



**5<sup>th</sup> ICEEE-2014 International Conference**  
**„Global Environmental Change and Population Health:  
Progress and Challenges”**

**Programme**  
and  
**Abstracts**



**Óbuda University**  
**Rejtő Sándor Faculty of Light Industry and**  
**Environmental Protection Engineering,**  
**Institute of Environmental Protection Engineering**  
**International Council of Environmental Engineering**  
**Education (ICEEE)**

**November 19<sup>th</sup> - November 21<sup>st</sup> 2014**

**III. District, Doberdó u. 6**  
**Budapest, Hungary**





**5<sup>th</sup> ICEEE-2014 International Conference**  
**„Global Environmental Change and Population Health:**  
**Progress and Challenges”**

**November 19<sup>th</sup> - November 21<sup>st</sup> 2014**

**Óbuda University**  
**Rejtő Sándor Faculty of Light Industry and**  
**Environmental Protection Engineering,**  
**Institute of Environmental Protection Engineering**



**Budapest, Hungary**

## Impressum

### **Programme, Abstracts and Proceedings of the 5<sup>th</sup> ICEEE-2014 International Conference „Global Environmental Change and Population Health: Progress and Challenges” Conference**

The official language of the 5<sup>th</sup> International Conference of ICEEE-2014 is English.

The Programme and Abstracts of the Conference is provided to all registered participants in printed form.

The accepted papers were reviewed by the members of international scientific committee of the Conference.

All accepted and reviewed papers for 5<sup>th</sup> International Conference of ICEEE-2014 will be published in the **Fifth Edition** of the Conference Proceedings of ICEEE with ISBN **978-615-5460-26-5** in CD-ROM format.

The Publisher of the Programme and Abstracts as well as the Proceedings of the Conference is the ICEEE, Sándor Rejtő Faculty of Light Industry and Environmental Protection Engineering, Óbuda University, Budapest, Hungary.

Website:

- [www.iceee.hu](http://www.iceee.hu) and
- [www.rkk.uni-obuda.hu](http://www.rkk.uni-obuda.hu)



The Conference is organized in the framework of the Hungarian Scientific Season (Hungarian Scientific Festival).

General Secretary: Prof. Dr. Hosam Bayoumi Hamuda





**Dear Distinguished Guests, Colleagues, Dear Friends!**

It's my great pleasure to welcome all of you to the 5<sup>th</sup> International Conference of ICEEE-2014 under the title: **"Global Environmental Change and Population Health: Progress and Challenges"**.

The main approaches of the 5<sup>th</sup> ICEEE International Conference are the next:

- Provide a platform to exchange emerging ideas and investigate key issues such as air-, water-, soil-, nuclear pollution, waste recycling, wastewater, renewable energy technologies, public health issues, etc.
- Provide an excellent international forum for researchers and practitioners to continue research, characterize the global environmental changes and how they affect population and environmental ecosystems health.
- Ability to work towards sustainable solutions within a team either personally or online, to identify problems to find solutions or to develop arguments.
- Think critically about the most important environmental issue currently facing humankind.
- Try to solve the problems with creative and innovative strategies and being conscious of global social, cultural and environmental issues in relation to engineering and technology.
- Highlighting some of the main frameworks in this area and recommending directions for future research.

The conference covered a wide range of highlighting potential issues and paths towards a sustainable future such as:

- Global climate change and public health
- Air, water and soil pollution
- UV-B radiation and ozone depletion
- Agriculture and soil degradation, fertilizer, food production and nutrition
- Changes of biodiversity and depletion of natural resource
- Urbanization
- Energy and renewable energy sources
- Monitoring of the environmental state and environmental management: protection and conservation
- Biogeochemical cycles, waste management and environmental engineering
- Biotechnology and food industry, Environmental biotechnology, nanotechnology and bioengineering
- Social, economic and demographic dislocation through effects on economy, infrastructure and resource supply as well as tourism and global environmental changes
- Implications for future research and scientific policy

I wish you a fruitful cooperational work during the Conference and I hope you will find some free time besides your scientific busy schedule to experience the vitality of Budapest to make your visit truly memorable. Also, I would like to thank the work of the organization committees, and wish you all the best.

Thank you.

**Prof. Dr. habil István Patkó**  
**Dean**



After a great successful of the last four ICEEE International Conferences which brought together the world's professions and practitioners from different fields of environmental applied sciences and environmental engineering, the Óbuda University Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering Institute of Environmental Protection Engineering and the International Council of Environmental Engineering Education (ICEEE) have the great pleasure to invite you to participate in the programme of the 5<sup>th</sup> ICEEE-2014 International Conference deals with „Global Environmental Change and Population Health: Progress and Challenges” during November 19<sup>th</sup> - November 21<sup>st</sup> 2014 in Budapest, Hungary.

### ***Organization Committee***

**Patron:** Prof. Dr. János Fodor Rector, Óbuda University, Budapest, Hungary  
**General Chair:** Prof. Dr. István Patkó Dean, Faculty of Light Industry and Environmental Protection Engineering, ICEEE President  
**Secretary:** Prof. Dr. Hosam B. Hamuda General Secretary, ICEEE

### ***Members of the Organization Committee:***

Prof. Dr.h.c. Miroslav Badida	(Technical University of Košice, Slovakia)
Prof. Dr. Milan Pavlovič	(University of Novi Sad, Serbia)
Prof. Dr. habil Vasyl Lendyel	(Uzhgorod National University, Ukraine)
Prof. Dr. Abdalla A. Ahmed	(UNESCO-CWR, Sudan)
Prof. Dr. Diana Milčić	(University of Zagreb, Croatia)
Prof. Dr. Sęp Jaeosław	(Rzeszów University of Technology, Poland)
Prof. Dr. Nicolae Ungureanu	(Technical University of Cluj Napoca, Romania)
Prof. Dr. Sikolya László	(College of Nyíregyháza, Hungary)
Dr. Pavlina Paraskova	(Agricultural Academy, Food Research and Development Institute, Plovdiv, Bulgaria)

### ***International Scientific Committee***

Prof. Dr. Ferenc Ligetvári	(Debrecen University, Debrecen, Hungary)
Prof. Dr. György Heltai	(Szent István University, Gödöllő, Hungary)
Prof. Dr. Juraj Ladomersky	(Technical University in Zvolen, Zvolen, Slovakia)
Prof. Dr. György Füleky	(Szent István University, Gödöllő, Hungary)
Prof. Dr. Zoltán Juvancz	(Óbuda University, Budapest, Hungary)
Dr. habil Ágens Bálint	(Óbuda University, Budapest, Hungary)
Dr. Ruslan Mariychuk	(Presov University, Presov, Slovak Republic)
Dr. Marek Moravec	(Technical University of Košice, Košice, Slovakia)
Dr. Lýdia Sobotová	(Technical University of Košice, Košice, Slovakia)
Dr. László Dióssy	(Óbuda University, Budapest, Hungary)





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*The purpose of the 5<sup>th</sup> ICEEE-2014 International Conference deals with „Global Environmental Change and Population Health: Progress and Challenges” is to familiarize the participants with the current environmental problems of the Global Environmental Change and Population Health to search for possible ways of solution, to present an account of main directions of work and achievements of professional and young scientists from the World in this domain as well as the collaboration among scientists from various World universities and institutions will contribute to our professional development, uniting our efforts in developing joint scientific projects and contracts. We hope the conference will yield positive results for all participants.*

**Organization Committee**

## **Programme at Glance**

### **19. 11. 2014 (Wednesday)**

- **Registration** (14:00 p.m. – 17:00 p.m.) Entrance Hall
- **Opening Ceremony** (15:00 p.m. – 15:20 p.m.) Gara Auditorium
- **Plenary Session** (15:20 p.m. – 18:00 p.m.) Gara Auditorium
- **Welcome Dinner** (18:00 p.m. – 21:00 p.m.) Aula

### **20. 11. 2014 (Thursday)**

- **Registration** (08:00 a.m. – 13:00 p.m.) Entrance Hall
- **Oral Scientific Sessions** (09:00 a.m. – 13:20 p.m.) Gara Auditorium
- **Poster Scientific Sessions** (09:00 a.m. – 15:00 p.m.) Gara Auditorium
- **Lunch** (13:40 p.m. – 15:00 p.m.) Room No. 103
- **Continuing the Scientific Sessions** (15:00 p.m. – 17:00 p.m.) Gara Auditorium
- **ICEEE 2013 Year Activities** (17:15 p.m. – 17:45 p.m.) Gara Auditorium
- **Awards Celebration and Closing ceremony** (17:45 p.m. – 18:00 p.m.) Gara Auditorium
- **Conference Banquet** (19:00 p.m. – 22:30 p.m.) Trófea Grill Rest.

### **21. 11. 2014 (Friday)**

**Only for those who will take part at the social programme: Post Conference Tour**



- Start: From 08:30 a.m. to 16:00 p.m.
- Scientific Excursion
- Social Programme
- Closing ceremony (late afternoon) with good bye lunch



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## **Detailed Programme**

	<p style="text-align: center;"><i>5<sup>th</sup> ICEEE International Conference on „Global Environmental Change and Population Health: Progress and Challenges” 19 – 21 November 2014, Budapest, Hungary Óbuda University Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering</i></p>	
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**19. 11. 2014 (Wednesday)**

**Registration** (14:00 p.m. – 17:00 p.m.) **Entrance Hall**

**Opening Ceremony** (15:00 p.m. – 15:20 p.m.) **Gara Auditorium**

*István PATKÓ* (Dean, Óbuda University): **OPENING**

*János FODOR* (Rector, Óbuda University): **CONFERENCE WELCOME**

**Plenary Session** (15:20 p.m. – 17:10 p.m.) **Gara Auditorium**

*Chairman: István PATKÓ*

**15:20** *Milan PAVLOVIC<sup>1</sup>, Mirjana SEVALJEVIC<sup>1</sup>, Bogdana VUJIC<sup>1</sup>, Aleksandar TOMOVIC<sup>1</sup>, Aleksandar DJURIC<sup>1</sup>* (<sup>1</sup>Technical Faculty “Mihajlo Pupin”, University of Novi Sad, Zrenjanin, **Serbia**):

**DETERMINATION OF THE DISSOLUTION VELOCITY CONSTANT OF ATMOSPHERIC POLLUTANTS IN THE WATERSTREAM AND INFLUENCES TO THE VERTICAL VELOCITY OF THE MOLECULS OF WATER**

**15:50** *Syed P. S. SHABUDEEN<sup>1</sup>, Bader Zead ALFARHAN<sup>2</sup>* (<sup>1</sup>Kumaraguru college of Technology, Coimbatore, **India**, <sup>2</sup>Saudi Patent Office, King Abdul-Aziz City for Science and Technology, **Kingdom of Saudi Arabia**):



**CARBON SEQUESTRATION ENABLES TO TREAT WASTE WATERS BY CULTIVATING ALGAE A RESOURCE FOR VALUE ADDED BIO-PRODUCTS AND BIO FUELS IN ORDER TO MITIGATE GLOBAL WARMING**

**15:50 – 16:10** **Coffee break**

**16:10** *Attila VERECZKEY, Éva MARGITTAI* (Versys Clinics Human Reproduction Institute, Budapest, **Hungary**):

**PERICONCEPTIONAL MEDICINE: A KEY FACTOR TO OUR CHILD'S HEALTH?**



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**16:40** *Hosam E.A.F. BAYOUMI HAMUDA (Óbuda University, Rejtő Sándor Faculty of Light Industry and Environmental Engineering, Institute of Environmental Engineering, Budapest, Hungary):*

**IMPACT OF GLOBAL ENVIRONMENTAL CHANGE ON INFECTIOUS DISEASES**

**Welcome dinner (18:00 p.m. – 21:00 p.m.) Aula of Faculty**

**20. 11. 2014 (Thursday)**

**Registration (8:00 a.m. – 15:30 p.m.) Entrance Hall**

**Oral Presentation (9:00 a.m. – 17:00 p.m.) Gara Auditorium**

*Chairmen: György HELTAI - P. S. Syed SHABUDEEN*

**09:00** *István PATKÓ (Óbuda University, Rejtő Sándor Faculty of Light Industry and Environmental Engineering, Institute of Environmental Engineering, Budapest, Hungary):*

**PROBLEMS OF SUN COLLECTOR OPERATION**

**09:15** *Filippo CIUFFI (IntraVidére Research Institute, Rome – Potenza, Italy):*



**GROUNDWATER CIRCULATION MODEL FOR DISCOVERING ENVIRONMENTAL CONTAMINATION OF SPRINGS**

**09:30** *Léocadie ODOULAMI, Brice Saturnin DANSOU, Bachirou TIDJANI SALAMI (Laboratoire Pierre PAGNEY, Climat, Eau, Ecosystème et Développement, Département de Géographie et Aménagement du Territoire, Faculté des Lettres, Arts et Sciences Humaines, Université d'Abomey, Calavi, République du Bénin):*

**PRODUCTION AND STRATEGIES MANAGEMENT OF WASTE IN MALANVILLE CITY (BENIN, WEST AFRICA)**

**10:45** *Timur BYKOVSKIY (Department: General technical disciplines, Faculty of Engineering-pedagogical Institute, National Pedagogical M.P. Dragomanov University, Kiev, Ukraine):*

**PREPARING FUTURE TEACHERS OF ECOLOGY FOR NON-FORMAL EDUCATION IN UNIVERSITIES UKRAINE**

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**11:00 – 11:15      Coffee break**

*Chairmen: György FÜLEKY - Filippo CIUFFI*

**11:15      Lydia SOBOTOVA, Miroslav BADIDA, Robert JENCO** (*Technical University of Kosice, Kosice, Slovakia*):

**ENVIRONMENTALLY FRIENDLY LASER CLEANING OF MATERIALS**

**11:30      Mohammad Altaf HOSSAIN<sup>1</sup>, Mohammad Kabel Hossain DEWAN<sup>2</sup>** (*<sup>1</sup>Soil Resource Development Institute, Ministry of Agriculture. <sup>2</sup>Krishi Khamar Sarak, Farmgate, Dhaka, Bangladesh*):

**LAND ZONING: CONCEPT AND ITS URGENCY IN BANGLADESH**

**11:45      Farid BENSALAH<sup>1</sup>, A. LABTAR<sup>1</sup>, S. LAROUCI<sup>1</sup>, C. DELORME<sup>2</sup>, P. RENAULT<sup>2</sup>** (*<sup>1</sup>Laboratoire de Génétique Microbienne, Es-Senia université, Département de Biologie, Oran, Algeria, <sup>2</sup>Michalis Institute, Département Microbiologie et Chaîne Alimentaire, INRA-CRJ, Jouy-en-Josas, France*):

**IDENTIFICATION BY DNA METHODS OF STREPTOCOCCUS THERMOPHILUS ISOLATED FROM ARTISANAL FERMENTED PRODUCT**

**12:00      Zoltán JUVANCZ<sup>1</sup>, Erzsébet VARGA<sup>2</sup>, Edit SZEKELY<sup>3</sup>, Rita BODANE-KENDROVICS<sup>1</sup>, Tamás SOHAJDA<sup>2</sup>, György BANSAGHI<sup>3</sup>, Béla SIMANDI<sup>3</sup>** (*<sup>1</sup>Obuda University Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering, Environmental Protection Engineering Institute, Budapest, Hungary, <sup>2</sup>CycloLab R&D. Ltd., Budapest, Hungary, <sup>3</sup>Budapest University of Technology and Economics, Department of Chemical and Environmental Process Engineering, Budapest, Hungary*):

**DEVELOPMENT OF A CHIRAL SELECTIVE ELECTROPHORETIC METHOD FOR ANALYSIS OF POPE-PEACHI DIASTEREOMERIC SALT RESOLUTION PRODUCTS**

**12:15 – 12:30      Coffee break**

*Chairmen: Milan PAVLOVIČ - Hosam B. HAMUDA*

**12:30      Ferenc LIGETVÁRI<sup>1</sup>, Ferenc ZSABOKORSZKY<sup>2</sup>** (*<sup>1</sup>Debrecen University, Debrecen, Hungary, <sup>2</sup>Research and Development, ENQUA Kft, Budapest, Hungary*):

**SOME ASPECTS OF WASTEWATER TREATMENT AND SLUDGE UTILIZATION IN HUNGARY**



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**12:45** *Ruslan MARIYCHUK, Viktoria BIRKNEROVA (Department of Ecology, Faculty of Humanities and Natural Sciences, University of Prešov in Prešov, Prešov, Slovakia):*

**THE KINETICS STUDY OF THE SILVER NANOPARTICLES GREEN SYNTHESIS**

**13:00** *Ágnes BÁLINT<sup>1</sup>, Zs. LENGYEL<sup>2</sup>, M. CZIKKELY<sup>2</sup>, B. TÖRŐ<sup>2</sup>, Albert SZANISZLÓ<sup>1</sup> (<sup>1</sup>Óbuda University, Institute of Environmental Engineering, Budapest, Hungary, <sup>2</sup>Szent István University, Department of Chemistry and Biochemistry, Gödöllő, Hungary):*

**MONITORING OF DIFFERENT HEAVY METALS IN SOIL SAMPLES DERIVED FROM VALLEY SAJÓ AND NEAR LAKE “VERESMART**

**13:15** *Victor Grigorievich BARYAKHTAR, Yaroslav Timurovich BYKOVSKIY (Physics-Mathematics, Faculty of Physics-Mathematics, National Pedagogical M.P. Dragomanov University, Kiev, Ukraine):*

**ATOMIC PROJECT: HISTORY AND MODERNITY**

**13:30** *Ahmed M. MUFTAH (Department of Earth Sciences, Faculty of Science, University of Benghazi, Benghazi, Libya):*

**PANORAMIC ENVIRONMENTAL HABITATS OF (PLIOCENE – RECENT) AS-SAHABI AREA, NORTHERN LIBYA**

**13:45 – 15:00**      **Lunch**

*Chairmen: Ruslan MARIYCHUK - Bhoop Singh PANWAR*

**15:00** *Jana CHOVANCOVÁ, Danica FAZEKAŠOVÁ, Juraj FAZEKAŠ (Department of Environmental Management, Faculty of Management, University of Prešov in Prešov, Prešov, Slovakia):*

**GREEN PURCHASING AS A TOOL OF IMPROVING ENVIRONMENTAL PERFORMANCE – CASE STUDY OF IMPLEMENTATION IN BUSINESS COMPANY**

**15:15** *Abdulla A. NOMAN<sup>1</sup>, Jawid AL-JAILANI<sup>2</sup> (<sup>1</sup>Faculty of Engineering, Sana’a University, Sana’a, Yemen, <sup>2</sup>Social Fund for Development, Sana’a, Yemen):*

**INVESTIGATION OF THE POTENTIAL OF FOGWATER HARVESTING IN THE WESTERN MOUNTAINOUS PARTS OF YEMEN**





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**15:30** *Tamás FRÁTER<sup>1</sup>, Tatjana JUZSAKOVA<sup>2</sup>, János LAUER<sup>3</sup>, László DIÓSSY<sup>1</sup>, Ákos RÉDEY<sup>1</sup> (1Chianti 3D Kft., Veszprém, Hungary, 2University of Pannonia, Veszprém, Hungary, 3Fire-Moon Kft., Pápa, Hungary):*

**UNMANNED AERIAL VEHICLES IN ENVIRONMENTAL MONITORING – AN EFFICIENT WAY FOR REMOTE SENSING**

**15:45** *M.S. GREWAL<sup>1</sup>, Mohammad Amin BHAT<sup>1</sup>, V.S. ARYA<sup>2</sup> (1CCS Haryana Agricultural University, Hisar, India, 2Haryana Space Application Centre, CCS HAU, Hisar, India):*

**GEOINFORMATICS FOR DELINEATION AND ESTIMATION OF SALT AFFECTED SOILS**

**16:00 – 16:15** **Coffee break**

*Chairmen: Lydia SOBOTOVA - László DIÓSSY*

**16:15** *Hosam E.A.F. BAYOUMI HAMUDA (Óbuda University, Rejtő Sándor Faculty of Light Industry and Environmental Engineering, Institute of Environmental Engineering, Budapest, Hungary):*

**ECOLOGICAL AND BACTERIOLOGICAL MONITORING OF DANUBE WATER QUALITY IN BUDAPEST REGION**

**16:30** *Mohamed S. E. AL FAITOURI, Osama A. ELFALLAH (University of Benghazi, Faculty of Science, Department of Earth Sciences, Benghazi, Libya):*

**GEOCHEMICAL SIGNALS FOR GLOBAL ATMOSPHERIC WARMING; NUBIAN AQUIFER, AL KUFRA BASIN, SE LIBYA**

**16:45** *Dániel KISS, Dániel STOJCSICS (Óbuda University, John von Neumann Faculty of Informatics, Budapest, Hungary):*



**EIGENVECTOR BASED SEGMENTATION METHODS OF HIGH RESOLUTION AERIAL IMAGES FOR PRECISION AGRICULTURE**

**17:00 – 17:15** **Coffee break**

*Chairmen: István PATKÓ*

**17:15 – 17:45** **ICEEE Activities in 2013-14** **Gara Auditorium**

**17:45 p.m.** **Awards Celebration and Closing Ceremony** **Gara Auditorium**

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19:00 – 22:30 p.m.

