujtim ZENA, 1725, 4093
Kutalmış GÖKKUŞ, 3081
Kültiğin ÇAVUŞOĞLU, 2139
Kürşad ÖZKAN, 565, 651
Kyaw Tha PAW U, XV
Kyoung-Woong KIM, XIV

L

L. DHASKALI, 4769
L. MEKLICHE 493
L. N. Ece ARIBURUN, 1449
L. TAFAJ, 4769
L. V. HUSEYNOVA, 3411
L. V. LIM, 2233
L. Van RENSBURG, 2701
L. YILMAZ, 1801
Laika GÖKÇEKUŞ, 1983
Lale GÜREMEN, 3353
Latifah MANAF, 2675
Laura SHABANI, 4783
Leel RANDENI, 3939
Leila VATANI, 399
Levent AKDUMAN, 4635
Levent ŞIK, 2029
Leyla AÇIK, 761
Leyla KALENDER, 3365
Li MINGYANG, 1113
Lidia V. SMOLOVA, 2485
Lidija VUJIČIĆ, 2569
Liliana VASILIU-OROMULU, 255
Liljana ELMAZI, 1323, 1427, 2123
Ljiljana MALOVIĆ, 3423
Luc HENS, III, XV
Luiz Antonio FERRARI, 3517
Lyoussi BADIAA, XI

M

M. A. YÜKSELEN, 3213
M. Ali KİRMAN, 5165
M. Aydın PEKİN, 3669
M. AZIMI, 2747
M. B. KHORSHIDI, 675
M. BORHANI, 2747
M. D. HASNAOUI, 2785
M. DUMITRU, 255
M. Erol KESKİN, 4280
M. F. ALTUNKASA, 2917
M. FALAHI, 5421
M. FALCA, 255
M. FRAHPOUR, 2747
M. Ghanbari MOTLAGH, 641
M. GHOLAMI, 5421
M. H. MAHDIAN, 4183
M. Hakan ARSLAN, 4655
M. Hakkı ALMA, 1931
M. Handan ÇUBUK, 1821
M. ISMAILI, 2225
M. KARAMAN, 4007
M. Kemal BEŞER, 1549
M. KITIS, 3019, 3523
M. KOLUKIRIK, 3227
M. M KAMEL, 3237
M. MAHDAVI, 4647
M. Mohseni SARAVI, 4647
M. Nasir SHAMSUDIN, XI
M. Nur EROĞLU, 5365
M. ÖVEZ, 4015
M. R. ASGHARIPOUR, 359
M. S. GÜNEY, 4059
M. Sedat KABDAŞLI, 5037
M. SEHABI, 493
M. SERİN, 695
M. Shamsher ALI, XV, 2369
M. T. ESETLILI, 2727
M. TABARI, 641
M. Talha GÖNÜLLÜ, 5225
M. TOUJI, 2785
M. UZUNKAVAK, 1767
M. Yaşar KALTAKCI, 4655
M. Zeki DOĞAN, 1515, 1521
M. Zeki YILDIRIM, 411
M. ZGUROVSKIY, 1609, 4199
Macid NURBAŞ, 3051, 3359
Maengsern KIM, 997
Mahir FİSUNOĞLU, 2869
Mahmut MUTLUTÜRK, 1641
Mahmut Parlak TUNA, XI
Mahmut SARI, 2527
Mahnaz ZAHEDMANESH, 1925
Majed Hamad Abu ZAHRAH, 2923
Majid Labbaf KHANEIKI, 3929
Majid YASOURI, 4207
Mamdouh NOUH, XV
Manfred DENICH, 475
Mannar FAYYAD XI
Manuel Benito CRESPO XI
Manzoor QADIR, XV
Marcel ARNOULD, XV
Marcel STIVE, XI
Marcial BLONDET, XV
Margaret ZIMBA, XI
Maria da CONCEIÇÃO, 37
Maria JONSTRUP, 3415
Mariele EVERS, 3887, 3899
Marilena ONETE, 645, 3197
Mark BYNOE, XI
Marko KIESSEL, 1021
Martha C. MONROE, XV
Martín CERVANTES, 1393
Martin Morgan TAYLOR, 5291
Mary SEELY, XV
Maryna YEPIK, 4491
Marzieh MOSAYEBI, 2739
Mayor John WILLIMAS, 5327
Mehmet A. MAZMANCI, 3509
Mehmet AKBULUT, 439
Mehmet Ali TALAT, XXXVII
Mehmet BERKUN, 3401, 3991
Mehmet BEYHAN, 851
Mehmet ERDOĞAN, 2421, 2549
Mehmet ERGİN, XV
Mehmet İŞLER, 2365
Mehmet KARACA, 3679, 3723
Mehmet KARAOĞLAN, 2775
Mehmet KITIS, 3149
Mehmet OKCAN, IX
Mehmet ÖZTÜRK, 295
Mehmet TÜRKMENOĞLU, 3961
Mehraj ABBOV, 237
Melih MICIK, 4741
Meltem Kutlu GÜRSEL, 2863
Meltem MARAŞ, 329, 2139
Mesude İŞCAN, 345
Mesut ANIL, 3961
Mesut YALVAÇ, IX
Mete FERİDUN, 4367
Mete TAYANÇ, 3723
Metin CAN, 5197
Metin ERGENEMAN, 3669
Michael WILHELM, XV
Mihaela PAUCA-COMANESCU, 645, 3197
Mikayel HARUTYUNYAN, 4237
Mine Uzbilek KIRKAĞAÇ, 587
Minodora STANESCU, 255
Mira LULIĆ, 4915
Mirela MERSINI, 1427
Mohamed AZAB, 4527
Mohamed. M. SHEREIF, 1989
Mohammad Esmaeil ASADI, 1033
Mohammad Reza NAGHAVİZADEH, 627
Mohammad Yousif Al HITY, 2615
Mohsen HOSSEINI XI
Mohsen MALEKI, 2739
Mohsen ROSHDI, 1737
Mohsin SHAIKH, 2307
Moneef R. ZOU'BI, XI
Moslem AKBARINIA, 399, 2823
Muaaz Mutaz Al-AJLANI, 2243
Muammer TUNA, 2441, 5133
Muhammad AKHTAR, 421
Muhammad Ali SHAMIM, 3687
Muhammad ARSHAD, 4753
Muhammad Azim KHAN, 551
Muhammad Naeem KHAN, 421
Muhammed ATAMANALP, 4318
Muhammet TURKOGLU, 439, 4935
Muhlis ÖĞÜTÇÜ, 2863
Mukesh B. JOSHI, 1617
Murat AYDEMIR, 2549
Murat ÇETİNKAYA, 111
Murat DOĞRUEL, 3723
Murat E. YAZGAN, 955
Murat ERTAŞ, 1931
Murat ŞAHİN, 987
Murat TAŞDEMİR, 1589
Murat TÜRKEŞ, 3657
Murat ÜNAL, 621
Murat ZENCİRKIRAN, 271
Musarrat JABEEN, 1695, 4425, 5209
Mustafa ALPASLAN, 439
Mustafa AYDIN, 2775
Mustafa CENGİZ, 3027
Mustafa DOĞAN, 3139
Mustafa Dursun ÇAĞLAR, 881
Mustafa IŞILOĞLU, 2365