Conference Banquet

Trófea Grill Restaurant

Poster's session

(09:00 – 18:00)

Aula

**Abdousalam ALGAIDI<sup>1</sup>, Hosam E.A.F. BAYOUMI HAMUDA<sup>2</sup>, Abdussalam Ashour KHALIF<sup>3</sup>, Hamed A. ABDORHIM<sup>4</sup>** (*<sup>1</sup>Sebha University, Sebha, Libya, <sup>2</sup>Obuda University, Budapest, Hungary, <sup>3</sup>Tripoli University, Tripoli, Libya, <sup>4</sup>Alzetona University, Tripoli Libya*):

**IMPACT OF LEAD AND CADMIUM ON SOIL RESPIRATION AND BACTERIAL CONTENT UNDER GREENHOUSE CONDITIONS**

**Abdussalam Ashour KHALIF, Ghazala OTHMAN, Ali ALAMMARI** (*Szent István University, Doctoral School of Management and Business Administration, Gödöllő, Hungary*):

**IMPACTS OF GLOBAL WARMING AND CLIMATE CHANGE ON THE ENVIRONMENT: A CASE STUDY IN IRELAND**

**Abraham Sombé Sylvain ILY<sup>1</sup>, Mahamadou SAWADOGO<sup>2</sup>, Amos MININGOU<sup>1</sup>** (*<sup>1</sup>University of Ouagadougou, Institute of Environment and Agriculture Research (INERA), <sup>2</sup>Laboratory of Genetics and Biotechnology, University of Ouagadougou, Ouagadougou, Burkina Faso*):

**ENGAGEMENT OF YOUTH IN AGRICULTURE IN BURKINA FASO: TOWARDS SUSTAINABLE DEVELOPMENT**

**Adrienn HANCZVIKKEL<sup>1</sup>, Brigitta BERTA<sup>2</sup>, Tamás TIRCZKA<sup>2</sup> Hosam E.A.F. BAYOUMI HAMUDA<sup>1</sup>, Ákos TÓTH<sup>2</sup>** (*<sup>1</sup>Óbuda University, Budapest, Hungary, <sup>2</sup>National Center for Epidemiology, Budapest, Hungary*):

**SURVIVAL OF HIGH RISK, MULTIRESTANT BACTERIAL STRAINS IN ABIOTIC ENVIRONMENT**

**Alaelddin A. ELFOUGHI<sup>1</sup>, Hosam E.A.F. BAYOUMI HAMUDA<sup>2</sup>, Laila M.H. ABUSRIWIL<sup>1</sup>, Gy. FÜLEKY<sup>3</sup>** (*<sup>1</sup>Environmental Sciences Ph.D. School, Szent István University, Gödöllő, Hungary, <sup>2</sup>Environmental Protection Engineering Institute, Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering, Óbuda University, Budapest, Hungary, <sup>3</sup>Soil Science and Agrochemistry Department, Szent István University, Gödöllő, Hungary*):

**CU AND ZN IMPACTS THE BIOLOGICAL ACTIVITY AND PLANT GROWTH IN SOIL AMENDED WITH COMPOST**



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*Ali ALAMMARI, Abdussalam Ashour KHALIF, Ghazala OTHMAN (Szent István University, Doctoral School of Management and Business Studies, Gödöllő, Hungary):*

**ARAB FOOD SECURITY CHALLENGES AND OPPORTUNITIES**

*Albert SZANISZLÓ<sup>1</sup>, Gy. KAMPFL<sup>2</sup>, Á. BÁLINT<sup>1</sup> (1Óbuda University, Institute of Environmental Engineering, Budapest, Hungary, 2Szent István University, Department of Chemistry and Biochemistry, Gödöllő, Hungary):*

**INVESTIGATION OF GAS EMISSION IN FOOD CHAIN REACTOR SYSTEM**

*Amel GUERMOUCHE, Chahra ZERROUKI, Saliha LAROUCI, Farid BENSALAH (Laboratoire Génétique Microbienne, Faculté des Sciences de la Nature et de la Vie, Université Oran, Oran, Algérie):*

**ISOLATION OF INDIGENOUS STREPTOMYCES SPP. FROM ARID AREA AND EVALUATION OF THEIR ANTIFUNGAL ACTIVITY**

*Andrea LAMI, Cecília TAMÁS-NYITRAI (Óbuda University, Rejtő Sándor Faculty of Light Industry and Environmental Engineering, Institute of Environmental Engineering Budapest, Hungary):*

**SAVING SOIL AND WATER USING DIFFERENT REMEDIATION TECHNIQS AT THE LEADER'S TERRITORY OF RAILWAY STATION**

*Andrea PAUKÓ (Óbuda University, Rejtő Sándor Faculty of Light Industry and Environmental Engineering, Institute of Environmental Engineering Budapest, Hungary):*

**COMPARATIVE ANALYSIS OF TIMBER QUALITY OF SPRUCE AND PINE PLANTATION**

*Beata HRICOVÁ, Ervin LUMNITZER, Miriama PIŇOSOVÁ, Henrieta NAKATOVÁ (Technical University of Košice, Faculty of Mechanical Engineering, Department of Environmentalistics, Slovakia):*

**ECODESIGN AS A PART OF PRODUCTION**

*Bogdana VUJIC<sup>1</sup>, Francisc POPESCUE<sup>2</sup>, Milan PAVLOVIC<sup>1</sup>, Aleksandar DJURIC<sup>1</sup>, Aleksandar TOMOVIC<sup>1</sup> (1Technical Faculty “Mihajlo Pupin”, University of Novi Sad, Zrenjanin, Serbia, 2Politehnica Timisoara, Timisoara, Romania):*

**CROSS-BORDER WATER STREAMS QUALITY IN THE BANAT REGION**

*Bhoop Singh PANWAR<sup>1</sup>, S. MOGHADASY<sup>2</sup>, M.S. GREWAL<sup>1</sup>, P. RAGULYI<sup>2</sup>, M. REKASI<sup>2</sup>, M. LÁSZLÓ<sup>3</sup>, K.R. VEG<sup>3</sup>, E. LEHOCZKY<sup>3</sup> (1Department of Soil Science, CCS Haryana Agricultural University, Hisar, India, 2Department of Soil Science, Ferdowsi*





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University, Moshhad, **Iran**, <sup>3</sup>Institute of Soil Science and Agricultural Chemistry,  
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**PHYTOREMEDIATION: BOOSTED CADMIUM UPTAKE BY ORGANIC,  
CHEMICAL CHELATES AND MICROBIAL INOCULANTS IN MAIZE (ZEA MAYS)**

**Danica FAZEKAŠOVÁ<sup>1</sup>, Juraj FAZEKAŠ<sup>1</sup>, Jana CHOVANCOVÁ<sup>1</sup>, Eva MICHAELI<sup>2</sup>,  
Vladimír SOLÁR<sup>2</sup>** (<sup>1</sup>Department of Environmental Management, Faculty of  
Management, <sup>2</sup>Department of Geography and Applied Geoinformatics, Faculty of  
Humanities and Natural Sciences, University of Prešov in Prešov, Prešov,  
**Slovakia**):

**DEVELOPMENT OF BASIC PHYSICAL PARAMETERS OF SOILS IN COLD  
MOUNTAIN CLIMATE CONDITIONS**

**Emese VÁGÓ, Cecília TAMÁS-NYITRAI** (Óbuda University, Rejtő Sándor Faculty of Light  
Industry and Environmental Engineering, Institute of Environmental  
Engineering Budapest, **Hungary**):

**HOW GRANULAR ACTIVATED CARBON ADSORPTION HELPS REMOVAL  
OF ORGANIC SUBSTANCES, FLAVOUR AND ODOUR AGENTS IN DRINKING  
WATER**

**Eva MICHAELI<sup>1</sup>, Martin BOLTÍŽIAR<sup>2</sup>, Vladimír SOLÁR<sup>1</sup>, Monika Ivanová<sup>1</sup>, Danica  
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University of Prešov, Prešov, **Slovak Republic**):



**THE NATURE OF THE SELECTED ENVIRONMENTAL BURDENS IN THE  
SLOVAK REPUBLIC**

**Farid BENSALAH, Billal BELABED, Saliha LAROUCI, Amel GUERMOUCHE** (Laboratoire  
Génétique Microbienne, Faculté des Sciences de la Nature et de la Vie, Université  
Oran, **Algérie**):

**SCREENING OF AUTOCHTHONOUS STREPTOMYCES SPP. ISOLATED FROM  
WESTERN ALGERIA AND DETERMINATION OF THEIR ANTIMICROBIAL  
ACTIVITY**

**Ghazala OTHMAN, Abdussalam Ashour KHALIF, Ali ALAMMARI** (Szent István  
University, Doctoral School of Management and Business Administration,  
Gödöllő, **Hungary**):

**ROLE OF WOMEN AND MEN IN RURAL COMMUNITY DEVELOPMENT IN  
NORTH AFRICA IN RELATION WITH GLOBAL CHANGES**

	<p style="text-align: center;"><i>5<sup>th</sup> ICEEE International Conference on „Global Environmental Change and Population Health: Progress and Challenges” 19 – 21 November 2014, Budapest, Hungary Óbuda University Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering</i></p>	
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**EFFECT OF PLANTED FORESTS ON CARBON CYCLE AND GROUNDWATER LEVEL IN JÁSZSÁG, HUNGARY**

**Hamed A. ABDORHIM<sup>1</sup>, Hosam E.A.F. BAYOUMI HAMUDA<sup>2</sup>, Abdousalam ALGAIDI<sup>3</sup>** (*<sup>1</sup>Azzaytuna University, Tripoli, Libya, <sup>2</sup>Óbuda University, Rejtő Sándor Faculty of Light Industry and Environmental Engineering, Institute of Environmental Engineering Budapest, Hungary, <sup>3</sup>Sebha University, Faculty of agriculture, General Trend Department, Sebha, Libya*):

**INVESTIGATION OF SOME EXTRACELLULAR ENZYMIC ACTIVITIES IN THE RHIZOSPHERE OF SPRING WHEAT CULTIVATED IN SOIL MIXED WITH BIOSOLID**

**Hosam E.A.F. BAYOUMI HAMUDA<sup>1</sup>, Ibrahim ISSA<sup>2</sup>** (*<sup>1</sup>Óbuda University, Rejtő Sándor Faculty of Light Industry and Environmental Engineering, Institute of Environmental Engineering, Budapest, Hungary, <sup>2</sup>Soil and Water Department, Agriculture Faculty, Sirte University, Sirte, Libya*):

**BIOAVAILABILITY OF CADMIUM AND LEAD IN SOIL AMENDED WITH SEWAGE SLUDGE**

**Jozef FEJER** (*Department of Ecology, Faculty of Humanities and Natural Sciences, University of Presov in Presov, Presov, Slovakia*):



**ACUMULATION OF ZINC BY AMARANTHUS CRUENTUS PLANTS**

**Juraj FAZEKAŠ<sup>1</sup>, Jana CHOVANCOVÁ<sup>1</sup>, Miroslav KARAHUTA<sup>2</sup>, Danica FAZEKAŠOVÁ<sup>1</sup>** (*<sup>1</sup>Department of Environmental Management, <sup>2</sup>Department of Mathematical Methods and Managerial Informatics, Faculty of Management, of University of Prešov in Prešov, Prešov, Slovakia*):

**ECOLOGICAL AND ENVIRONMENTAL LITERACY OF THE YOUNG GENERATION IN THE PROCESS OF EDUCATION FOR SUSTAINABLE DEVELOPMENT**

**Krisztina DEMÉNY<sup>1</sup>, Csaba CENTERI<sup>2</sup>** (*<sup>1</sup>Óbuda University, Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering, Budapest, Hungary, <sup>2</sup>Szent István University, Faculty of Agricultural and Environmental Sciences, Department of Natural Conservation and Landscape Ecology, Gödöllő, Hungary*):

**NATURALNESS OF FOREST IN THE GÖDÖLLŐ HILLSIDE, HUNGARY**

	<p style="text-align: center;"><b>5<sup>th</sup> ICEEE International Conference on „Global Environmental Change and Population Health: Progress and Challenges” 19 – 21 November 2014, Budapest, Hungary Óbuda University Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering</b></p>	
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**DELIMITATION OF VEGETATION PATCHES FOR ENVIRONMENTAL MONITORING: A QUANTITATIVE METHOD**

**Laila M.H. ABUSRIWIL<sup>1</sup>, Hosam E.A.F. BAYOUMI HAMUDA<sup>2</sup>, Alaelddin A. ELFOUGH<sup>1</sup>, Ágnes BÁLINT<sup>2</sup>** (*<sup>1</sup>Environmental Sciences Ph.D. School, Szent István University, Gödöllő, Hungary, <sup>2</sup>Environmental Protection Engineering Institute, Óbuda University, Budapest, Hungary*):

**GROWTH OF ALFALA IN HEAVY METAL CONTAMINATED CLAY LOAM BROWN FOREST SOIL**

**Lóránt SZABÓ, István PATKÓ** (*Óbuda University, Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering, Institute of Environmental Protection Engineering, Budapest, Hungary*):

**EXAMINATION OF AIR-SOURCE HEAT PUMP AND POSSIBILITY OF ITS SEPARATION FROM NATIONAL ELECTRICITY NETWORK**

**Lucia BEDNÁROVÁ, Natália JERGOVÁ** (*Department of Commercial Business, University of Economics in Bratislava, Faculty of Business Economy with seat in Košice, Tajovského 13, 041 30 Košice, Slovakia*):

**CURRENT WASTE MANAGEMENT IN THE SLOVAK REPUBLIC**

**Maamar LAIDI** (*Department of Physics, Faculty of Science, Blida 1 university, Blida, Algeria*):

**ENVIRONMENTAL LIFE CYCLE ASSESSMENTS FOR WATER TREATMENT PROCESSES AN ALGERIAN CASE STUDY OF AN URBAN WATER CYCLE**

**Marek MORAVEC, Pavol LIPTAI, Miroslav BADIDA** (*Technical university of Kosice, Faculty of mechanical engineering, Košice, Slovakia*):

**ANALYSIS OF MATERIAL POTENTIAL F END-OF-LIFE PHOTOVOLTAIC PANELS IN SLOVAK REPUBLIC**

**Marian HURAJT, Miroslav BADIDA, Tomas JEZNY, Radoslav RUSNAK** (*Department of Process and Environmentalistics Engineering, Kosice, Slovakia*):

**THE IMPACT OF ACID MINE WATER ON THE BIO AVAILABILITY OF HEAVY METALS IN THE ABANDONED MINING DEPOSITS IN THE TOWN SMOLNIK**





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**RISK ASSESSMENT IN THE ENVIRONMENT**

**N. MOULAI-MOSTEFA<sup>1</sup>, R. KHALLADI<sup>1</sup>, F. BENTAHAR<sup>2</sup>** *(<sup>1</sup>LME, Faculty of Sciences and Technology, University of Medea, Ain d'Heb, Medea, Algeria, <sup>2</sup>LPT, Faculty of Mechanical and Process Engineering, USTHB, Bab ezzouar, Algiers, Algeria):*

**REMEDIATION OF PAH CONTAMINATED SOILS BY SURFACTANTS**

**Ruslan MARIYCHUK<sup>1</sup>, Maksym FIZER<sup>1,2</sup>, Mikhailo SLIVKA<sup>2</sup>, Sergij SUKHAREV<sup>2</sup>, Vasil LENDEL<sup>2</sup>** *(<sup>1</sup>Department of Ecology, Faculty of Humanities and Natural Sciences, University of Prešov in Prešov, Prešov, Slovakia, <sup>2</sup>Faculty of Chemistry, Uzhhorod National University, Uzhhorod, Ukraine):*

**SYNTHESIS OF 5-AMINO-4-BENZOYL-1,2,4-TRIAZOLE-3-THIONES AS LIGANDS FOR THE DETERMINATION OF HEAVY METALS IN ENVIRONMENT**

**Ruzena Králiková** *(DPaEE, Faculty of Mechanical Engineering, Technical University of Kosice, Slovakia):*

**THERMAL COMFORT IN THE WORKING ENVIRONMENT - ASSESSMENT THROUGH OBJECTIVE AND SUBJECTIVE APPROACHES**

**Saliha LAROUCI, Amel GUERMOUCHE, Farid BENSALAH** *(Laboratoire de Génétique Microbienne, Dpt. de Biologie, Université Es-Sénia Oran, Algérie):*



**PCR IDENTIFICATION OF LACTOBACILLI STRAINS FOR POTENTIAL PROBIOTIC IN POULTRY**

**Tomas JEZNY, Miroslav BADIDA, Radoslav RUSNAK, Marian HURAJT** *(Department of process and environmentalistics engineering, Kosice, Slovakia):*

**VALIDATION OF METHODS FOR FAAS DETERMINATION OF CU, PB, ZN, CD EXTRACTANT WITH HNO<sub>3</sub> AND EDTA EXTRACTS ULTRASONIC EXTRACTION**

**Zoltán JUVANCZ, Dóra Jecsak MAKLÁRI** *(Óbuda University Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering, Environmental Protection Engineering Institute, Budapest, Hungary):*

**INVESTIGATION OF CHIRAL SELECTIVITY OF VARIOUS DERIVATIVES OF ENVIRONMENTALLY IMPORTANT MANDELLIC ACID**

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**Zoltán JUVANCZ, Zita LACZKÓ, András SZEDER** (*Óbuda University Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering, Environmental Protection Engineering Institute, Budapest, Hungary*):

**CHIRAL SEPARATION OF ENVIRONMENTALLY IMPORTANT PYRETHROID ACIDS**

**Yurij DMYTRUK, Ol'ga STUZUK, Vasyl' CHERLINKA** (*Chernivtsy national university, Chernivtsy, Ukraine*):

**CERTAIN METHODOLOGICAL APPROACHES TO THE ASSESSMENT OF CONTAMINATION OF AGRICULTURAL LANDSCAPES' SOIL**



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## IMPACT OF LEAD AND CADMIUM ON SOIL RESPIRATION AND BACTERIAL CONTENT UNDER GREENHOUSE CONDITIONS

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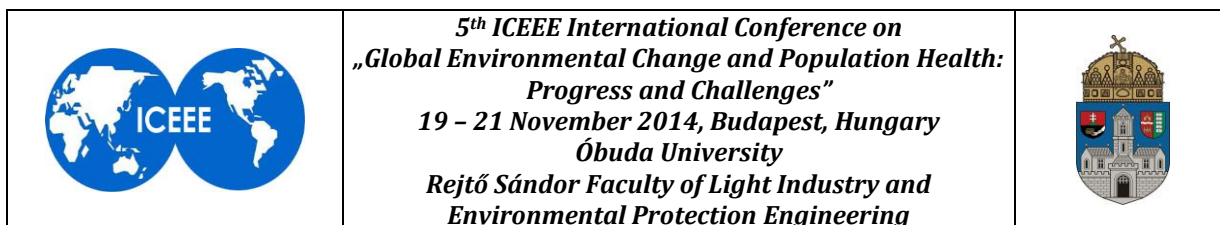
### ABSTRACT

The effect of lead and cadmium ions on the activity of aerobic soil heterotrophic bacteria was studied in cultivated variants of brown forest soil originating from Gödöllő, Hungary under greenhouse conditions. Soil samples were incubated in glass vessels in the greenhouse at 28°C for one, three or six weeks. The metabolism of soil-borne aerobic heterotrophic bacteria was activated by adding C, N and P in the form of glucose, sodium nitrate and potassium phosphate, respectively, prior to the determination of substrate-induced respiration (SIR). Measurements were made on changes in the total mobilizable heavy metal fraction, the total aerobic heterotrophic bacterial count and the quantity of CO<sub>2</sub> produced during the incubation period under the stress of different concentrations of lead and cadmium as soil contaminants. The heavy metal compounds examined became immobilized largely within a week, but after further incubation, they gradually became re-mobilized. The addition of lead and cadmium ions reduced the total aerobic heterotrophic bacterial count and the physiological activity of the bacteria in the soil. In general, the aerobic heterotrophic bacterial populations declined to a similar extent as the CO<sub>2</sub> production in response to the toxic effect of the tested metal ions. The inhibition in the biological activity of the soil samples could already be observed after a period of three weeks, but this effect only became substantial at the end of the 6 week incubation period. Lead had lower effects on decreasing CO<sub>2</sub>-production at different incubation intervals. The strongest inhibition of the gas production was detected by the influence of cadmium ions.

**Keywords:** *cadmium, CO<sub>2</sub>-production, lead, soil bacterial activities, soil respiration.*

### INTRODUCTION

The fertility of natural soil ecosystem depends significantly on the rate of turnover of soil organic matter, mediated by the soil microbial biomass. In agricultural ecosystems, soil fertility can be increased by applications of inorganic or organic fertilizer. The fertility of natural ecosystem, however, depends almost entirely on natural microbial processes, including N<sub>2</sub>-fixation, the mineralization of organic matter of N, C, P and S, and organic matter transformations, all mediated by the soil microbial biomass. Soil microbial biomass is considered to be the agent of breakdown of organic matter in the soil, although the importance of its size in relation to nutrient cycling and decomposition processes is poorly understood. The gradual increase in atmospheric CO<sub>2</sub> concentration and potential climatic changes are likely to affect plant, soil and ecosystem processes, including carbon flux from plants to soil and from soil to atmosphere (Pajari, 1995). In a typical forest ecosystem, the components of soil CO<sub>2</sub> efflux include (1) respiration due to litter decomposition, (2) root respiration, (3) rhizo-microbial



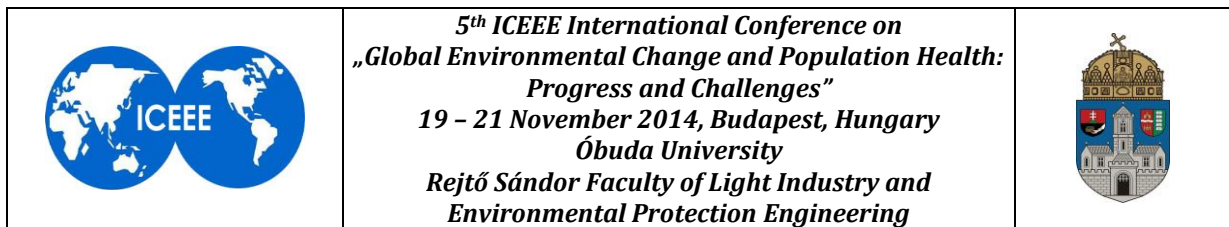
respiration (i.e. microbial respiration utilizing C directly derived from living roots), and (4) microbial respiration utilizing native soil organic matter (Cheng, 1999).

Bayoumi Hamuda and Kecskés (2003) mentioned that the biological activity in a soil is usually evaluated by measuring CO<sub>2</sub> evolution. The results obtained from different studies on the influences of heavy metals on CO<sub>2</sub> evolution in contaminated soils by the addition of sewage sludge have been at variance. It was established that the addition of sewage sludge containing high amount of Cd, Pb to the soil increase the CO<sub>2</sub> evolution. Soil respiration and microbial biomass can be useful indicators of soil contamination, combining the two measurements to give amounts of CO<sub>2</sub> evaluated per unit of biomass (µg CO<sub>2</sub>-C/g soil). Soil microorganisms, the living component of soil organic matter, are responsible for mineralization of nutrients, decomposition, and degradation or transformation of toxic compounds. Being a labile fraction of soil organic matter, the microbial biomass can be a useful early indicator of change and future trends and can reflect organic matter changes and soil development. The microbial biomass in soils comprises a substantial pool of nutrients, which depending on the stage of growth, can be a source or sink of plant nutrients. Close relationship between microbial biomass and soil fertility indices has been noted. Mineralizable N has been related to microbial C and N in a wide range of soils. It has been shown that a considerable proportion of the enhanced level of N and P in soils after drying is derived from the microbial cells killed by desiccation. Microorganisms play a unique role in the soil ecosystem, because of their contributions to soil fertility. Contrasting trends, reported on toxic effects of heavy metals including Cd, Pb on soil microorganisms and their activities, are attributable to short-term studies often limited to a single soil type and conducted under controlled laboratory conditions. The bioavailability of Cd, Pb and associated toxicity to soil biota vary with time, soil type, speciation, ageing, Cd, Pb sources, organisms, and the environmental factors. The available fraction or soil solution Cd, Pb and not the total concentration of Cd, Pb seem to correlate well with the toxicity parameters (Vig et al., 2003). There appear to be no comparable reports in which the effects of heavy metals, singly or in combination, on soil microorganisms *in vivo* have been compared. Similarly, there is little information on the suppression of growth or tolerance developed by individual microorganisms *in vivo* with respect to combinations of metals. However, there are some positive and negative interactions between metals upon their toxic effects on microorganisms *in vitro*. The natural content of heavy metals in soils is known as the biogeochemical background. The occurrence of heavy metals in soils is closely dependent on the chemical composition of parent rock (Siebielec et al., 2012).

Some heavy metals play an extremely important role in biochemical reactions which are significant for the growth and development of microorganisms, plants and animals (Kavamura, Esposito, 2010). Heavy metals when present in amounts equal to the geochemical background do not interfere with the soil metabolism, which is associated with the growth and development of soil microorganisms as well as the processes of synthesis and re-synthesis, governed by intra- and extracellular enzymes. In the said concentrations, heavy metals do not cause undesirable changes in the development of plants. On the contrary, such elements as copper and zinc are essential constituents of physiological processes in all living organisms, including microorganisms and plants. Some soils suffer from zinc and copper deficits, which is why they are enriched with fertilizers containing copper or zinc to satisfy the nutritional requirements of crops. Cadmium is different in that its essential role in the proper functioning of living organisms has not been proven yet (Jadwiga et al., 2013).

A variety of methods exists to estimate the size of the microbial biomass in soil. Of these methods, the most simple and rapid is substrate (glucose) induced respiration (SIR), which stimulates a maximal respiratory response from the soil biomass, measured conductimetrically as CO<sub>2</sub> evolution, and methods currently available are those involving direct counting in which





microorganisms can be variously stained, and relates this respiration to biomass C (Anderson and Domsch, 2000).

Metals are introduced into the environment during mining and refining of ores and from other sources, such as the combustion of fossil fuels, industrial processes, spraying of pesticides, and disposal of industrial and domestic wastes etc. One particular uncertainty is whether the toxic effects of combinations of metals are synergistic, additive, or antagonistic. There have been numerous reviews on the effect of metals on microorganisms (e.g., Trevors et al., 1996) that have dealt mainly with in vitro studies of the biochemical and physiological mechanisms whereby metals exert their effects on microorganisms. Collins and Stotzky (2001) stated that microorganisms interact with metals in various ways: many metals are essential to microorganisms, because they are electron acceptors or cofactors in enzymes, whereas other metals are toxic.

Leita et al. (1995) studied influence of Pb, Cd, and Tl on microbial biomass survival and activity during a laboratory incubation of soil. In comparison to uncontaminated soil, the microbial biomass C decreased sharply in soil contaminated with Cd and Tl, whereas the addition of Pb did not have any significant inhibitory effect on the level of microbial biomass C. Heavy metals influenced microorganisms by affecting their growth, morphology, and biochemical activities. The supply of mineralized C, N and P from soil organic matter, the decomposition of plant and animal residues and the maintenance of soil structure are all dependent upon the correct functioning of the soil microbial ecosystem (De Haan et al., 1999). Therefore, it is important to determine and predict the adverse effects of heavy metals and other pollutants on soil microorganisms (Baath, 2002).

The short-term effects of Pb in sand were distinct. In sandy loam, the inhibitory effect was not significant, but after 43 weeks, it had increased significantly. In silty loam and clay, no significant inhibitory effects were found. In general, the heavy metals were found to be more toxic during the first eight weeks than after an extended period. It was decreased in this study that toxicity of heavy metals in soil decreases with time. Clay (Dutch clay soils mainly contain illite) as abiotic factor was found to be the dominant factor in decreasing the toxicity of Pb and to a lesser extent of Cd.

The objectives of present investigation were:

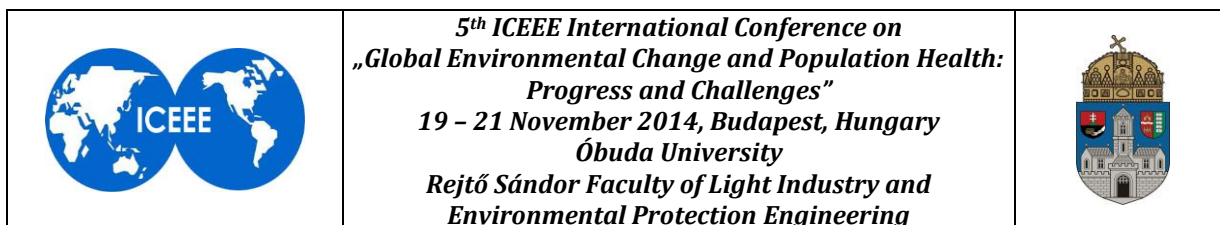
- 1) To study the availability of investigated metals under greenhouse conditions.
- 2) To determine whether measurements of CO<sub>2</sub> evolution is a suitable bioindicator parameter of soil contamination under greenhouse incubations.
- 3) To study the effect of heavy metals on the population of aerobic heterotrophic bacteria in treated soil under greenhouse condition.

## **MATERIALS AND METHODS**

### ***Soil and treatments***

#### **Soil and treatments:**

The acidic sandy brown forest soil samples were collected from wheat cultivated area in Gödöllő, Hungary. The soil samples were air-dried. The availability and the effect of heavy metals (Cd and Pb) on CO<sub>2</sub>-production and bacterial population were studied. Chemical materials in the form of sodium nitrate (170 mg/kg), potassium phosphate (50 mg/kg), and glucose (3 g/kg) as sources of N, P, and C, respectively were added to the soil samples for activating the soil samples. The soil sample was divided into two groups according to the number of heavy metals used. Each group was divided into three sub-groups which were treated with three concentrations of



Cd in CdCl<sub>2</sub> (1.5, 3, and 6 ppm), or Pb in the form of PbCl<sub>2</sub> (40, 80 and 160 ppm). The treated soil samples were incubated for one, three and six weeks. The soil samples were collected for measuring the total aerobic heterotrophic bacterial population and the amount of CO<sub>2</sub>-production after 1<sup>st</sup> week, 3<sup>rd</sup> week and 6<sup>th</sup> week of incubation at 28°C. The experiment was carried out in triplicates. For measurement of CO<sub>2</sub>-production, a fixed plastic tube containing 50 ml 10 M NaOH solution for trapping the evolution of CO<sub>2</sub> was placed in the centre of 1.5 l glass vessel filled by 0.5 kg of the heavy metal treated soil sample and vessel was closed tightly. The NaOH was titrated with HCl (1 M) to calculate the volume of CO<sub>2</sub> of soil respiration, which represented the 1) respiration due to litter decomposition, 2) root respiration, 3) rhizomicrobial respiration (i.e. microbial respiration utilizing C directly derived from living roots), and 4) microbial respiration utilizing native soil organic matter. Method of Erdey (1989) was applied for simultaneous determination of NaOH and Na<sub>2</sub>CO<sub>3</sub> content in the experimental soil samples.

MI -08-1735-1990 is the Hungarian technical directive method which was used to detect and measured the availability of Cd and Pb content in the soil samples. Five g of air-dried soil samples were ground to pass through a 2 mm stainless steel sieve for use. Soil samples were shaken by 25 cm<sup>3</sup> 1.5 M nitric acid at 20°C for two hours. The elemental analysis of the filtrate was performed by jobin-Yvon 24 type ICP atomic emission spectrometer. The study was carried out in three replicates.

#### ***Determination of total number of bacteria:***

The total aerobic heterotrophic bacterial count was carried out in all soil amendment with different concentrations of Cd and Pb. Under sterile conditions, serial dilution technique was used for this purpose. Ten gram of fresh soil sample of each soil treatment was suspended with 90 cm<sup>3</sup> sterile distilled water. After shaking for 30 minutes, in rotary shaker, this suspension was diluted gradually from 10<sup>-1</sup> to and 10<sup>-6</sup>. The dilution range from 10<sup>-4</sup> to and 10<sup>-6</sup> were selected and from each of these dilutions 1 cm<sup>3</sup> was pipetted to Petri dish, and thoroughly mixed with Nutrient agar. The developed bacterial colonies were counted after 48 h incubation at 28°C. The investigations were done in triplicates.

## **RESULTS AND DISCUSSION**

These previous results are in accordance with the results found by De Haan et al. (1999) who reported that the supply of mineralized C, N and P from soil organic matter, the decomposition of plant and animal residues and the maintenance of soil structure are all dependent upon the correct functioning of the soil microbial ecosystem. The effect of SIR and heavy metals (Pb and Cd) on CO<sub>2</sub>-production and bacterial population of acidic sandy clay brown forest soil samples which were collected from wheat cultivated area in Gödöllő (Hungary) was studied in laboratory conditions. After a week incubation, the recovery of Cd and Pb concentrations added to SIR treated acidic sandy brown forest soils was determined in the nitric acid soluble fraction.

Data presented in Figures 1 and 2 show that the addition of inorganic forms of Cd and Pb significantly increases the mobile (HNO<sub>3</sub> soluble) fraction of these metals during the different incubation time intervals and their concentration does not reach the 100% recovery.

In figure 1, it was found that the availability of Pb concentration in soil samples increased by increasing the incubation intervals and the dose applied to the soil samples under greenhouse conditions.

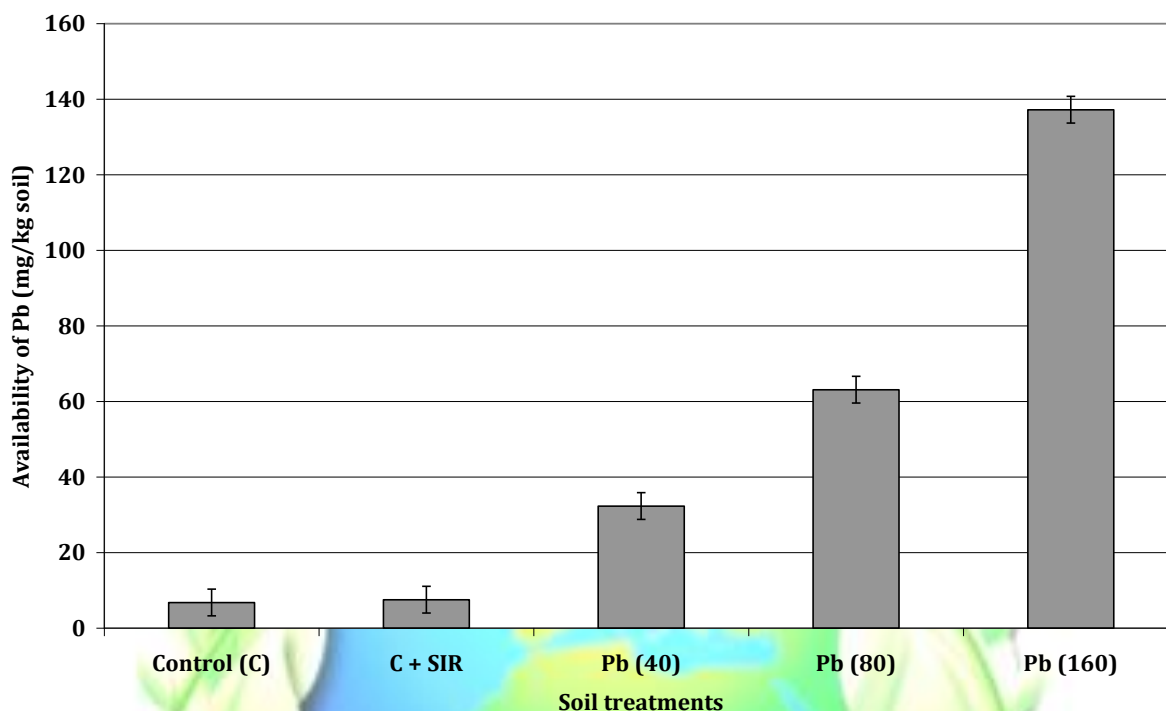


Figure 1: Average lead availability at 28°C in sandy clay brown forest soil treated by SIR and various concentrations of lead at different three time intervals

The beneficial effects of sewage sludges due to the extra organic matter N or P supplied may be short lived. These results are also in accordance with investigation of Hossain et al. (2005). Hossain et al. (2005) have discussed the effects of fertilizer. It was reported that only the lime plus P and N plus P treatments significantly affected soil microbial biomass C content. The N plus P treatment increased biomass C content.