Mustafa KARABOYACI, 3027
Mustafa N. İLHAN, 2257
Mustafa ÖZER, 1219
Mustafa ÖZTÜRK, 2343
Mustafa ÖZYURT, 3471, 5063
Mustafa TÜRKMEN, 3081, 3089, 3559
Mustafa VAR, 393
Mustafa YILDIRIM, 3059, 4350
Mutasem EL-FADEL, XI
Muthana SHANSHAL , XV
Muzaffer YÜCEL, 3735
Müberra PULATKAN, 393
Müge BAHÇECİ, 963
Münevver ELELE, 2687
Münir ÖZTÜRK, III, XV, 2935
Müslüm BEYAZGÜL, 2935
Mykola SHESTAVIN, 4491
Myqereme RUSI, 5281

N

N. A. BERESFORD, 1953
N. A. SALIMOVA, 3411
N. AYMAN ÖZ, 3227
N. Ç. BEZİR, 1767, 1947, 3555
N. DURKAN, 3595
N. Ferah AKINCI, 829

N. Gamze TURAN, 1665
N. IGNATYEVA 4047
N. KALOYANOVA, 3465
N. KHUSSAINOVA, 2233
N. KONAKLI, 2917
N. N. JIBIRI, 3105
N. O. YİĞİT, 3019, 3523
N. ÖZEK, 1767, 1947
N. ŞAHİN, 695
N. Ülkü Karabay YAVAŞOĞLU, 2029
Nadejda TODODROVA, 1331
Nader YEHIA, 4527
Naim H. AFGAN, XV
Naim UZUN, 2603
Nandkishor MORE, 515
Naser AKHONDI, 1737
Naser Jafari GHAVZAN, 4292
Nasreddıne SAADOULI, 4264
Nawneet VIBHAW, 2889
Nazan Deniz KOÇ, 4797
Nazım BURGUL, 5371
Nazlı BÖKE, 2029
Nazmi ORUÇ, 881, 889
Nedim GÜRSES, 4859
Nerkis KURAL, 2497
Neslihan SARUHAN, 595
Nesrin ÇİLİNGİROĞLU 2205
Nesrin MENEMENCİ, IX, 5429
Neşet KILINÇER, XI
Nezaket ADIGÜZEL, 761
Nezihe KÖKSAL, 467, 753
Nguyen THI HAI YEN, 4067
Nicholas MASCIE-TAYLOR, XV
Nicholas ORNSTON, XV
Nicolas JARRAUD, 4443
Nihal KUTLU, 595
Nihâl Yıldırım MIZRAK, 1219
Nilay TAŞER, 3313
Nilden BEKTAŞ, 3481
Nilgün BALKAYA, 3481, 3495
Nilgün BİLEN, 2281
Nilgün Göktürk BAYDAR, 4801
Nilgün ÖZDEMİR, 4318
Nilgün ÖZTÜRK, 2333
Nilsun İNCE, 5269
Nilüfer SEYİDOĞLU, 271
Ning ZHOU, 4597
Nives MAZUR, 4915
Norhayati Mohd TAHİR, XV
Nuray TERZİ, 1399
Nuray TOKGÖZ, 83
Nurdan ATAMTÜRK, 4551
Nurdan ERDOĞAN, 1535, 2163
Nuri Onur AZİZOĞLU, 1975
Nurkan KARAHANOĞLU, 4105
Nusret ŞEKERDAĞ, 3037, 5075
Nüket SİVRİ, 2275
Nükhet GÜNBEYAZ, 1665
Nükhet YILMAZ TURGUT, XI, 2807
Nüzhet Cenk SESAL, 4797
Nüzhet DALFES, 3679