Figure 2 illustrates the availability of Cd concentration in soil samples increased by increasing the incubation intervals and the dose applied to the soil samples under greenhouse conditions. It can be observed that the methods used for CO<sub>2</sub>-evolution and total aerobic heterotrophic bacterial number, are both suitable to be indicators for measurements the contamination rates of tested metals which give an idea about the soil fertility.

It is known that microbial biomass plays an important role in mineral nutrition of soil. The effect of heavy metal treatments on CO<sub>2</sub> reduction in SIR fertilized soil is showed in Figure 3. It is clear from data presented that SIR treated acidic sandy clay brown forest soil showed higher rate of CO<sub>2</sub>-production.

Results recorded in Figure 4. indicated that SIR treated acidic sandy clay brown forest soil samples have higher bacterial population (which are representing in term of log<sub>10</sub> of bacterial colonies) than in untreated control soil samples during the three different periods (1<sup>st</sup> week, 3<sup>rd</sup> week and 6<sup>th</sup> week) of incubations.

Microbial specific respiratory activity was higher in the unfertilized treatments. Nannipieri et al. (1990) stated that the changes in CO<sub>2</sub>-evolution were related to glucose concentrations of mineral nutrients. Higher initial rates of CO<sub>2</sub>-evolution were noted after the addition of P and glucose to N amended soil at C: P ratios greater than 30:1. It's also shown from such data presented in Figure 3. The heavy metals, Cd and Pb have significant effect on CO<sub>2</sub>-production of tested acidic sandy brown forest soil at different incubation periods (1<sup>st</sup> week, 3<sup>rd</sup> week, and 6<sup>th</sup>



week). Pb at different concentrations, 40, 80, and 160 mg/kg have the smallest effect on decreasing CO<sub>2</sub>-production either in acidic sandy brown forest soil incubated at different periods.

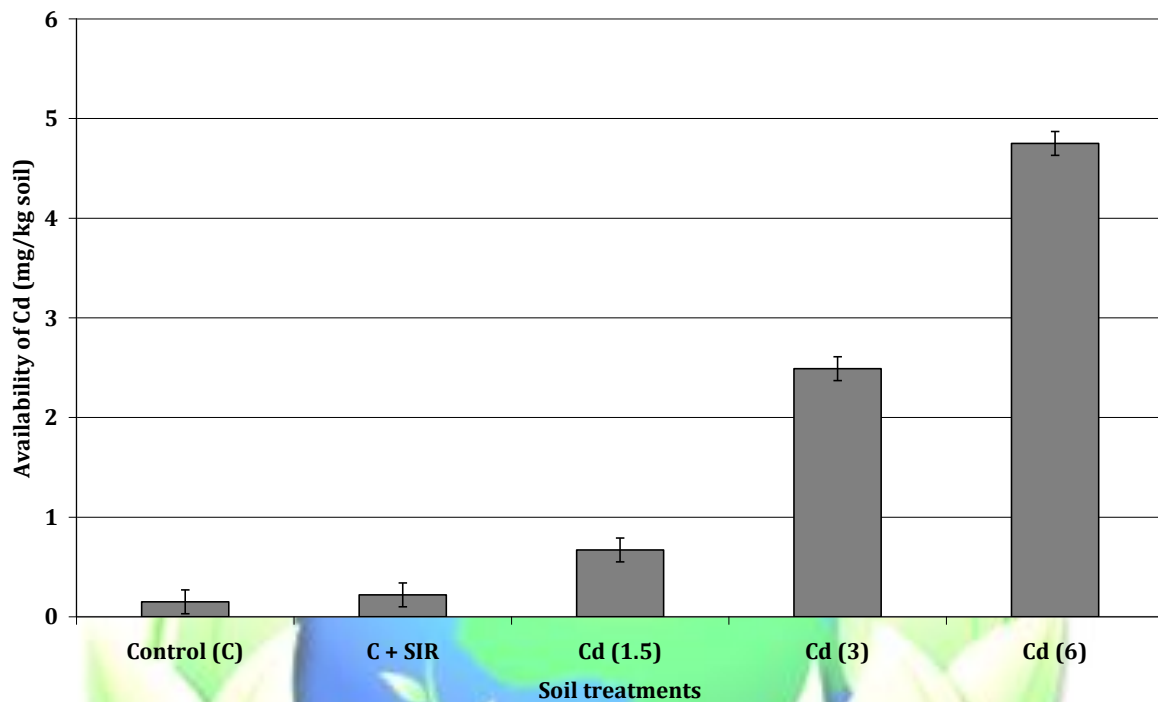


Figure 2: Average cadmium availability at 28°C in sandy clay brown forest soil treated by SIR and various concentrations of cadmium at different three time intervals

It can be shown also from data that Cd has higher effects in decreasing the amount of CO<sub>2</sub>-production at the different concentration used, 1.5, 3, and 6 ppm for Cd either in acidic sandy brown forest soil at the three different periods.

Baath (2002) studied the effect of heavy metals in soil microbial processes and populations. He established that the relative toxicity of different metals decreased in the order Cd > Cu > Zn > Pb. His results were similar to my result in which my investigation showed that the relative toxicity of tested metals decreased in the order Pb > Cd.

A significant effect of lead and cadmium on bacterial population has been found in SIR treated or untreated soils (Figure 4). It is shown that Cd has much more significant effect in decreasing bacterial population than Pb that has a little effect. It is also clear that the higher concentration of Pb and Cd cause decreases in total bacterial population.



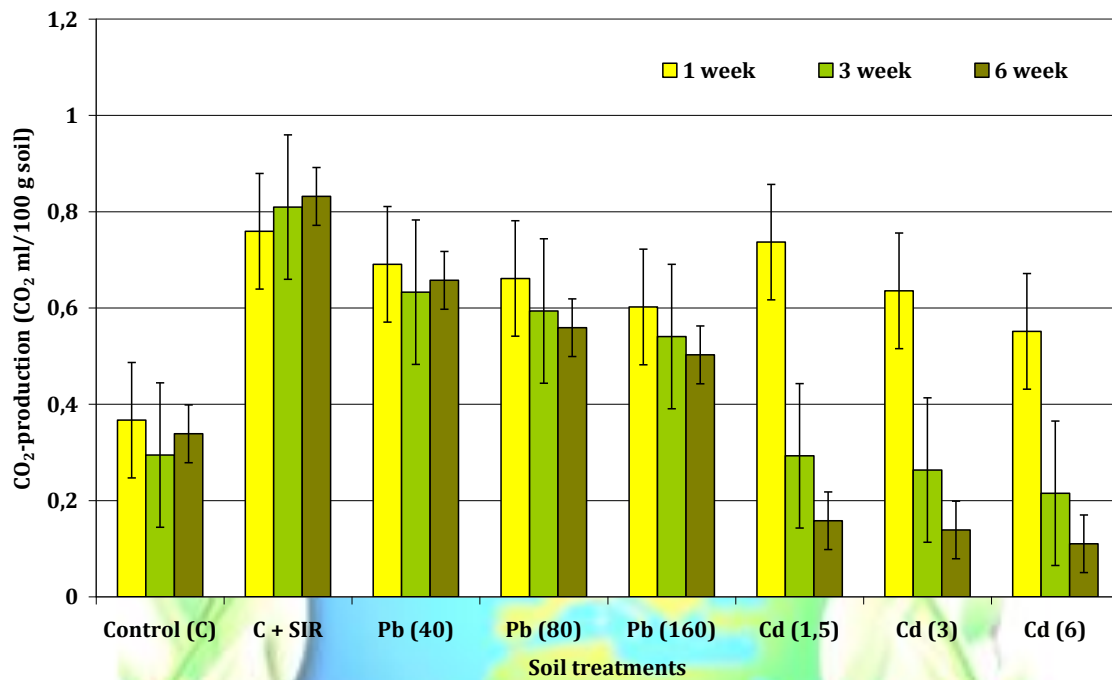


Figure 3: Average volume of CO<sub>2</sub>-production at 28°C from sandy clay brown forest soil treated by SIR and various concentrations of lead and cadmium at different three time intervals

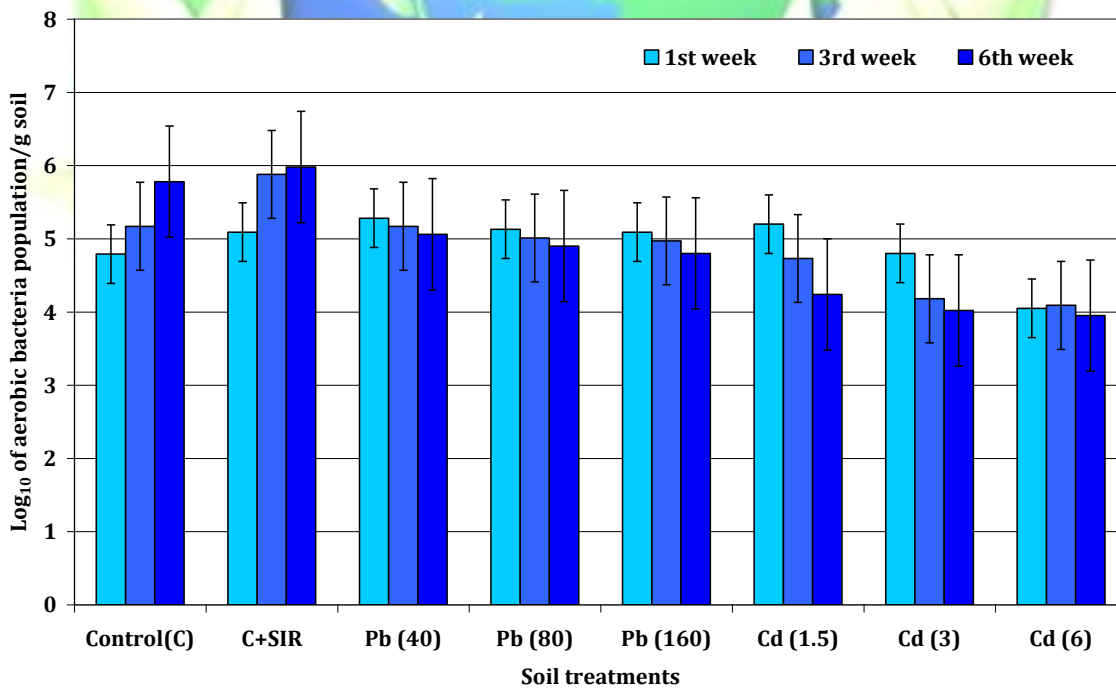
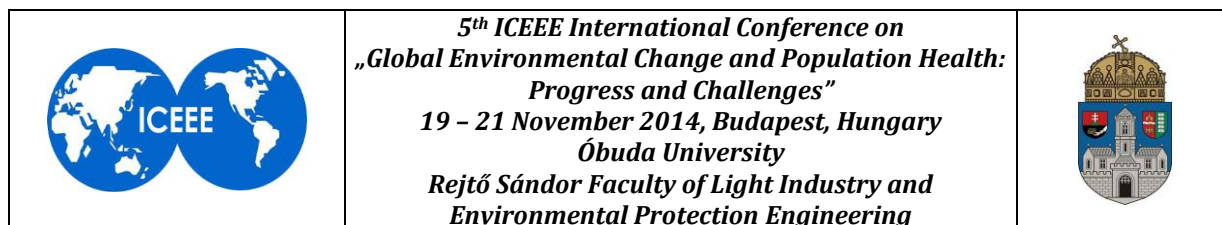


Figure 4: Average of log<sub>10</sub> of total aerobic heterotrophic bacterial number in sandy clay brown forest soil treated by SIR and contaminated by different concentrations of lead and cadmium and incubated under greenhouse conditions for three time intervals



Concerning the effect of Pb and Cd on the CO<sub>2</sub>-production and its relation to the sampling time, it is obvious that there is a clear trend. In the two heavy metal treatments, (Pb and Cd), the highest CO<sub>2</sub>-production was measured after the 1<sup>st</sup> week incubation followed by the 3<sup>rd</sup> and 6<sup>th</sup> week respectively. The same effect was found for the bacterial population. This result is in accordance with the result of Leita et al. (1995) who reported that the addition of Pb did not have any significant inhibitory effect on the level of microbial biomass C.

## CONCLUSION

The results indicated the following points:

- 1) The inhibitory effect of Cd applied in pot experiments under greenhouse conditions on CO<sub>2</sub>-production and total number of aerobic heterotrophic bacteria is significant higher than the soil samples contaminated with Pb.
- 2) Measurement of CO<sub>2</sub> is appropriate indicator for Pb and Cd soil contamination better than the bacterial indicator.

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## **IMPACTS OF GLOBAL WARMING AND CLIMATE CHANGE ON THE ENVIRONMENT: A CASE STUDY IN IRELAND**

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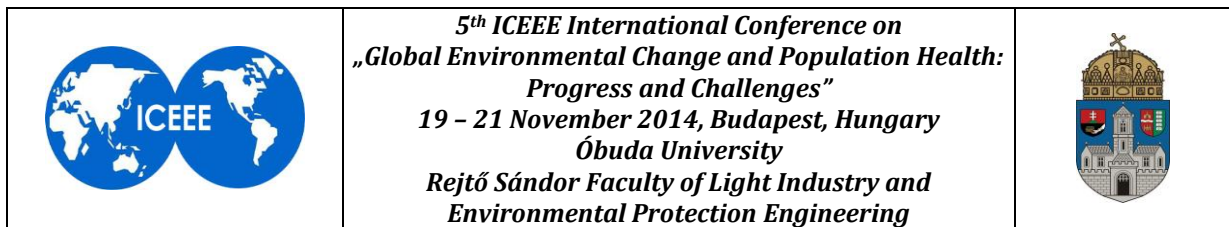
### **ABSTRACT**

Globally, 1998 was the warmest year of the last millennium. Such fluctuations were capable of being associated with changes in a diverse set of physical and biological indicators in many parts of the world. In this study, indicators of climate change showed that an average increase in annual temperature of 0.6°C overall has been observed over the course of the 20<sup>th</sup> century. This warming has been concentrated in two periods but most significantly in the 90s, of the century. On a shorter time scale, the seasonal maximum and minimum temperatures are increasing at a number of locations. Globally, it is minimum temperatures that are increased. This is also observed in Ireland, particularly for the summer months. Increases in both winter maximum and minimum temperatures mean that this season has experienced the greatest warming. The main finding is that signals consistent with global warming/climate-change effects, due to the increasing of greenhouse gases in the atmosphere, are evident in the primary meteorological record and that there is evidence of linked ecosystem changes in secondary indicators. Human health, energy and other economic factors are complicated by changing social behaviour and economic development. There is evidence that anthropogenically induced climate change is influencing Ireland's climate and ecosystems. However, analysis of the full impacts, particularly on ecosystems, is limited due to the absence of long-term monitoring sites or the development of systematic phenological observations beyond the phenological gardens. Climate change impacts are projected to increase in future years which may result in major environmental changes as well as economic and social difficulties.

**Keywords:** *Climate change, Global average temperature, Greenhouse gases, Global warming*

### **INTRODUCTION**

It is important to distinguish between climate and weather. Climate is described as an average of weather conditions, such as temperature and rainfall, over a long period of time (typically 30 years). In contrast, weather changes rapidly over hours and days and is highly variable. Climate change, therefore, refers to a significant change in the average temperature or rainfall, over periods of decades to centuries. Over the Earth's history, the climate has changed for many reasons including changes in the orbit of the Earth around the sun, changes in the energy from the sun and geological changes. What is different now is that human activities, that release emissions of gases and other pollutants into the atmosphere, are changing the energy balance of the planet and causing our climate to change. The gases, which are known as greenhouse gases, trap energy which then warms the planet somewhat akin to what happens in a greenhouse. The impact of this warming includes increased air and ocean temperatures, drought, melting ice and snow, rising sea levels, changes in rainfall patterns and flooding. Over the last 200 years, the concentrations of the main heat-trapping greenhouse gases have increased significantly in our atmosphere; CO<sub>2</sub> by 40%, CH<sub>4</sub> by 150% and N<sub>2</sub>O by 20%. These three gases are now higher than

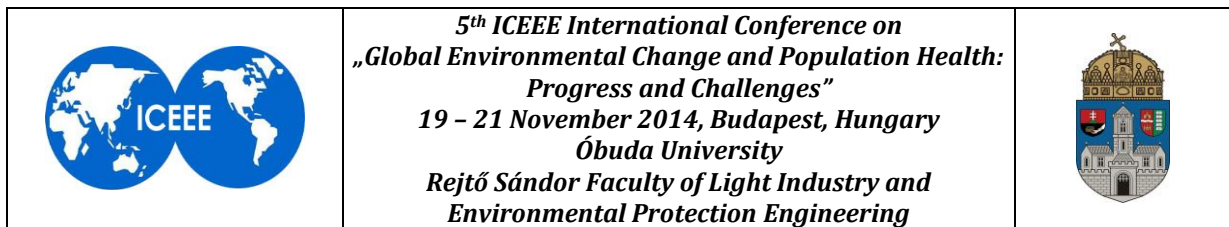


they have been for at least 800,000 years. The consequences of this are most clearly evident in the global temperature records, which show that, on average, the global temperature has increased by 0.85°C since records began in the mid-19<sup>th</sup> century. Continued emissions at or above current levels will cause further warming and result in changes in the global climate system during the 21<sup>st</sup> century that would very likely be larger than those observed during the 20<sup>th</sup> century (Environmental Protection Agency: EPA, 2013).

The increased concentration of greenhouse gases in the atmosphere, which are largely attributable to human activity and economic growth, are causing climate to change. There is conclusive scientific evidence that climate and weather patterns are changing (European Environment Agency: EEA, 2005). Climate change will result in a range of impacts across a number of sectors that are likely to exacerbate existing vulnerabilities. Adaptation actions will be required to avoid or reduce the adverse impacts of climate change and take advantage of any positive impacts. For Ireland, it is important to be able to build on positive opportunities that may be presented to respond effectively to reduce any negative impacts and to prepare for longer term consequences (Department of the Environment, Community and Local Government, 2012). Changing climate has implications for a range of issues such as economic activity, flooding, storms, agriculture, fisheries, and energy demand. Policy actions are now being undertaken to lessen the negative impacts of climate change. Anticipated changes in Irish climate due to global climate change are a gradual increase in temperature, increased precipitation and an increased frequency of severe storms and flooding (EPA, 2004). The human activities through the burning of fossil fuels, land use changes and more intensive agriculture have resulted in an increase in the levels of greenhouse gases in the atmosphere, especially CO<sub>2</sub>. This increase in greenhouse gases enhances the atmosphere's ability to trap heat leading to an increase in the average surface temperature of the Earth. Since the industrial revolution, the global average temperature is estimated to have increased by 0.6°C. Rising temperatures can have a number of possible consequences. These include more powerful and destructive hurricanes, fuelled by warmer seas and rising sea levels due to the melting of ice sheets in Antarctica and Greenland and a decline of more than 7% in the Arctic sea ice between 1978 and 2003, which would endanger low-lying regions of the world. The United Nations Framework Convention on Climate Change (UNFCCC, 1992) defines climate change “as a change of climate, which is attributed directly or indirectly to human activity that alters the composition of the global atmosphere and which is in addition to natural climate variability observed over comparable time periods”. More recently, the Intergovernmental Panel on Climate Change (IPCC, 2001) defines climate change as “any change in climate over time, whether due to natural variability or as a result of human activity”. Human beings, like other living organisms, have always influenced their environment (IPCC, 1994). It is only since the beginning of the Industrial Revolution, the impact of human economic activities has begun to extend to a much larger scale, continental or even global. Human activities, in particular those involving the combustion of fossil fuels for industrial or domestic usage, and biomass burning, produce greenhouse gases which affect the composition of the atmosphere.