O

O. BOYACIGİL, 2917
O. EYİCE, 3227
O. G. ARINOLA 2133
O. İNCE, 3227
O. K. ULUTAŞ, 3459
O. KVITKA, 4199
O. M. AKINOSUN, 2133
O. O. OYETAYO 2133
O. PAVLOVA, 4047
O. SUSAREVA, 4047
Obasohan QUEEN, 5327
Obradović ZAREMA, 2115
Oğuz KURT, 295
Oğuz ÖZDEMİR, 2441
Oksal MACAR, 353
Oktay YILDIZ, 339
Olcay GÜLÇİÇEK, 2793
Olcayto KESKİNKAN, 3043
Olivier BOIRAL, 169
Onur KOYUNCU, 2333
Orhan ALTAN, XI
Orhan KÜÇÜKGÜL, 3059
Orhan ÜNAL, 2327
Osman N. ÖZDEMİR, 4463
Osman Nuri ERGÜN, 3601
Osman SÜNGER, 1975
Ozan M. GÖKTÜRK, 3679

Ö

Ö. ÇINAR, 3523
Ö. Faruk TEKBAŞ, 2063
Ömer APAYDIN, 5225
Ömer EKER, 4001
Ömer LÜTFİ ŞEN, 3679, 4965
Ömer Tuğrul KARAGÜZEL, 1881
Öner ÇETİN, 4255

Özcan ÖZEN, 439
Özden AĞRA, 1821
Özgül İNCEOĞLU, 3227
Özgür CENGİZ, 439
Özgür Emek İNANMAZ, 439
Özgür YILMAZER, 1275, 4635
Özlem ESENGİN, 2775
Özlem ŞENYİĞİT, 829
Özlem UNAL, 1339
Özlem YILMAZER, 1275, 4635
Öznur ÖZDEN, 4567

P

P. GÜREL, 4015
P. J. Jansen Van RENSBURG, 2701
P. K. GOGOI, 1195
P. MANOHARAN, 199
P. MUTLU, 695
P. S. SHEHRAWAT, 1141
Pall HERSTEINSSON, XV
Paqui BLANQUES, 3415
Parisa NIKZAD, 1925
Patricia MAURICE, XV
Paul Ravn JEPSEN, 2387
Paul W. JOWITT, XV
Paulo B. LOURENCO, XV
Pecora VANESSA, 1685
Pelin AKLIK, 3577
Pernille ALMLUND, 53
Peter BRIMBLECOMBE, XV
Peter KRUMBIEGEL, XV
Peter NOVAK, XV
Petra ADOLFSSON, 1793
Peyman YALÇIN , XI
Phil-Eze, 5155
Philip E. LAMOREAUX, XV
Philip M. Fearnside, XV
Pınar İŞMEN, 439
Pınar KUŞ, 3119
Pranav VYAS, 369

Q

Qamar Shahid SIDDIQUI, 2543
Qarayev Siyavush FARKHAD, 2479
Qasem Abdul JABER XI
Qiang LUO, 4597
Qorban ELMI, 4735