In 2002, Ireland along with the other European Union (EU) countries, ratified the Kyoto Protocol to the UNFCCC, which established international emissions reduction targets for greenhouse gases. In Ireland the National Climate Change Strategy (NCCS), which provides a pathway for achievement of national emissions targets (Department of the Environment and Local Government, 2000), while the UNFCCC provides the international structure for actions to address climate change issues. The ultimate objective of the UNFCCC is stabilisation of atmospheric greenhouse gas concentrations at a level that would prevent dangerous anthropogenic interference with the climate system. However, the most immediate challenge for Ireland is achievement of national emissions targets established under the Kyoto Protocol.





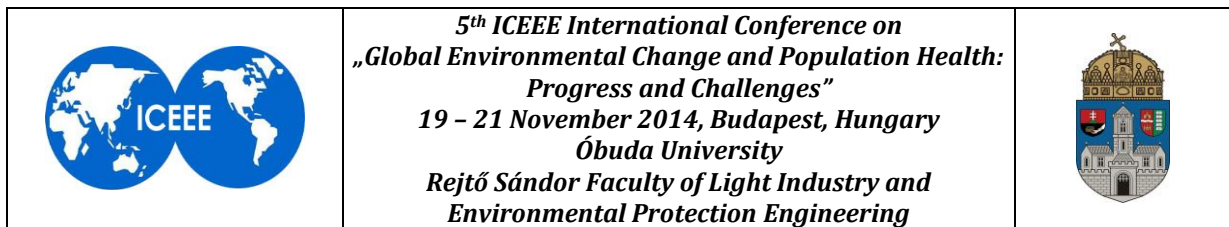
Furthermore, the Kyoto Protocol commits industrialised or developed countries to reduce their combined emissions of a basket of six greenhouse gases (CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub> these emissions primarily due to fossil fuel combustion, industrial processes, transport and agriculture) by at least 5% compared to 1990 levels by the first commitment period 2008-2012. While in the case of the collective EU-15 a target reduction of 8% is specified. In relation to other emissions to air in Ireland, between 1990 and 2000 emissions of SO<sub>2</sub> decreased by 29% as well as NO<sub>x</sub> emissions decreased by 25% at the same period. However, the most significant and sustained increase in greenhouse gas emissions has been in the transport sector, mainly due to road transport. (WATSON, 2003). The present study has highlighted on many ways in which, over the past decade and more, cumulative pressures deriving from growth and change in economic sectors have influenced on the Irish environment affecting climate change on the basis of both the national and the international levels. Continual improvement of monitoring and information systems, particularly on ecosystems and biodiversity, are needed if they are to understand and mitigate human influence on the environment.

### **CLIMATES OF THE PAST**

The Earth's climate has evolved and changed throughout its history. For approximately 94% of the past 850.000 years the earth's climate was colder than at present (BARRY & CHORLEY, 1998). The last major glacial episode reached a maximum 25.000-18.000 years ago when sea surface temperatures in the vicinity of Ireland were probably 10°C below those of today. CHURCH & WHITE (2005) found that a sea-level rise from January 1870 to December 2004 of 195 mm, equal to an average sea-level rise of  $1.7 \pm 0.3$  mm / year in the 20<sup>th</sup> century. This yearly rise is also increasing by  $0.013 \pm 0.006$  mm / year. This is an important confirmation of climate change simulations. The North Sea waters have warmed by 1.1°C over the past 30 years (PERRY, 2005). Sea temperature rise is causing fish species in the North Sea to shift their ranges northward in latitude and/or deeper to find colder waters. Changes in North Sea fisheries, already under stress from over-fishing, are likely to accelerate with climate change. More recently, the European annual means temperatures have increased by 0.3-0.6°C since 1900. A further increase of 2°C above the 1990 level is predicted for 2100 (EEA, 1998). This will have increasing impacts on natural and agriculture, ecosystem, human health, and water resources. Some of the climate driving forces may be sudden, having an immediate impact, while others may take much longer to be felt.

In the past 100 years the number of cold and frost days has decreased in most parts of Europe, whereas the number of days with temperatures above 25°C increased the 1990s was the warmest decade in the observational record; 1998 was the warmest year, followed by 2002 and 2003 also, the average annual growing season in Europe lengthened by about 10 days between 1962 and 1995 (EPA, 2005). The global mean temperature has increased by 0.6°C over the past 100 years, and the 1990s was the warmest decade for 150 years (EEA, 2003). Since the late 19<sup>th</sup> century, the global average sea surface temperature has increased by 0.5-0.7°C. Glaciers are retreating, ice sheets are melting and collapsing, and early snowmelt is augmenting warming rates (COOK, 2005). The loss of ice from Greenland doubled between 1996 and 2005, as its glaciers flowed faster into the ocean in response to a generally warmer climate also, the ice mass loss resulting from enhanced glacier flow increased from 63 km<sup>3</sup> in 1996 to 162 km<sup>3</sup> in 2005. In Ireland there has been an increase in winter maximum and minimum temperatures; a reduction in the number of frost days; an increase in the number of hot days. However, precipitation trends in Europe in the last decade show northern Europe being 10-40% wetter and southern Europe up to 20% drier than previously. In Ireland there has been a significant increase in rainfall in the north and west. Natural causes can only explain a small part of the recent rapid







changes in global climate; changes that far exceed all natural climate variations of the last millennium (EPA, 2005). Rapidly economic growth and human activity is largely responsible for the increase in the concentration of CO<sub>2</sub> in the atmosphere from a level of some 280 ppm in the pre-industrial period before 1750 to 375 ppm at present. PEZZA & SIMMONDS (2005) concluded that there has been an increase in hurricane intensity and attribute this trend in part to climate change, while it is still uncertain whether the number of hurricanes/year is correlated. Scientists also are drawing a link between climate change and the first-ever South Atlantic hurricane, which hit and made landfall along the coast of southern Brazil in spring 2004, and named Catarina, (in the state of Santa Catarina).

MCELWAIN & SWEENEY (2007) reported that evidence for an anthropogenic influence on climate change is now stronger than ever before, with the IPCC Fourth Assessment Report assertion that “It is very likely that anthropogenic greenhouse gas increases caused most of the observed increase in globally averaged temperatures since the mid-20<sup>th</sup> century” (IPCC, 2007). Global average temperature has increased by 0.74°C over the past 100 years with the rate of warming almost doubling over the last 50 years. Climate indicators for Ireland are based primarily on daily synoptic station temperature and precipitation data from Met Éireann’s monitoring network. Some of the key findings include:

- Mean annual temperature records closely resemble global trends, with warming evident in 2 periods, 1910 to the mid-1940s, and 1980 to 2004. The warming in the latter period occurred at a much greater rate than the global temperature increase. Nearly all stations reveal increases in annual and seasonal mean maximum and minimum temperatures.
- For the 1961 to 2005 period, the majority of stations recorded minimum temperatures increasing at a faster rate than maximum temperatures in spring, summer and autumn. In winter, 6 of the 11 stations have maximum temperatures increasing at a faster rate than minimum temperatures, and these are predominantly on the east coast.
- Heat waves are a cause for concern because of their impact on, for example, human health, agriculture and water supply. With global warming, it is thought that heat waves may increase in severity, frequency or duration in the future. The number of heat waves has increased at a number of stations annually, with greater increases in winter, spring and summer heat waves. Similarly, cold waves have also decreased at a number of stations. Cold waves generally occur in autumn and winter.
- Changes to precipitation patterns are more spatially and seasonally variable than temperature changes. There are increases in precipitation to the north of the country, with 4 out of 5 of the wettest years on record at Malin Head occurring since 1990.
- The greatest increases for maximum number of consecutive wet days occur at the west, north, and southwest coast stations of Belmullet, Malin Head and Valentia respectively.
- Rainfall intensity is an important indicator of climate change. The number of days where daily precipitation is greater than or equal to 10 mm reveals significant annual increases on the west coast and non-significant decreases at the east coast.

In addition, by 2012, global temperatures had increased by nearly 1°C above pre-industrial temperatures (Jones *et al.*, 2012), equivalent to about 0.01°C yr<sup>-1</sup> with about 20cm sea-level rise (Church and White 2011), and there are increasing numbers of unusual weather events that have been attributed to climate change (Trenberth and Fasullo 2012). By the time, temperature increases reach 2°, or sea level rise reaches 40cm, would impacts be twice as bad or increase more sharply? If impacts increase sharply with increasing perturbations, then overall damages would be largely determined by impacts at the times of highest perturbations, whereas with a less steep impact response function, impacts at times with lesser perturbations would contribute more to overall damages (Kirschbaum, 2014).

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## CLIMATES OF THE FUTURE

The Third Assessment Report of the IPCC (2001) represents the most authoritative contribution on the topic. Among the principal conclusions of the Third Assessment Report are the following:

- Global average temperature has increased by  $0.6^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$  since the mid-19<sup>th</sup> century and the trend seems to have accelerated in the past three decades. A further increase of 1.5-6.0<sup>o</sup>C is projected for the period to 2100.
- The 20<sup>th</sup> century was the warmest century of the last millennium in the Northern Hemisphere. The 1990s was the warmest decade and 1998 was the warmest year.
- A widespread retreat of mountain glaciers outside the Polar Regions has taken place in recent decades and sea-ice thickness in the Arctic has decreased by 40% during late summer/early autumn.
- Sea level has risen by 10-20cm since 1900, and a rise of approximately 50-80cm is considered likely during the period 1990–2100.
- Precipitation has increased over the land masses of the temperate regions by 0.5-1% / decade with some signs of increased intensities being measured. In the tropics, decreases in rainfall have been observed.

*EPA (2005) established that without intervening policy measures, anticipated changes in climate will include:*

- Cold winters almost entirely disappearing in Europe by 2080, while hot summers are projected to become much more frequent. This has implications for oil demand for heating and electricity demand for air conditioning, as well as health implications, e.g., heat waves in France resulted in mortalities especially among the elderly.
- From 1990 to 2100, the global average temperature is projected to increase by 1.4-5.8<sup>o</sup>C and by slightly more in Europe. Such dramatic changes in temperature will impact many aspects of life including agriculture and tourism trends but it will also impact on wildlife and nature.
- For the next century sea levels are expected to rise by 2.2 to 4.4 times higher than the rate in the 20<sup>th</sup> century, and sea level is projected to continue to rise for centuries. Consequently the risk of coastal flooding will increase threatening many urban areas.
- The European Alps could lose some 80% of their glacier cover by the end of this century if summer air temperatures rise by 3<sup>o</sup>C and become almost completely ice-free by 2100, in the case of a temperature increase of 5<sup>o</sup>C.

Climate change have a profound influence on life on earth, this is part of the daily experience of human beings and is essential for health, food production and well-being. Many consider the prospect of human-induced climate change as a matter of concern. The IPCC (2001 and 2007) reports assert that the evidence for a human influence on global climate is now stronger than ever before and states that “increasing concentrations of anthropogenic greenhouse gases have contributed substantially to the observed warming over the last 50 years.” Therefore, the average atmospheric CO<sub>2</sub> concentration has increased from 280 ppm in 1850 to 365ppm at present, and could exceed 700 ppm by the end of the present century if emissions continue to rise at current rates (IPCC, 2001).

*IPCC (2007) reported that future projections of climate suggest that:*

- Globally-averaged surface temperature is likely to increase by between 1.8<sup>o</sup>C (low emissions) and 4<sup>o</sup>C (high emissions) over the course of this century.
- There is likely to be an increase in maximum temperatures and in the frequency of hot days.
- Precipitation increases are likely in the mid- to high-latitudes in winter by the middle of the present century. However, there will be large spatial and seasonal variations.



- More intense precipitation events are also very likely over mid- to high-latitude areas of the Northern Hemisphere.
- Global mean sea-level rise over the present century range of 18 to 38 cm for the low emissions and 26 to 59 cm for the high emissions.

SWEENEY *et al.* (2002) established that indicators of climate change show a response to changes that have occurred in the recent past and that are continuing to occur today. These involve the detection of change in both primary (climatological or meteorological) and secondary (biological, sociological and economic) indicators. The Organisation for Economic Co-Operation and Development (OECD, 1993) defined an indicator as “a parameter, or a value derived from parameters, which points to provides information about describes the state of a phenomenon of an environmental area with a significance extending beyond that directly associated with a parameter value”. Primary indicators are the instrumental observations of climate over time. Secondary indicators are systems or organisms the vitality and responses of which change in response to environmental conditions changed by human economic activities. The OECD produces a core set of thirty-three indicators for environmental performance based on the Driving Force - Pressure - State - Impact - Response (DPSIR) framework (OECD, 1993 and EEA, 1999) as presented in Figure (1).

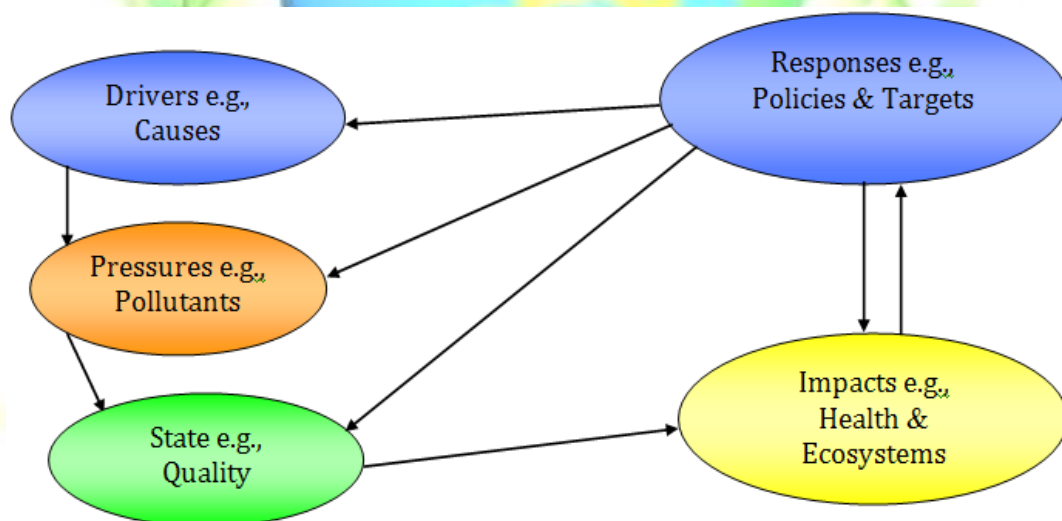


Figure 1. The DPSIR Framework (Source: OECD, 1993 and EEA, 1999)

Indicators simplify a complex reality and communication is their major function (EEA, 1999). Indicators of climate change enable communication of critical information regarding climatic conditions. They also provide an essential early warning system by making available observational data that may point to an environmental problem and provide a representative picture of environmental conditions. Most national and international bodies base their sets of indicators on the DPSIR framework or a subset of it. According to this system, social and economic developments exert a *pressure* on the environment and, as a consequence, the *state* of the environmental changes. This leads to *impacts* on human health in an ecosystems and materials that may elicit societal *response* that feeds back on the *driving forces* or on the impacts directly, through adaptation or curative action. The PSR framework is used to identify indicators of environmental pressures (P), state or conditions (S) and responses (R) as shown in Figures (2 and 3) for use in the state of the environment reports produced by each of the EU member states.



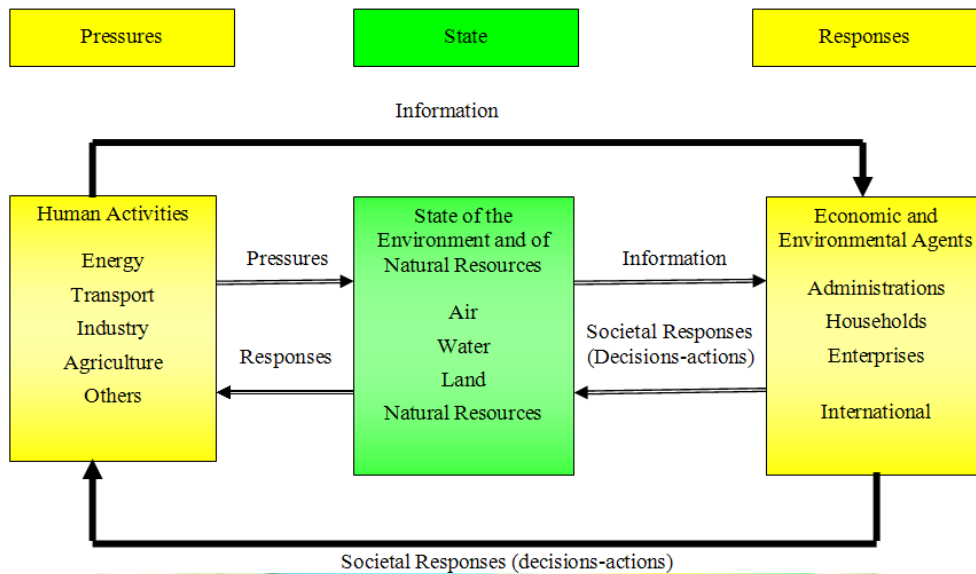


Figure 2. Pressure-State-Response (PSR) Framework (Source: OECD,1993)

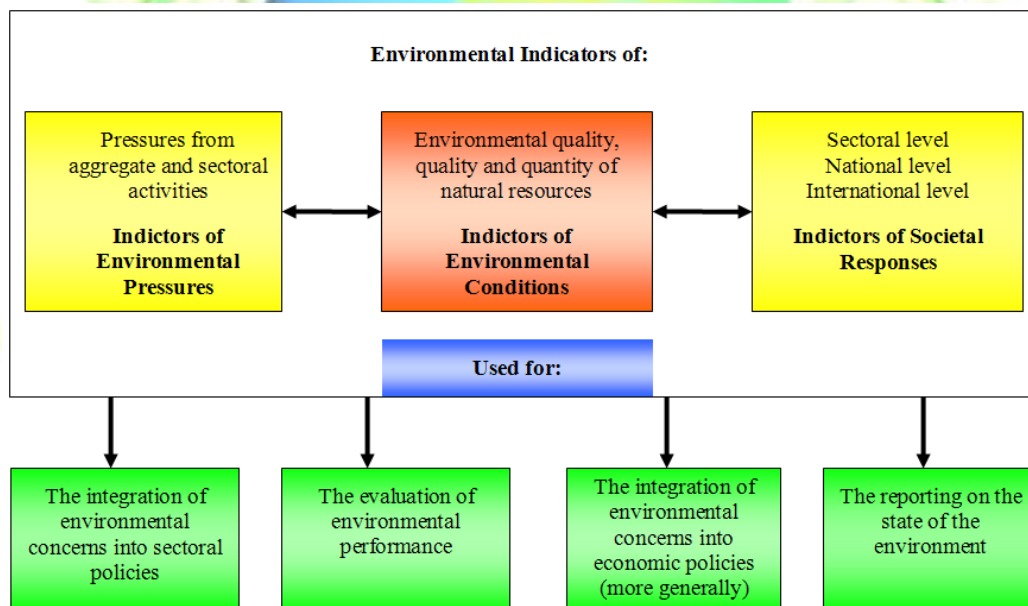
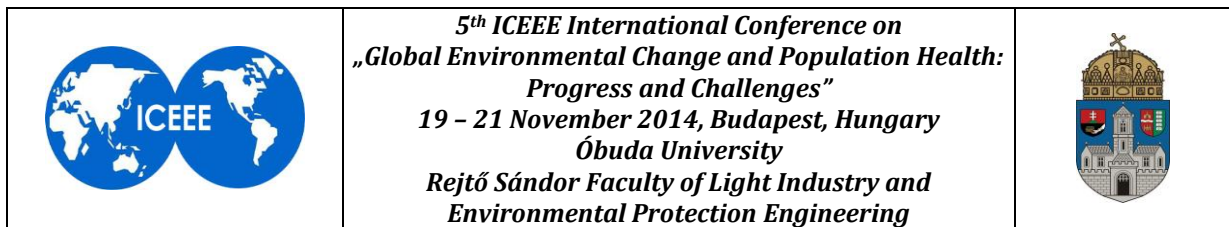


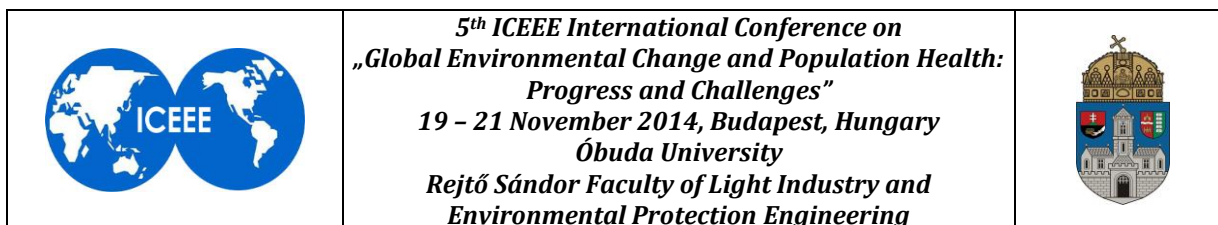
Figure 3. Nature and Use of Environmental Indicators (Source: OECD,1993)

### PRIMARY INDICATORS OF CLIMATE CHANGE

Primary indicators such as temperature, precipitation, cloud cover, sunshine, wind, atmospheric pressure, and humidity. While secondary indicators are important as they provide valuable information for early warning on how climate change affects important ecosystem, economic and social activities, such as the effects of climate change on natural flora and fauna which are complex, problematic, multifaceted and subject to large uncertainty. Also, secondary indicators may be valuable in areas where direct meteorological measurements are not available to pinpoint vulnerable parts of the ecosystem. In establishing indicators, a distinction can be made between primary indicators, based on analysis of directly observed meteorological data, and



secondary indicators, based on the responses of the living world to climate changes which provide a response in living microorganisms and human health. The warming is not linear, with greatest warming being observed in the temperature record since the mid-1970s (MCELWAIN & SWEENEY, 2007). According to the Climate Research Unit (2005) was the second warmest year globally (JONES, 2006). The trend in global temperatures provides the clearest signal that greenhouse gases are trapping more energy in the atmosphere. This is sometimes referred to as global warming. The average temperature in Ireland increased by 0.7°C during the period 1890-2004, at an average rate of 0.06°C/decade. In Ireland this warming is most evident during the periods 1910 to 1949 and 1980 to 2004. The temperature increase in the latter period has been larger, and the rate of increase more rapid than in the 1910-1949 period. The decade beginning 1990 has been the warmest decade in the instrumental record for Ireland. Temperature records indicate that global trends have been largely replicated in Ireland, albeit with an observed tendency for a lag of a few years. A warming episode from the first decade of the 20<sup>th</sup> century to the mid-1940s was followed by a cooling trend to the end of the 1970s. Thereafter, a rapid warming was apparent which continues to the present. A stronger warming trend was apparent in Ireland in the 1930s and 1940s than globally and this resulted in the warmest year of the last century being 1945 in Ireland. The temperature observations indicate that most warming has occurred in the winter period. Maximum temperatures appear to be increasing more than minimum temperatures during winter season. A global analysis of mean daily maximum and minimum temperatures, point to an increase in minimum temperatures at a rate nearly twice that of maximum temperatures since approximately 1950 (FOLLAND *et al.*, 2001). This may be associated with global changes in precipitation and cloud cover. On a global level, the greatest seasonal warming has occurred during the Northern Hemisphere winter and spring. As a result, the disparity between summer and winter has decreased. Overall, two of the most visible impacts of higher temperatures in Europe are melting ice and reduced snowfall. Eight out of nine glaciated regions in Europe show significant retreat of glaciers in the past century. Across Europe, climate change already appears to be impacting many sectors of society. Higher temperatures and more intense droughts are producing a rising trend in the number and severity of forest fires in the Mediterranean. These threaten forestry, farming, tourism and the suitability of the land for habitation. In 2003 heat wave saw 20.000 more people die in Europe than in the same period in other years, some 14.000 of them in France. Most people died from heat stroke, and heart and respiratory ailments, as daily maximum temperatures rose to 40°C and, perhaps of equal importance, night-time minimum temperatures stayed above 25°C on the warmest nights. Climate extremes are creating ever-greater risks of catastrophic events of all sorts. Changes in rainfall and flows from glaciers are altering river flows, sometimes causing floods or emptying reservoirs. Flood events in particular have soared in Europe and, although better warning and rescue systems have prevented a commensurate rise in deaths, the loss to property has been substantial. The severe flooding in Austria, the Czech Republic, Germany, Hungary and Slovakia in August 2002 caused economic and insured losses of about EUR 25 billion (EEA, 2005). Climate change is affecting precipitation and hydrological cycles (DORE, 2005). One of the expected impacts of climate change is that snow and ice levels reduce and that snowmelt occurs earlier in the spring season. Wet regions increasingly experience higher levels of precipitation, and arid areas reduced levels, becoming drier. The IPCC (2001) concluded that increases in global total cloud amount over the Northern Hemisphere mid- and high-latitude continental regions had occurred at a rate of 2% since the beginning of the 20<sup>th</sup> century. These increases have been positively correlated with decreases in the diurnal temperature range and increases in precipitation (FOLLAND *et al.*, 2001). The diurnal temperature range is defined as the difference between the daytime maximum temperature and night time minimum temperature.



EPA (2006) published that climate change will cause changes in weather patterns including the amounts and characteristics of precipitation. Precipitation in Ireland is generally in the form of rain or drizzle, with hail and snow accounting for very small percentages of annual totals. An intensified hydrological cycle, i.e. heavier rain over short periods is expected. Heavy or extreme precipitation events can be defined as days with precipitation greater than a given threshold (e.g., 10 mm or 50 mm). Extreme precipitation events are of great importance, as they affect many people through loss of life and cause much economic damage and disruption. Greatest rainfall totals more than 3 days are important from the perspective of flooding and vulnerability of local populations and environment. MCELWAIN & SWEENEY (2007) concluded that the annual precipitation has increased on the north and west coasts, with decreases or small increases in the south and east. However, the wetter conditions on the west and north coastal regions appear due to increases in rainfall intensity and persistence. There is an increase in precipitation events over 10 mm on the west coast with decreases on the east coast. The increases in intensity and frequency of extreme precipitation events provide a cause for concern as they may have a greater impact upon the environment, society and the economy. Additionally, continued monitoring and updating of the mentioned indicators will support policy decisions on the climate change in Ireland or any where of the world.

### SECONDARY INDICATORS OF CLIMATE CHANGE

SWEENEY *et al.* (2002) mentioned that secondary indicators are including agricultural, biological, social and economic factors, which are a comprise phenomena, especially in the biological environment, which might be expected to show a response to changes in primary climatic parameters. As indicators, they will inherently be subject to a complex, multifactor set of influences of which climate may be only one component. The problems of confounding factors were particularly evident in agricultural systems. Management practices, market forces, subsidy payments, genetically modified cultivars and all these made the isolation of climatic influences difficult. Some possible future indicators did emerge, most notably changes in the production area of warm weather crops such as forage maize and vines. Here, we summarized the secondary indicators in Table (1).

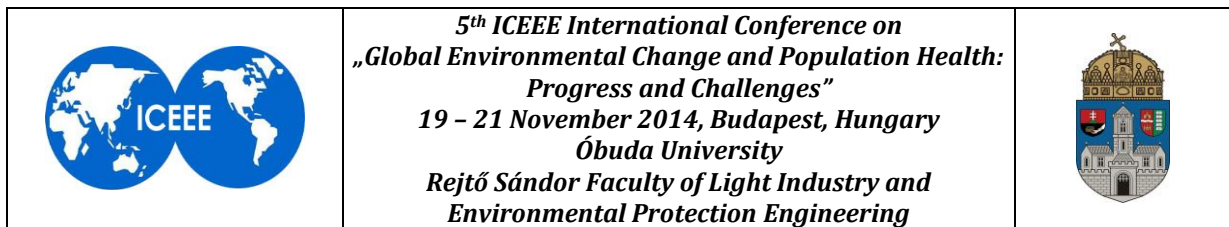
Table 1

*Summarised the Secondary Indictors of Climate Change in the Same Time Mainly in 20<sup>th</sup> Century*

Secondary Indictors		
Biological Activity	Agriculture Productivity	Economic and Social Activities
Changing in birds, butterflies, insects and bats activity	Use of irrigation	Changes in energy consumption
Changing in fish stocks (Salmon run)	Change in warm-weather crops	Changing in Tourism (domestic holidays)
Changing in the beginning and growing season of the trees	Change in grass production in late summer	Insurance claim for storm damage
Changing in microbial activity		
Changing in plants distribution	Change in crop yield especially potato in Ireland	Effecting human health

PERRY (2005) reported that some species of marine fishes are already migrating out of their historic ranges to avoid changing climate conditions. Plants and animals associated with certain geographic regions are moving or dying. Habitats are becoming reduced as a result of climate change. Food chains have changed. Further alterations in ecosystem provisioning services,



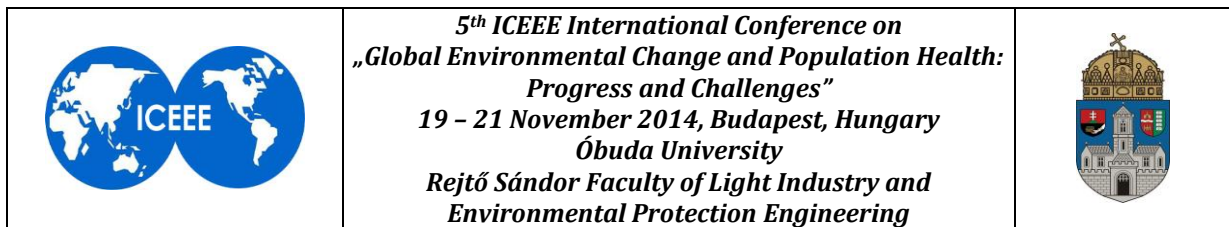


including wood products, drinking water supply, and agriculture productivity can be expected as climate change continues to alter entire ecosystems. Agricultural data are influenced by factors such as management, market forces, subsidy payments and agricultural policy. It is, therefore, difficult to identify suitable agricultural indicators for climate change. By developing the technology, in particular the breeding of new cultivars tolerant of adverse environmental conditions, make it difficult to isolate climatic influences on agricultural crops (BURKE, 2001). The Irish agricultural sector contributes €24 billion to the national economy annually, accounts for almost 10% of Irish exports and provides 7.7% of national employment (Teagasc, 2013). The sector accounts for about 7% of Irish Gross Domestic Product (GDP) with primary agriculture accounting for 2.5% (Central Statistics Office, 2013). Investigations of socio-economic data in Ireland show that as indirect indicators of climate change, which included changes in energy consumption, insurance claims for weather-related damage and changes in domestic tourism. In Ireland, since 1990, there has been a sharp decline in “home holidays” and a sharp increase in “foreign holidays”. This suggests that there is something other than increased summer temperatures influencing the number of domestic holidays being taken by Irish residents (SWEENEY *et al.*, 2002). The growth in the economy during the 1990s is undoubtedly responsible for part of the decline seen in domestic holidays.

Finally, there have been substantial reductions in Ireland’s greenhouse gases emissions in recent years, due in significant part to the impact of the economic downturn. Ireland is on track to meet its Kyoto Protocol commitment for the 2008-2012 period. This is a first step in achieving a longer-term goal of a low-carbon society and economy. The next key step is to meet the emissions reductions required under the EU 2008 Climate and Energy Package. The European Commission Roadmap for moving to a competitive low-carbon economy by 2050 points to EU-wide greenhouse gases emission reduction requirements of up to 80% by 2050. Within the EU, Ireland has an unusual emissions profile, with emissions from agriculture being proportionally higher than for most other Member States and projected to increase in the period to 2020. Projections by the Common Agricultural Policy indicate that even in the best-case scenario, Ireland will breach its annual obligations for greenhouse gases emissions under the EU 2020 target in 2017. Accordingly, further cost-effective actions need to be identified, assessed, adopted and implemented to reduce greenhouse gases emissions in the near term. The impacts of climate change are already occurring in Ireland and are projected to intensify over the coming decades; this must be factored into future planning and investment choices. The vulnerability of existing systems and infrastructure should be assessed and a national framework for climate change adaptation prepared (EPA, 2012).

## CONCLUSION

The atmosphere and ocean have warmed, the amounts of snow and ice have diminished, sea level has risen, and the concentrations of greenhouse gases have increased. Each of the last three decades has been successively warmer at the Earth’s surface than any preceding decade since 1850. Ireland has temperate climate and principally influenced by the North Atlantic Ocean and the Gulf Stream circulation. The significant indications of changes in climate can be detected in data from the west coast. Some changes could be regarded as being positive (higher minimum temperatures decrease in occurrence of frost days and longer growing season). The changes such as increased winter-time precipitation levels and decreased sunshine may not be regarded as beneficial developments. The build-up of greenhouse gases in the atmosphere is projected to increase climate changes in future. The more energetic atmosphere is likely to be more erratic and less predictable than today with more extreme weather events occurring. There may be

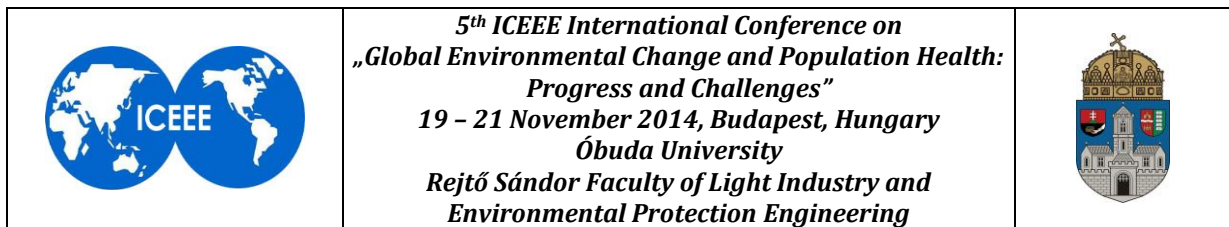


surprises, which have significant environmental, social and economic impacts that will be difficult to deal with. Ireland should support efforts to understand the impacts of climate change through research and the further development of observational systems as required under the Kyoto Protocol. There is a need for increased co-ordination and commitment to long-term monitoring of primary (climatologically) and secondary (ecological, health and economic) indicators in Ireland. In order to have an effective monitoring program it is essential to carefully consider the choice of measurements and sampling design. These must be linked to objectives to ensure that the results are useful, which would contribute to the development and implementation of environmental policy. Finally, reaching climate stabilization of the world economy must be totally transformed in a climate friendly and sustainable manner.

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Environmental Protection Engineering**



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## **INVESTIGATION OF THE POTENTIAL OF FOGWATER HARVESTING IN THE WESTERN MOUNTAINOUS PARTS OF YEMEN**

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### **Abstract:**

The Republic of Yemen is located in an arid to semi-arid region. Rainfall rates range from none at certain parts of the country to about 400 mm/yr in its mountainous parts. Rainfall has been harvested and collected in cisterns existed in the mountainous region for generations. In the dry season (October - February), and after the stored water is consumed, people, mainly women and children, have to travel long distances down wadis to fetch water from the nearest water source, which is often not suitable for human consumption. This is the case in the western mountainous region, namely Hajja Governorate, which heavily depends on rainwater for drinking, animal watering, domestic uses and irrigation. However, during the dry season this region experiences foggy conditions. This has prompted conducting a fog collection field study in this region to investigate the potential of providing an alternative source for water supply during the dry season. The study consisted of installing 26 standard fog collectors (SFC) of one m<sup>2</sup> of polypropylene mesh at 19 sites in Hajja, and measuring the daily fogwater amounts collected during the period from 1 January to 31 March, 2003. The results indicated that fog collectors located closest to the red sea with an elevation ranged between 2,000-2,200 meters above sea level and winds from the west direction have produced the highest water output, reaching a maximum of about 4.5 liters per square meter of mesh per day over the three winter months period. The conclusion drawn is that though this technique is cheap, simple and promising, more investigations are still needed on the various parameters contributing to fog collection, such as, relative humidity, temperature, and SFCs technologies.

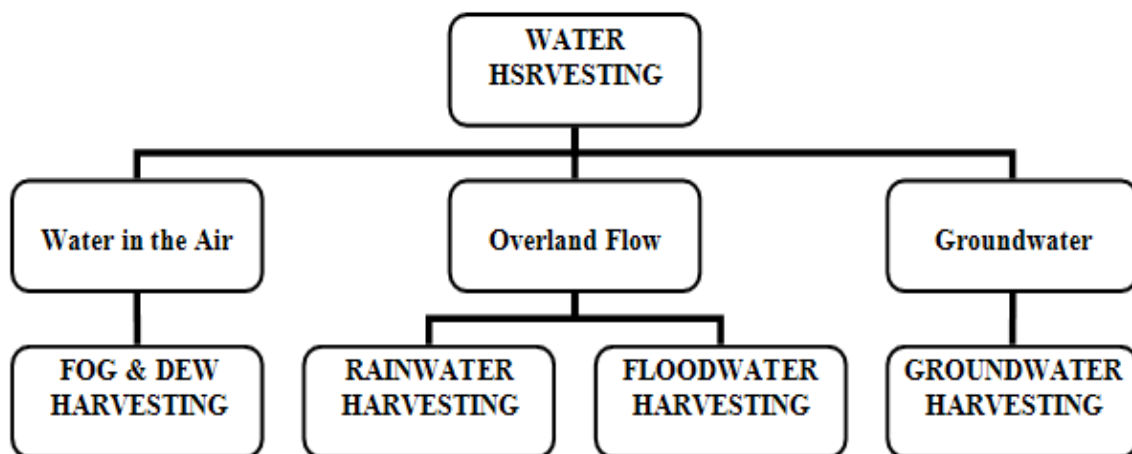
**Keywords:** *fogwater harvesting, arid and semi arid, mountains, Yemen*

### **INTRODUCTION**

Water scarcity is considered as one of the major threats to humankind in this century. This is especially true in the arid regions of the world, where it is expected that available water resources in streams, rivers and groundwater in most of these regions will not be sufficient to meet the future ever-increasing needs of agriculture and urban areas. Therefore, there is a need to reassess indigenous irrigation methods to find their potential value to alleviate future water scarcity (Prinz, 1996). These methods, if associated with water saving techniques, modern hydrological and technological tools, may supplement other water sources and help in securing future water supply.