R

R. Erdem ERKUL, 4417
R. Esra DEMİRDÖĞEN, 129, 1747
R. K. BAXI, 2307
R. KANANI, 675
R. N. PATI, 1995
R. SOLTANI, 487
R. Süleyman GÖKTÜRK, 2327
R. TIPIRDAMAZ 537
R. ÜNAl, 3551
Rabiye TERZİ, 595
Rafet KISTIR, 1641
Rahmi ERDEM, 931
Rahmi KOÇ, XXIII
Rahşan TAMSÜ, 1005
Ramazan AKMEŞE, 5357
Ramazan MERAL, 4344
Ramazan ŞEVİK, 305
Ramzi SANSUR, XI
Rasa GLINSKIENĖ, 95
Raşit ALTINDAĞ, 1641
Ravi JAIN, XV
Raza ALI, 3687
Reha SAYDAN, 1575
Reinhold STEINACKER, III, XI
Remzi KARAGÜZEL, 1641
Renee RICHER, XI
Richard MOLES, XI
Richard R. ERNST, XIII
Richard ROBINS, XV
Rifat REŞATOĞLU, IX
Robert GIFFORD, XVI
Robert J. LETCHER, XVI
Roberto DANOVARO, XVI
Romeu ROVAI FILHO, 3517
Rosanna SALVIA, 4109
Roshan T. RAMESSUR, 5021
Rouhi-Moghaddam EINOLLAH, 387
Ruhangiz ISMAILOVA, 1633
Rüstem KIRIŞ, 3747

S

S. A. UTELBAYEVA, 2233
S. AYAN, 501
S. BAŞLAR, 3595
S. BATGI, 1859
S. CLAASSENS, 2701
S. DINEVSKA, 2225
S. DÜZGÜN, 4619
S. Gonca DEPREM, 5365
S. H.R. SADEGHI, 4183
S. HARUTYUNYAN, 4791
S. M. R FATEMI, 5421
S. Mohsen HOSSEINI, 2823
S. P. BINDRA, 5117
S. SAKAR, 1463
S. SAM, 3213
S. SARKAR, 1597, 3279
S. Serkan NAS, 3541
S. STRATIEVA, 3465
S. TAHMİSCİOĞLU, 4007
S. TANIK, 4015
S. Yousefi KHANGAH, 379
Saadet TOKER, 781
Sabri AZGÜN, 1589
Sabri RAZA, 2105
Sabri ŞENER, 1057
Saeed A.K. LODHI, 67
Saeid GORGİN, 581
Saffa B. RIFFAT, XVI
Said DAĞDAŞ, 3747
Saime ÖNCE, 83
Salah Y. Awad ALLA, 1255
Salek Zamani ALI, 1573, 2613, 5495
Salek Zamani MARYAM, 1573, 2613, 5495
Salek Zamani YAGHOUB, 1573, 2613, 5495
Salih GÜCEL, IX, 295
Sam KACEW, XVI
Sami ÖZÇELİK, 2091
Sanda MAICAN, 255
Sanda Midzic-KURTAGIC, 2387
Sandor KEREKES, XVI
Sandra M. APOLINARIO, 1777
Santosh Kumar PRAJAPATI, 2983
Sarp ÜNER, 2187
Satoru OISHI, 4067
Savaş AYBERK, 3319
Saye Nihan ÇABUK, 889
Scott SLOVIC, XVI
Sebahat K. OZMAN-SULLIVAN, 4741
Sebsebe DEMISSEW, 475
Sedef ELKER, 3127
Sedef ERYİĞİT, 1411
Sefer AYCAN, 2257
Seher Arıkan TEZERGİL, 143
Selahattin GÖKMEN, 3313
Selcen BABAOĞLU, 761
Selçuk KILINÇ, 2343
Selim KAPUR, XI
Selma YEL, 4453
Selnur UÇAROĞLU, 3059
Semih EKERCIN, 2657, 2667

Semra İLHAN, 2321, 3097
Semra SOYDAM, 651
Serap YAMAN, 5269
Serdal SAKÇALI, 2935
Serdar ALTINOK, 111
Serkan ÖZDEN, 439
Serkan ÖZTÜRK, 4719
Serkan YILMAZ, 5269
Serpil OPPERMAN, XII, 2375
Servet ARMAC, 1275
Seunghoe CHOI, 997
Seval SÖZEN, XII
Sevda ÇALIŞKAN, 2853
Sevgi SARYAL, XII
Sevil YALÇIN, 571
Sevim BUDAK, 4399
Seyed Hamidreza SADEGHI, 4727
Seyed Mohsen HOSSEINI, 387
Sezgin ÇELİK, 557, 565, 2327
Sezginer TUNÇER, 439
Shafiqul I. BHUIYAN, XVI
Shahamat U. KHAN, XVI
Shahida HASNAIN, 2243
Shian-chee WU, XVI
Siaka, SIDIBE, XVI
Siarhei PAZNIAK, 1673
Sibel ALİOĞLU, 2005
Sibel ASLAN, 5075
Sibel BAYIL, 2099
Sibel ULUDAĞ-DEMİRER, 3127
Silva ORLANDO CRISTIANO, 1685
Sílvia Maria STORTINI GONZÁLEZ VELÁZQUEZ, 1685, 1777
Sima NART, 1575
Sinan GÜNEYSU, 2275
Sinan SARISOY, 1549
Sinem AKCALI, 2353
Skender OSMANI, XII
Škultétyová İVONA, 4081
Sladjana KLJAJEVIĆ, 3423
Slavka SUFI-MIĆIĆ, 181
Sokefun Olusola BOLARINWA 3343
Solmaz KARABAŞA, 1357
Somlata SHARMA, 3759
Songül Acar VAİZOĞLU, XII, 1975, 2173, 2539, 5357
Sorin STEFANUȚ, 3197
Sourav KUMAR KESHRI, 4481
St. ALEXIEVA, 3465
Staika STRATIEVA, 1331
Stefan TRESSL, 3887
Stephen P. MC CARTHY, XVI
Suani Teixeira COELHO, 1685, 1777
Suat ATEŞ, 439
Suat GÜNHAN, 1473
Suat İ. GÜNSEL, IX, XVII
Suavi TUNCAY, 5453
Subramanya Sirish TAMVADA, 369
Sujith RATNAYAKE, 3939
Sukhong YOON, 997
Sulejma ČEHIĆ, 3251
Sultan BEKİROĞLU, 4001
Sumana V. PANDEY, 2295
Sungyun LEE, 3149
Suresh Chandra SAXENA, 1313
Süha BERBEROĞLU, 187
Süheyla KIRMIZIGÜL, 2029
Süheyla Sıramkaya BÜYÜKŞAHİN, 917
Süleyman KOÇBAŞ, 2085
Süreyya A. KADIOĞLU, 3187
SV Sven Bienert MRICS, 3707
Svetla BACHVAROVA, 1331
Syed MUZAMMILUDDIN, 1781

Ş

Ş. Doğanay YAYIM, 263
Ş.Gülin BEYHAN, 851
Şafak URAL, XI
Şakir ALEMDAR, IX
Şebnem ELLİALTIOĞLU, 761
Şebnem Önal HOŞKARA, 977
Şennur DABAK, 2075
Sevket DURUCAN, XVI
Şifa ABİK, IX
Şule ELHAKAN, 823
Şükran CIRIK, 439
Şükran ŞAHIN, 1101, 4155
Şükrü GÜNEY, 1833

T

T. C. KUMASİ, 3863
T. GJYLADIN, 2225
T.SCHEYTT, 4059
Tadesse WOLDEMARIAM, 475
Tahsin ERTUĞRULOĞLU, XXIX
Tahsin Gökhan TELATAR, 2187, 5365
Tamer ATABARUT, 2287
Tamer İrfan KAYA, 2265
Tamer ŞANLIDAĞ, 2353
Tania FLOQI, 4783
Tarzan LEGOVIC, III, XII, XVI
Tayfun KINDAP, 3679
Temel FEHMINAZ, 1975, 2105, 2205, 2539
Teoman KESERCİOĞLU, 637
Tetsuo YUHARA, XII
Tevfik ISMAILOV, 1633
Thade CLAMSEN, 249
Theodore A. ENDRENY, 4219
Thomas MADRITSCH, 1293
Tomasz ZYLICZ, XVI
Tufan NAYİR, 2343
Tuğba ALP, 3169, 3177
Tuğra İNCEER, 5371
Tuğrul URAL, 2505
Tuluhan YILMAZ, XII
Tuncay M. SEVER, 5055
Tuncer KATAĞAN, 5051
Tuncer ÖZDİL, 1379
Turan ÖZTURAN, XII
Turgay AVCI, XXX
Tülay ÖZDEMİR, 861
Tümer GARİP, IX
Türkay YILDIZ, 1527
Türkekul KURTTEKİN, XXXII
Tynybekov AZAMAT, 1657

U

U. S.YILMAZ, 4655
Uğur ÖZEKİNCİ, 439
Uğur YILDIRIM, 4399
Ulaş AKIN, 1281
Ulaş İM, 3723
Ulric ROTT, III , XVI
Umit GÖKKUŞ, 4995, 5083, 5095, 5105
Umut TÜRKER, III, IX, 2923, 5037

Ü

Ü.Gülsüm TER, 1411
Ülgen BEKİŞOĞLU, 1101
Ümit ERDEM, XII, 2711
Ümit HASSAN, III, IX , XIX
Ümit KEBAPÇI, 411
Ünsal AÇIKEL, 3169, 3177

V

V. ALTAY, 695
V.DAVTYAN, 4791
V.H. KABAMBE, 3847
V. M. SARODE, 2037
V. NIMMIE, 199
V.S.MAZUMDAR, 2307
V.SANDA, 255
V.TOPRAK, 4619
V. V. KOZHANOV, 2233
Vakur SÜMER, 4507
Valentina YANKO-HOMBACH, XII
Vedat DOYURAN, III , XVI
Vedat TOĞAN, 3991
Vedat TOPRAK, 2631
Veysel GÜLDAL, 3981
Veysi ÖZEL, 5063
Victor G. PRIETO, XVI
Vildan GÜNDOĞDU, 2687
Vinil AKBULUT 2105
Vinka UZELAC, 2559
Violeta HOXHA, 4093
Viorica HONCIUC, 255
Vivek P. KAPADIA, 1617
Vladas ŽULKUS, 911