In general, water harvesting methods can be classified based on the source of the harvested water (Figure 1), which can be water in air, overland flow, or groundwater (Prinz, 1996; FAO, 1997). Of particular interest to this study are the methods of fogwater collection (water in air), which were developed in areas without permanent rivers, and where people have to rely on rainfall, dew and fog. These methods are based on the principle that water can be collected from fog under favourable climatic conditions to provide water for small rural

communities in arid and semi-arid regions. This innovative, non-classical water harvesting method has the advantages of being simple, can be applied without large investments, and can be maintained and managed by the users themselves, and hence offers good prospects for future development (FAO, 1997). However, the challenge in implementing these methods effectively is to identify suitable communities and favourable environmental conditions, and ensure that the system meets user demand sustainability, and to develop an efficient system to collect water for regional agricultural purposes.



**Fig. 1.** Water harvesting methods (Prinz, 1996)

Literature indicate that the modern era of fog collection has started in 1987 with the construction of a pilot project of 50 fog collectors at El Tofo district, located in the mountainous region of Chile (Schemenauer and Cereceda, 1994a). In 1992, water from these collectors was taken to the village of Chungungo. In the following years, the number of fog collectors on the mountains of El Tofo district was increased to 100, and the average fogwater production reached about 15,000 liters per day during a year. Since then, the number of fog collectors has varied somewhat depending on the needs and conditions. As a result of these successful projects, other fog collection projects have been initiated in other parts of Chile, as well as in other countries such as Peru, Ecuador, South Africa and the Canary Island of Spain (Canto, 1998). In addition, several evaluation studies have been carried out in many countries, such as Mexico (Schemenauer and Cereceda, 1994b) and Sultanate of Oman (Alesh, 2003; Hildebrandt *et al.*, 2005).

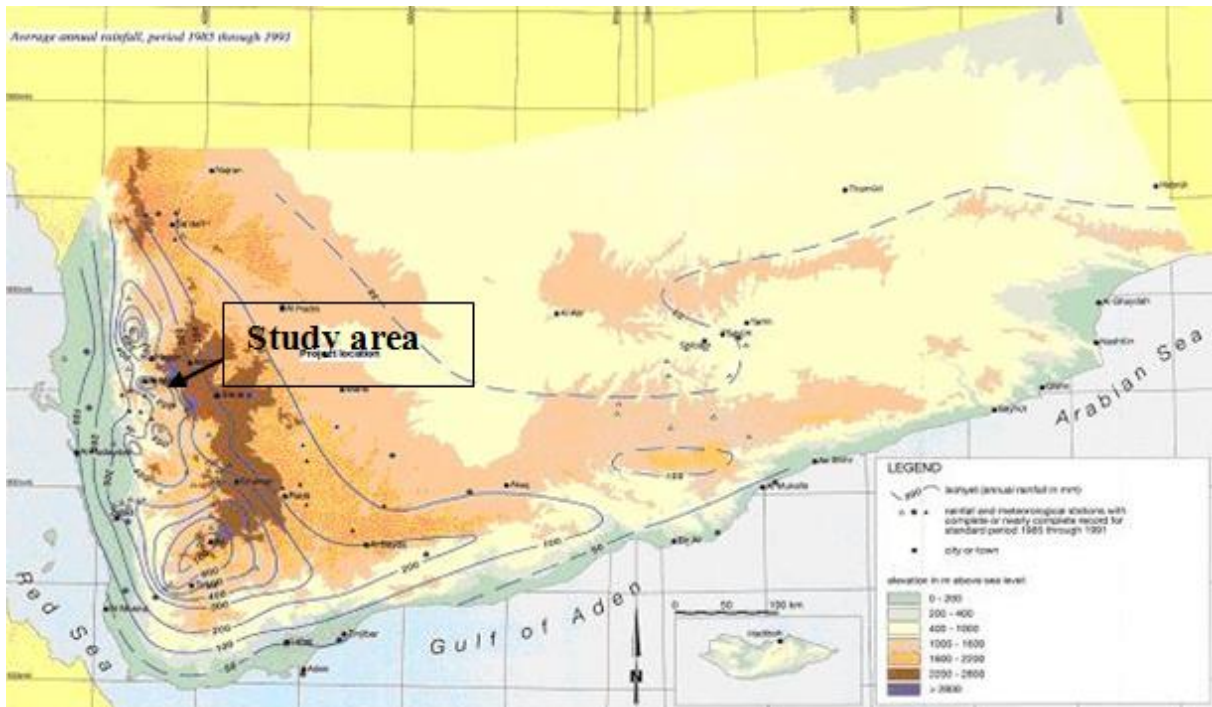
The objective of this study was to investigate the potential applicability of fogwater harvesting in the mountainous region of Yemen, and to get sufficient data for making reliable estimates of the daily yield that can be achieved during the foggy season. Furthermore, an analysis of the relationship between the collected amounts and seasonality, best placement and orientation of the collectors is made to help in the future design process to ensure the best performance at an affordable cost.

### Study Area

The Governorate of Hajja, located in the western mountainous region of Yemen, was selected for the fogwater harvesting field experiment (Figure 2). Hajja Governorate is located northwest of the Capital City of Sana'a, Yemen, and inland from the Red Sea, with an altitude range between 1,650 and 2,480 meters above sea level (masl). Many people in Hajja depend heavily on rainwater for drinking, animal watering, domestic uses and irrigation. In Hajja,



precipitation occurs in two periods, between the months of March and May, and between the months of July and September. During the dry season (October-February), Hajja experiences foggy conditions, and hence it was chosen for the study.



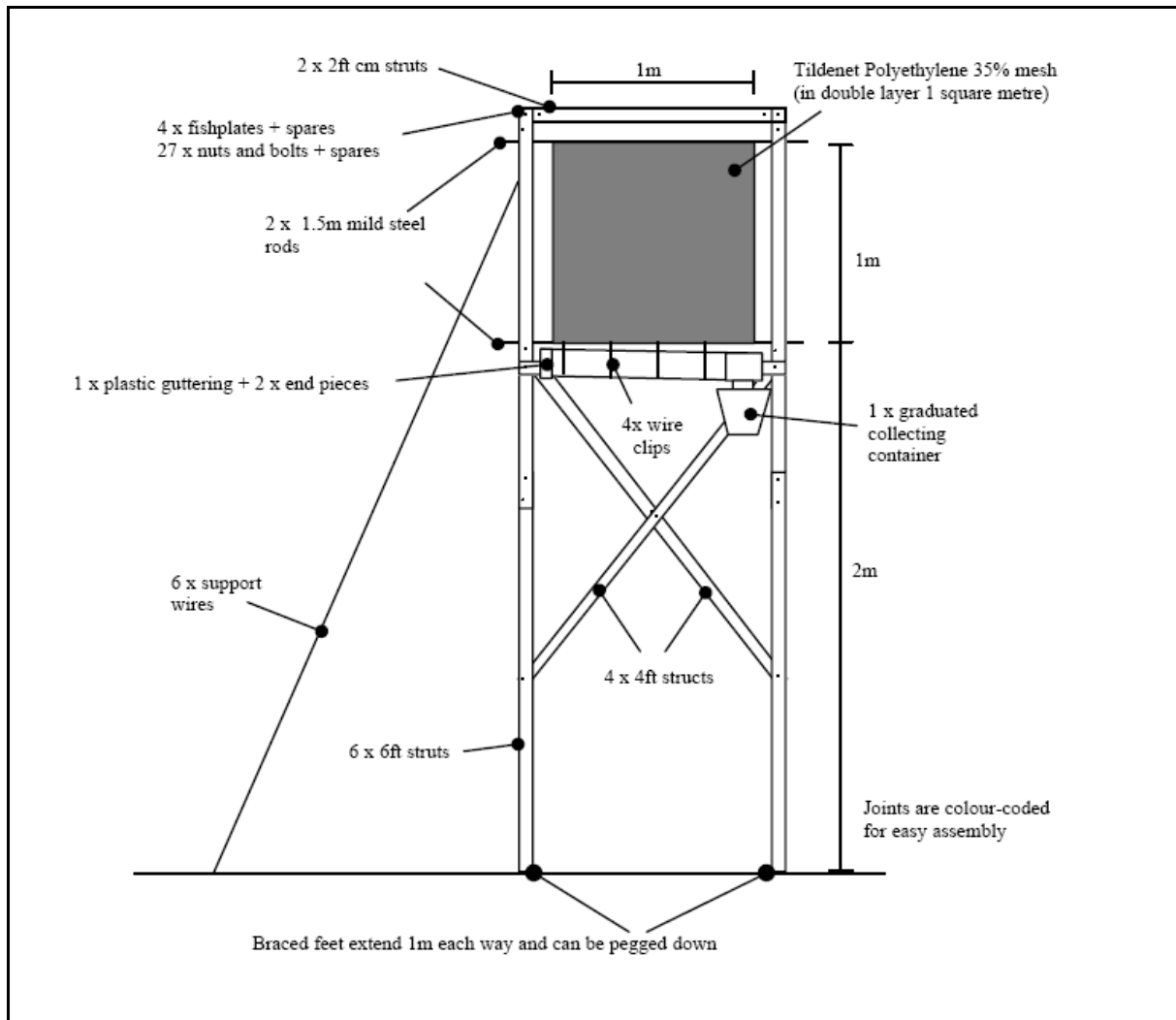
**Fig. 2.** Location of the Pilot study area in Yemen and rainfall contour map (Van Der Gun and Ahmed, 1995)

## Materials and Methods

Twenty-six Standard Fog Collectors (SFCs) were constructed with locally available materials and local workmanship, except for the mesh that was imported. These SFCs were installed in December 2002 and January 2003 at 19 different sites that were chosen for the field study. The data of the amounts of the fogwater collection were measured in the period from 1<sup>st</sup> of January 2003 to 31<sup>st</sup> of March, 2003.

The Standard Fog Collector (SFC) was designed by Schemenauer and Creceda (1994a). The collector is relatively simple and flat; rectangular nets (mesh) of nylon supported by a post at both ends arranged perpendicular to the direction of the prevailing wind. The SFC used in this study consisted of a 1 m<sup>2</sup> panel of mesh, located 2 m above the ground by a supporting structure (Figure 3). The collection of fog or cloud is achieved by the collision of suspended droplets on a mesh. The droplets coalesce on the mesh and run down into a collecting drain and then into a tank or distribution system. Fog collection can be thought of as an aerial spring; the piping and delivery system is similar to a standard spring-fed gravity water supply (FAO, 1997).

The complete system can be easily build or assembled on site. The installation and connection of the panels is quick and simple, and the assembly is not labor intensive and requires little skill. No energy is needed to operate the system or transport the water, capital investment is low, and maintenance and repair are minimal (IDRC, 1997).



**Fig. 3.** Diagram of Standard Fog Collector (SFC) used in the study area (Schemenauer and Cereceda, 1994a)

The variables required quantifying the magnitude and reliability of supply and the orientation and sturdiness (Schemenauer and Cereceda, 1994b) required by Fog Collection Units (FCU), include:

- Fog-water yield ( $\text{m}^3 \text{m}^{-2} \text{day}^{-1}$ )
- Annual variation and seasonality of yield
- Rainfall ( $\text{mm day}^{-1}$ )
- Wind speed ( $\text{m s}^{-1}$ )
- Wind direction during fog events

In order to get a comprehensive assessment of the fog harvesting potential, it is necessary to make daily measurements for the whole year. However, if the location of the study area has known fog season such as the monsoonal fog of Oman (Alesh, 1998) then the study period may be shortened to that season. In this study, measurements were made only during the foggy season (i.e., January-March).



## PARAMETERS INFLUENCING FOG COLLECTIONS

### *Wind patterns*

Conditions for fogwater harvesting are considered best where there are persistent winds in one direction to transport low-level cloud and fog. Figure 4 shows a schematic west-east cross section of an idealized case for the Tihama coastal plain in Yemen and Saudi Arabia (Furey, 1998). However, this is a very simplistic explanation, and fog in these desert areas can be caused by much more complex atmospheric and oceanic interactions that need further investigation understanding.

### *Mountain range*

The topographic relief must intercept the cloud. In the case of low-level coastal fog the interception can be made by isolated hills or dunes. For higher clouds, larger mountains are needed. In the latter case, the cloud can be pre-existing or orographically induced (Schemenauer and Cereceda, 1994a).

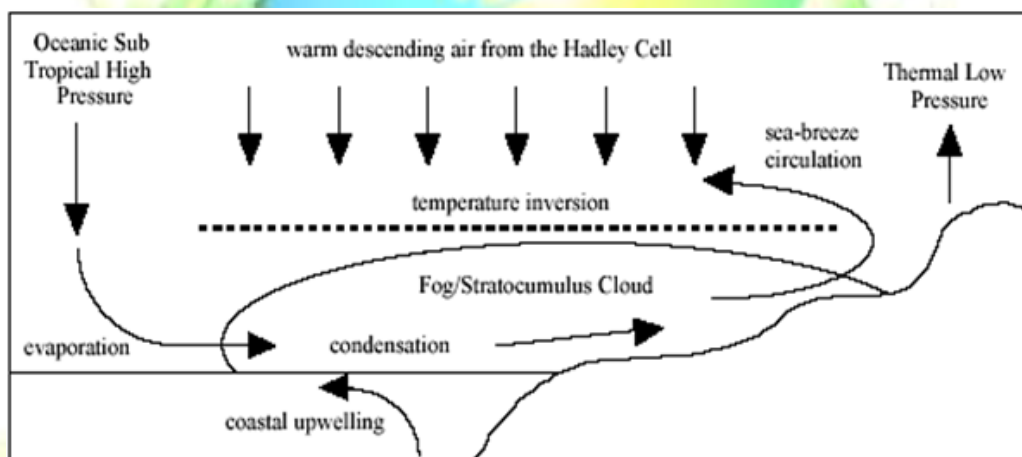


Fig. 4. Mechanisms of the formation of the West Coast advection fog (Furey, 1998)



### *Distance to the coastline*

Marine clouds and fog decks generally dissipate further inland due to evaporation. It is often therefore desirable to have collectors located within 5 km of the coast and usually not more than 25 km (Furey, 1998). This distance must be balanced against topography in relation to the cloud deck. Observations and experiments are needed to determine the optimum location. In high elevation areas where cloud is intercepted or induced by the topography, the distance to the coast becomes irrelevant (Furey, 1998)

### *Orientation of the topographic features*

It is important that the longitudinal axis of the mountain range, hills, or dune system be approximately perpendicular to the direction of the wind bringing the clouds from the ocean. The clouds will flow over the ridgelines and through passes, with the fog often dissipating on the downwind side. If the orientation of the SFCs is not directly facing the fog movement then the yield is likely to be underestimated. In Namibia, the use of a bi-directional fog collector was suggested to provide more accurate information for choosing the best orientation for the large collectors (Furey, 1998).



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### **Rainfall seasonality**

Rainfall in Yemen depends on two main mechanisms, the Red Sea Convergence and the Monsoonal Inter-tropical Convergence Zone. The former mechanism influence is most noticeable in the west of the country; this mechanism is active from March to May and to some extent during autumn (i.e., October-November). The latter mechanism reaches the country in July-September, moving north and then south again, so that its influence lasts longer in the south. Seaward exposed escarpments such as the western and southern slopes receive more rainfall than the zones facing the interior (Meteorological Service, 2000).

### **FIELD WORK AND MEASUREMENTS**

Planning for the fieldwork began in November 2002, and subsequently 26 SFCs were constructed in nineteen different sites in Hajja region. Table 1 shows the locations, orientations and the elevations of the SFCs in the study area.

The SFCs were preferentially sited on ridges and saddle points in positions where experience has shown that there will be strong enough winds to push the fog through the mesh of the collectors. The SFCs were located facing the south and west directions depending on the local topography based on the prevailing wind direction during the months of December, January, February and March, which are from the south and sometimes west (Meteorological Service, 2000).

The harvested fogwater was measured on a daily basis; measurements were made during the period from 1<sup>st</sup> of January to the 31<sup>st</sup> of March, 2003. These are the dry months in winter when rainfall is virtually non-existent and the need for water is very high.

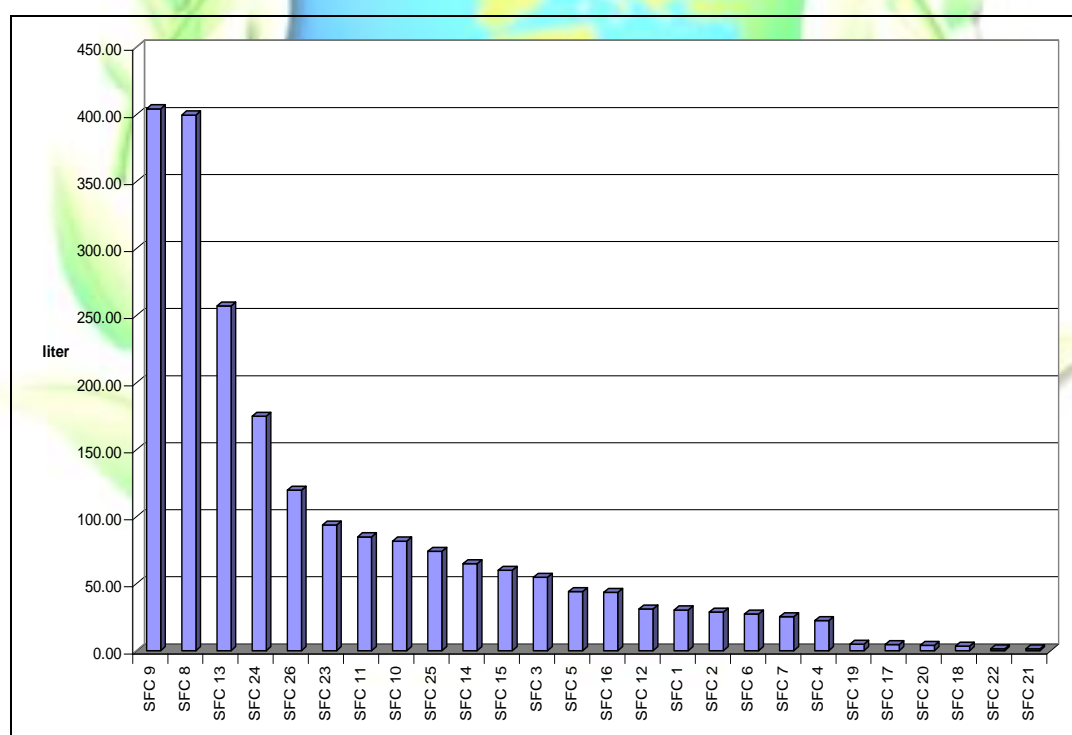
**Table 1.** SFCs details in the study area

<b>Area name</b>	<b>Site Number</b>	<b>SFC Number</b>	<b>Location UTM E N</b>	<b>Orientation</b>	<b>Elevation (masl)</b>
Schiraqi	1	1	352061 - 1729727	180	2260
Schiraqi	1	2	352061 - 1729727	270	2260
Schiraqi	2	3	352530 - 1730131	170	2450
Schiraqi	2	4	352530 - 1730131	270	2450
Schiraqi	3	5	352662 - 1730058	240	2450
Schiraqi	4	6	352887 - 1730132	180	2450
Schiraqi	5	7	352312 - 1729695	190	2300
Mabyan	1	8	346743 - 1739771	230	2020
Mabyan	2	9	346622 - 1739871	215	2030
Mabyan	3	13	347000 - 1739300	270	2000
Mabyan	4	10	347416 - 1737470	200	1650
Hajja City (Antenna)	1	11	350366 - 1735330	225	1820
Hajja City (MOA)	2	12	350114 - 1734950	180	1750
Humlan	1	14	351331 - 1733100	230	1775
Humlan	2	16	351420 - 1732770	270	1835
Humlan	3	15	351520 - 1732080	250	1890
Aschmur	1	17	366230 - 1735710	270	2840
Aschmur	1	18	366230 - 1735710	180	2840

Aschmur	1	19	366230 - 1735710	0	2840
Maswar Bait Sheim	1	20	357050 - 1728100	180	2640
Maswar Bait Sheim	1	21	357050 - 1728100	250	2640
Maswar Bait Sheim	2	22	357220 - 1728100	0	2660
Maswar Bait Saad Salah	3	23	355000 - 1727600	0	2440
Maswar Bait Saad Salah	3	24	355000 - 1727600	270	2440
Maswar Bait Saad Salah	4	25	355000 - 1727350	180	2485
Maswar Bait Saad Salah	4	26	355000 - 1727350	270	2485

## RESULTS AND DISCUSSION

Analysis of the data of the harvested fogwater during the study period (1 January - 31 March 2003) indicates that fogwater collection rates observed in the majority of the collectors were not acceptable according to Schemenauer and Cereceda (1994a), while the collection rates in collectors numbers 9, 8, 13, 24, 26 and 23 were moderate averaging about 1 liter per day (Figure 5).