W

W. CHO, 3533
Waleed Khalil ZUBARI, XII
Walid A. ABDERRAHMAN, XVI
Walter KOFLER, III , XVI
William J. MANNING, XVI
Wim DE KEYSER, 1081
Wiranto ARISMUNANDAR, XVI

Y

Y. BERİVAN, 839
Y. Bhg. DATO, 2761
Y. DOĞAN, 3595
Y. KURUCU, 2727
Yaakov ANKER, 4121
Yalçın TEPE, 3081, 3089, 3325
Yalçın TÖRE, 3089
Yasemin LEVENTELİ, 1275
Yaşar AVŞAR, 5225
Yavuz Bülent KÖSE, 659
Yavuz GÜNALAY, 11
Yeliz AŞÇI, 3051, 3359
Yeliz IŞIKLI, 4105
Yesim BÜYÜKATEŞ, 439, 4935
Yeşim Sağ AÇIKEL, 3051, 3359
Yeva TOROSYAN, 4237
Yılmaz İCAĞA, 277
Yılmaz OCAK, 3393
Yigal RONEN, XII
Yuan T. LEE,, XIII
Yusuf BAYRAK, 4719
Yusuf HÜSEYİNOĞLU, 611
Yusuf POLAT, 1005
Yusuf SERENGİL, 1133, 3875
Yusuf Ziya TER, 941
Yüksel İZCANKURTARAN, 187

Z

Z. ÇETECİOĞLU, 3227
Z. Damla UÇA AVCI, 4709
Z. DURAN, 871
Z. Fuat TOPRAK, 823
Z. J. MAMMADOVA, 545
Zafer BEKİROĞULLARI, 2591
Zafer DOĞU, 287, 305
Zafer ÖZER, 2793
Zafer YENAL, 5269
Zakia SHOAB, 67
Zalkid HADZIBEGOVIC, 2387
Zehra BAŞARAN, IX
Zehra GÜL, 2, 4399
Zekai ŞEN, III, XII , 3623
Zeki KODAY, 4308
Zekirija IDRIZI, 1725, 4093
Zeliha Selamoğlu TALAS, 2311
Zeynel DEMİREL, 2793
Zhang YANG, 3149
Zhihong XU, XVI
Zohra Ben LAKHDAR, XII
Zuhal DİLAVER, 521
Zulfiqar ALİ, 421
Zülküf KAYA, 3961
Zvjezdana SANDIĆ, 3423

SOME INFORMATION ABOUT NEAR EAST UNIVERSITY

Near East University was established in 1988 and since then has grown to become one of the fastest growing universities in the world setting itself the strategic goal of joining the “top 500 universities in the world”.

From 1988 until now, the University has managed to expand its physical infrastructure and improve its quality of education and scientific research to meet international standards. Near East University is a member of the European University Association, the International Association of Universities and the Federation of the Universities of the Islamic World. The University has over 3,000 staff, of which 1,000 are academic personnel. 17,000 students from 53 different countries are attending 14 faculties and more than 60 departments at the university. It has luxury halls of different sizes which in total cover an area of 350,000m^2 and have the capacity to hold a total of 5,000 people. There are also 14 dormitories with a capacity of 5,000 students, but the construction of new dormitories is also planned.

Near East University has adopted life long education as its main mission. Thus, we begin with our Kindergarten, Junior College and Secondary High School which have a total number of 2,000 students. The faculties and departments offering undergraduate and graduate degrees are as follows:

FACULTIES

1. Faculty of Architecture
    - Architecture
    - Interior Design

2. Faculty of Arts and Sciences
    - English Language & Literature
    - Mathematics
    - Turkish Language & Literature
    - Psychology

3. Faculty of Economics & Administrative Sciences
    - Banking & Finance
    - Business Administration
    - Computer Information Systems
    - Economics
    - European Union Relations
    - Human Resources Management
    - International Business
    - International Relations
    - Marketing
    - Political Sciences
    - Information & Records Management

4. Faculty of Communication
    - Radio-Television-Cinema
    - Motion Picture Production
    - Journalism
    - Public Relations & Advertising

5. Atatürk Faculty of Education
    - English Language Teaching
    - Computer & Teaching Technologies
    - Pre-school Teaching
    - Elementary Teaching
    - Turkish Language Teaching
    - Guidance & Psychological Counseling
    - Human Resources
    - History Teaching

6. Faculty of Engineering
    - Civil Engineering
    - Computer Engineering
    - Electrical & Electronic Engineering
    - Mechanical Engineering
    - Biomedical Engineering

7. Faculty of Fine Art & Design
    - Graphic Design
    - Plastic Arts

8. Faculty of Maritime Studies
    - Department of Deck
    - Maritime Management
    - Marine Engineering

9. Faculty of Law
    - Law

10. Faculty of Performing Arts
    - Dramaturgy & Dramatic Authorship
    - Acting

11. Faculty of Pharmacy
    - Pharmacy

12. Faculty of Dentistry
    - Dentistry

13. Faculty of Health Sciences
    - Nutrition and Dietetics
    - Nursing

14. Faculty of Medicine

SCHOOLS

1.School of Physical Education & Sports
-Coaching Education
-Physical Education and Sports Teaching
-Sports Administration

2.School of Tourism & Hotel Management
-Tourism & Hotel Management

3. School of Maritime
-Deck
-Marine Engineering
-Maritime Management

INSTITUTES

-Institute of Education Sciences
-Institute of Sciences
-Institute of Social Sciences
-Institute of Health Sciences

With the opening of the NEU Grand Library in December 2005, the University has passed a new and critical mileage stone entering truly the information age. The Grand Library is fully computerized and linked to many major world libraries and research institutions throughout the world. The library has a collection of more than 600,000 printed materials and access to more than 110 million electronic articles. The library has recently been elected as the central library for the Turkic world and now serves universities of several different countries such as Azerbaijan, Kyrgyzstan and Turkmenistan. The library is open 24 hours a day serving not only the university but the whole community.

The University has until now organized 14 International Conferences & Congresses and many local and regional conferences, seminars and panel discussions on a variety of subjects. Near East University believes that the role of the University is not merely to provide formal education but to establish close relations with the wider community. As such, it places special emphasis on strengthening and developing campus-community relations. The University set up a Lifelong Education Centre (YABEM) which provides a wide variety of adult education courses. The University also makes the use of its facilities for cultural, sports and recreation activities available to the public.

As you can see, NEU is one of the fastest growing Universities of the world. The last two years has been devoted towards Health Sciences. This year, we began education in the Faculty of Dentistry, Faculty of Pharmacy and Faculty of Health Sciences. Another important improvement that has been made in our university regarding Health is that in September 2008, education has begun in the Faculty of Medicine. The Faculty of Medicine Research Hospital will be opened in July 2009. The Hospital will have a capacity of 500 beds with a 4,5000m^2 closed area. The faculty will be giving full service but a special emphasis will be given to researches on Oncology and Cardiology.

NEU does not have boundaries in development. Therefore, a protocol was signed with IBM International in June 2007 for the construction of the NEU Innovation Centre. The building having a closed area of 8,500m^2 was opened last year. It consists of 3 sections: NEU-IBM Innovation Centre, NEU-IBM Advanced Research Centre and the NEU Technopark. The ‘super computers’ used in the building have a capacity of 12 trillion processes per second. The research areas consist of Global Warming, Earthquake Stimulation, Defense Research (military), Space Research, High Physical Energy, Nanotechnology and Biotechnology research and product design, Medical, Pharmaceutical, Microbiological, Health Science and Social Sciences. NEU Innovation Centre is unique with its facilities in Eastern Europe, Middle East, Central Asia and Northern Africa.

BRIEF INFORMATION ABOUT TURKISH REPUBLIC OF NORTHERN CYPRUS

History: Cyprus has been occupied successively by Assyrians, Babylonians, Egyptians, Persians, Romans, Lusignans and Venetians who have sought the island's wealth of minerals and timber since the 8th century BC. The Ottoman Empire conquered the island in 1571 and ruled it until the island was leased to the British Empire in 1878. In 1963, the Republic of Cyprus was established by the Turkish Cypriot and Greek Cypriots, based on political equality. The Turkish Cypriots were forcefully ejected from the state mechanism in 1963. Intercommunal clashes which broke out in 1960 continued until 1974. A military coup by Greece in 1974 aiming to annex the island to Greece was aborted by the intervention of Turkey, which was one of the Guarantor Countries. Following the Exchange of Populations Agreement in 1975, Turkish Cypriots moved to the north and Greek Cypriots moved to the south of the island. Consequently, the Turkish Cypriots established their own administration and in 1983, the Turkish Republic of Northern Cyprus was proclaimed.

Negotiations between the two sides under the auspices of the UN started in 1968, with the aim of finding a comprehensive settlement in Cyprus. The latest negotiation process came to an end when the compromise plan, Annan Plan, prepared by the then UN Secretary General Kofi Annan, was overwhelmingly rejected by the Greek Cypriot people. During the referendum held on 24 April 2004, whilst 65% of the Turkish Cypriots voted "Yes", 75% of the Greek Cypriots voted against the plan; thus, eliminating the possibility of establishing a new partnership republic. Despite their obstructionist attitude, the Greek Cypriot administration unilaterally entered the European Union under the usurped title of the "Republic of Cyprus", on 1 May 2004. The then UN Secretary General Kofi Annan, expressed his regret and noted that *"he hoped ways would be found to ease the plight in which the (Turkish Cypriot) people find themselves through no fault of their own"* (24 April 2004). In his report to the Security Council, he called upon the international community to *"cooperate both bi-laterally and in international bodies to eliminate unnecessary restrictions and barriers that have been the effect of isolating the Turkish Cypriots and impeding their development"* (S/2004/437). The current UN Secretary General Ban Ki-moon also referred to the economic and social isolation of the Turkish Cypriot people in his report to the UN Peacekeeping Force in Cyprus (UNFICYP) in December 2007, pointing out that promoting the development of the Turkish Cypriot people would make the reunification of the island "occur in as seamless a manner as possible." Observing the injustice against the Turkish Cypriots, who have been experiencing all kinds of inhuman restrictions for years, the EU also expressed its will to enhance the economic development of Turkish Cypriots through an aid package. The EU Commission adopted a proposal, which had foreseen the transfer of 259 million Euros financial aid. However, the Turkish Cypriots have not been effectively benefiting from the EU aid due to Greek Cypriot administrations' pressures.

After the Presidential elections in February 2008 on the Greek Cypriot side, President Mehmet Ali Talat has reiterated once again his readiness for a new process of full-fledge negotiations and expressed his sincerity towards a solution.

Places to visit: In Lefkoşa (capital): Selimiye Mosque, Mevlevi Museum, Sultan Mahmut Library, Dervish Pasha Mansion and Lapidary Museum. In Gazimağusa: Antique Ruins of Salamis, Kantara Castle, Othello Castle, Lala Mustafa Paşa Mosque, Canbolat Museum, Ruins of Ayios Philion, St. Barnabas Icon Museum and Apostolos Andreas Monastry. In Girne: Kyrenia Castle, Bellapais Abbey, St. Hilarion Castle and Buffavento Castle, and in Güzelyurt: Soli Ruins, St. Mamas Monastry and Vouni Palace.

Nature: North Cyprus hosts over 1,600 plant species (22 are endemic), 350 species of birds (7 are endemic), and there are 26 different species of reptiles and amphibians. Every year, 250 different kinds of birds, around 100 million, migrating from Europe to Egypt pass through North Cyprus. The country also became home to some 50 different varieties of butterflies. Visitors are amazed to see that there are 30 different varieties of orchids on the island, 7 of them unique to North Cyprus. Rich underwater plant life and 200 different types of fish are making the blue Mediterranean waters attractive for sea lovers. 30% of the turtles in the Mediterranean, amongst them Carretta Caretta, Chelania Mydas (Green Turtle) and Dermachelys Corniacea, come to the coasts of North Cyprus for breeding.

Life-style, Culture: Turkish Cypriots are well-educated, social and hospitable people. North Cyprus is popular with its handicrafts, cuisine, traditional music and folk dancing. The Turkish Cypriot Cuisine is famous for its kebab dishes and starters called “mezes”. Daily fresh fish, meat, vegetables and fruit used in the Turkish Cypriot cuisine make the dishes both tasty and healthy. Local alcoholic drinks include rakı, brandy and red and white wine. Baklava, kadayıf and katmer are deserts favoured by most and Turkish Coffee is a must at the end of every dinner. The cultural and art facilities make the country attractive both for the tourists and foreign students. During the hot summer months, people prefer to relax by the sea whereas during the fall season, people go on picnics and long walks in the mountains and countryside. Indoor activities like exhibitions, cinemas, theatres and concerts are always available.

Electricity: 240 volts A/C. 50 Hz.

Traffic: Driving is on the left and international traffic and road signs are used. Maximum speed on highways is 100 km/hr. Vehicles entering North Cyprus must be insured upon arrival. Please refer to the Turkish Embassy or TRNC Representative Office in your country to check visa requirements.

Climate: North Cyprus enjoys a Mediterranean climate with long, dry summers and short wet winters. The average annual temperature is 19ºC. The weather in winter is very mild with temperatures ranging between 9ºC-12ºC. Average annual rainfall is 500mm.

Emergency telephone numbers: Fire 199, Police 155, First Aid 112


International Conference on
Environment: Survival and Sustainability
19-24 February 2007 Nicosia-Northern Cyprus
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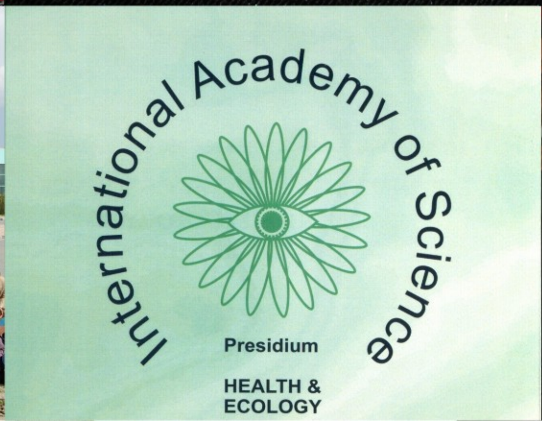
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