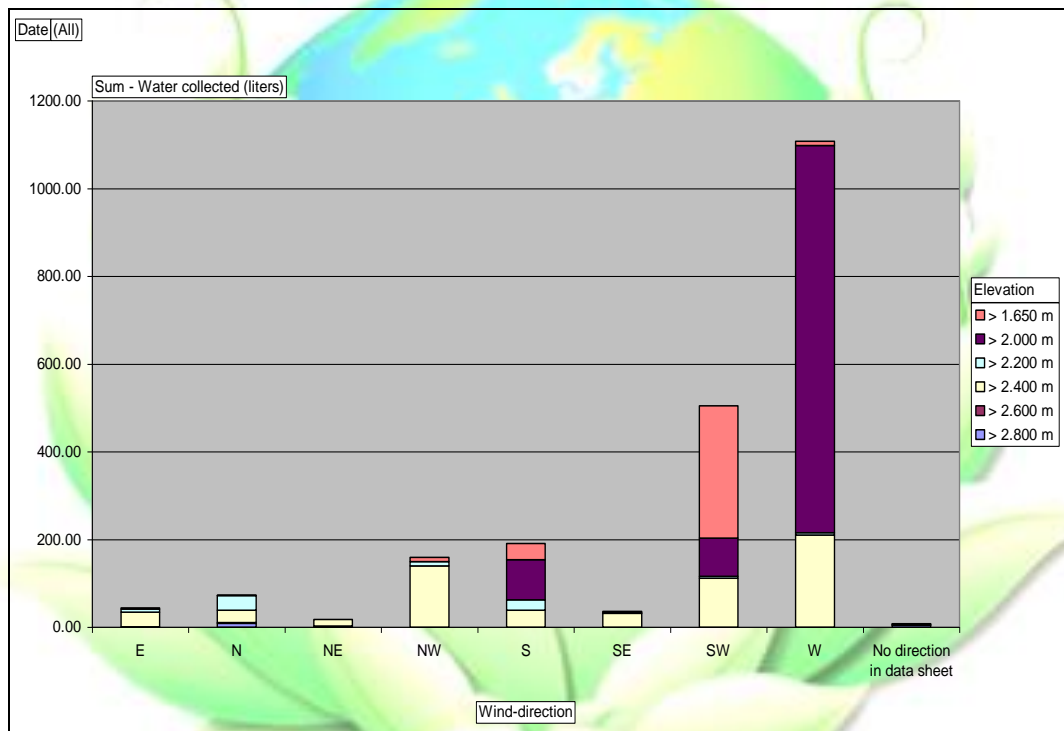


**Fig. 5.** Total fogwater collection amounts in the project area for the period 1 January - 31 March 2007.

In general, Mabyan area collection sites collected the highest water output (9, 8, and 13), with site 9, the closest site to the red sea, producing the highest measured rate (a total of 400 liters). Furthermore, analysis of the data trends during the study period have shown that the period from mid-January to the end of February is a dry period with lower water production, while during the month of March water production rate was excellent. The data also show that

some of the collectors on the highest altitude sites did not produce a significant amount of water. It is worth noting that as the climate may vary from one year to another, and therefore, determining the daily, weekly, monthly and annual climatic parameters variations is important in order to determine both the water availability and the water storage requirements.

Figure 6 shows the variation of fog collection with wind direction, which indicates the west winds are the most productive. Humid air comes from the Red Sea, with Mabian being the first mountain range encountered in its movement inland. Examination of the data of sites 9 and 8, which have the best collection rates, indicates that these sites are well exposed to winds coming from the west up a major wadi. Site 13 is in the same area but had lower collection rates, as the exposure to the west winds was not as good as the others. However, in light of the observations that collection rates were also high with southwest winds, it would be valuable to examine several new sites to the north of the city, which might be proved to be productive.

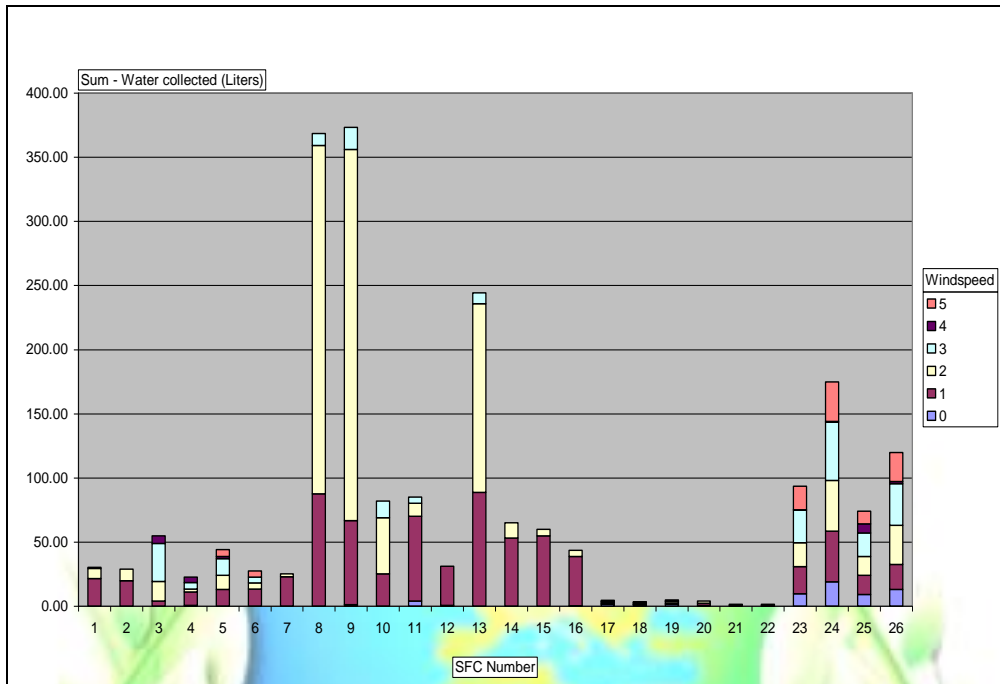


**Fig. 6.** Variation of fogwater collection with wind direction

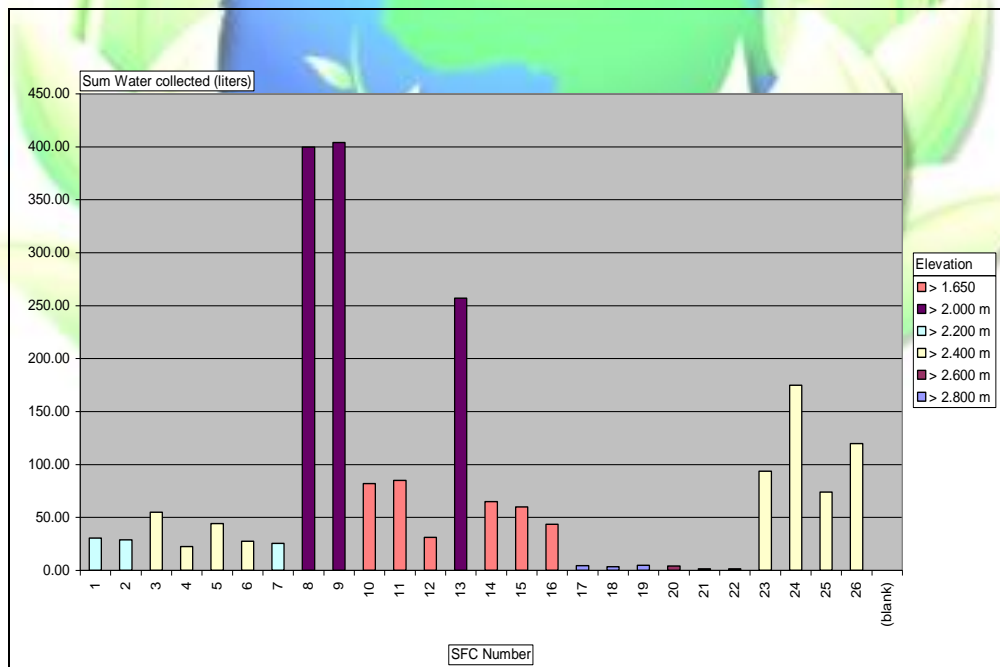
Figure 7 shows the variation of fogwater collection with different wind speeds. In Hajja governorate, fog occurs under low wind speed conditions. Almost 50% of the water collection occurred when the wind speed was around 2 of the Beaufort wind speed.

The variation of the fogwater collection with elevation is illustrated in Figure 8. the results indicate good collection amounts between elevations of approximately 2,000 and 2,500 masl. The collection rates for these sites are from 1.12 to 4.5 liters per square meter of mesh per day in the Mabian and Maswar districts.





**Fig. 7.** Variation of Fogwater collection with wind speed



**Fig. 8.** Variation of fogwater collection with altitude

This range of altitudes is a good starting point to continue testing fog collection in Yemen, especially since many villages are located at these altitudes. In general, all the ridges and mountain chains located from the north to the south that are above 2000 masl would be potentially good productive sites and need to be evaluated.



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## CONCLUSION AND RECOMMENDATIONS

The field study on fogwater collection in the western mountainous areas of Yemen indicated that, in principle, fogwater could represent an important water resource for the inhabitants with maximum water amounts occurring in the dry winter months of January to March. Fogwater harvesting might be an appropriate technological solution that can be built, managed and maintained by rural communities to be used for watering plants and afforestation.

The field study results indicated that fog collectors located closest to the red sea with an altitude range between 2,000-2,200 masl and westerly winds have produced the highest water output, reaching a maximum of about 4.5 liters per square meter of mesh per day over the three winter months period. It is recommended that more investigation is made on the relationship and impact of various climatic parameters contributing to the fog collection, such as relative humidity, temperature, and the distance from the coastline, as well as SFCs technologies. Operational requirements should be investigated, which include measurement of the volume collected and recording of meteorological data, either manually or by automatic weather station, since changes in weather conditions may change the operational design of the harvesters. Furthermore, more sites should be studied and investigated, either in Hajja or elsewhere in Yemen such as in the eastern parts of the country.

Furthermore, it is recommended that research is made on the dynamics and chemistry of fog in order to optimize quality and yield, and on the design of more efficient meshes needed to increase the yield to decrease the cost and space requirements.

## ACKNOWLEDGEMENT

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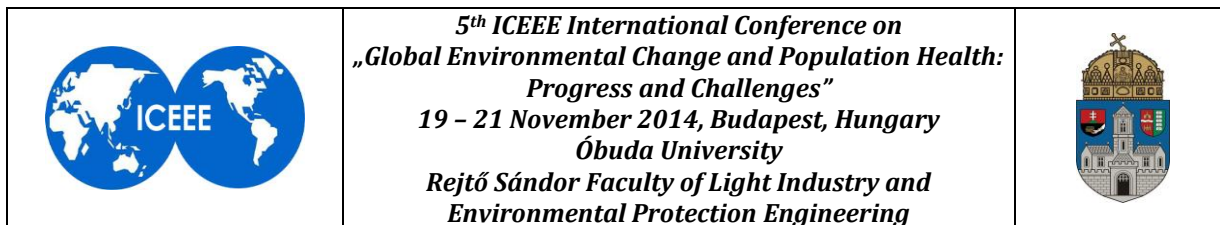
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## **ENGAGEMENT OF YOUTH IN AGRICULTURE IN BURKINA FASO: TOWARDS SUSTAINABLE DEVELOPMENT**

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### **ABSTRACT**

Africa is very vulnerable. The climatic distresses already compromise the conditions of life of the populations on a continent victim of poverty, the deterioration of the ecosystems and the civil and social unrests. More than 40,5% of Africans live in a extreme poverty and, among them, 70% live in farming zones, essentially subsisting thanks to agriculture. The climatic changes touch the agriculturists in all four corners of Africa. The entry of a big number of youth in this sector is going to accelerate probably of rhythm and to give a stroke of shoot to this sector of activity. Agriculture is recognized by African's leaders like source of growth, an instrument to improve food security, and a means to preserve the continent of the precious natural resources. But attention!!! Agriculture's already the biggest employer of Africa with an aging work hand. The present levels of investments on the projects of youth for the Agricultural and Environmental research aren't even sufficient to get the conclusive results and good outputs. Too few things have been dedicated to palliatives, as: the formations of the relief, the subsidies of the inputs, the mechanization, and the improvement of the technologies and the practices of long term management. The efforts are in progress to solve the constraints bound to the environment and the climatic risks. Agricultural and Environmental Research must as well as the structures and private Institutes, operating in these domains, greatly redoubled of effort. Some very definite programs must be established, to bring resolution at the end to the problems bound to the needs of the young in the environment but also in agriculture. Although in the past agriculture in Africa, has always been achieved by aged people, according to the requirements of the society and the profession, this tendency must turn around actually toward the African youth that is possessor of the energy and the physical strength. In Burkina, the climatic and environmental conditions don't encourage the agriculture in a general way too much: soils are poor, dry and arid, the inaccessibility of the agricultural inputs, devastating of cultures, the lack of adequate technologies. It's exactly for these reasons that youth do not take to agriculture, what has for consequence the farming exodus and the increase of the unemployment rate, and yet the economy and the development of the country depend strongly on agriculture. One very often says to Burkina that" Agriculture is the basis of the economy of the Country".

**Keywords:** *Youth, Agriculture, Environment, Research, Economy, Burkina*

### **INTRODUCTION**

Africa counts 200 millions of youngsters aged of 15 to 24 years, either more than 20% of the population. The continent knows a fast growth of its population and entered in a phase of nit demographic transition that is going to increase the pressure to which the countries are confronted in terms of creation of employment. The big majority of the young is of the farming that work mainly in the agriculture where they represent 65-70% of the total employment. More than 40,5% of the Africans live in the extreme poverty and, among them, 70% live in the

farming zones, essentially subsisting thanks to agriculture. The African youth doesn't form a homogeneous group and its perspectives of employment however not vary according to several factors (region, sex, level of instruction, etc.), what implies interventions differentiated on behalf of the public powers. Nevertheless, the entry of a big number of youngsters in this sector is going to accelerate probably of rhythm and to give a stroke of shoot to this sector of activity. Agriculture is recognized by the leaders of Africa like source of growth, an instrument to improve the food security, and a means to preserve the continent of the precious natural resources. So this survey aims to collect some information in Burkina on the implication of youth of today in agriculture and the environment at the hour of the ICT in Agriculture to put in evidence the problems and to propose some solutions.

## MATERIALS AND METHODS

- The investigation started from November 13<sup>rd</sup>, 2013 to June 31<sup>st</sup>, 2014. They investigated should answer to a set of questions. In all, 8.915.801 people have summers investigated on the period.
- The synthesis contains statistics corresponding to the answers below, as well as a summary of the commentaries received. According to the reactions and the interests expressed, new proceedings and exchanges on this topic could be thrown during the year.

- Pictures



Figure A



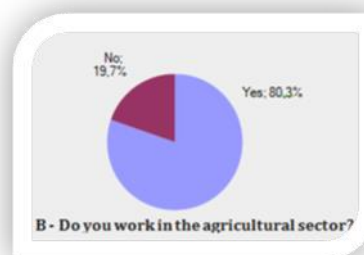
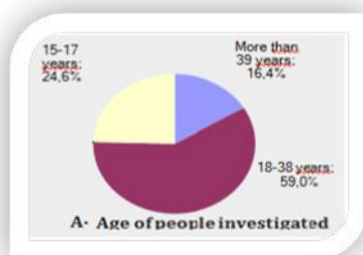
Figure B



Figure C

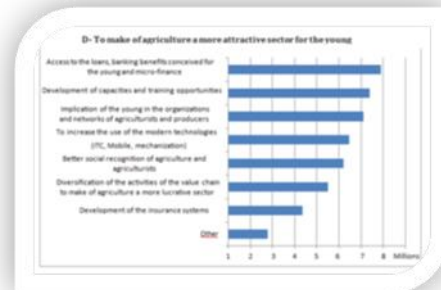
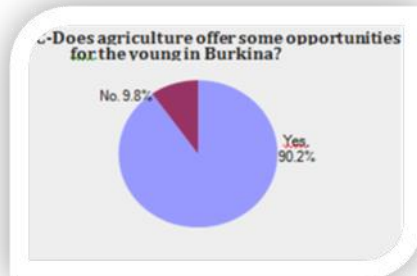
- A. Young Scientist in a experimental field
- B. Young boy weeding a field of maize
- C. Investigated zones

## RESULTS





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## CONCLUSION

Most farming youngsters don't glimpse a prosperous future in the agricultural sector, mainly because the agricultural activities are not sufficiently profitable and that the farming zones lack infrastructures and services (social in particular). However some inhale and want to become modern agriculturists and benefit the news ICT to learn new agricultural techniques and to facilitate the merchandising of their products. Conscious of the effects of the climatic change on the environment and the reduction of the natural resources, the farming youngsters are of excellent guards of the environment who promote the lasting agriculture

## ABBREVIATIONS

INSP: National institute for Statistics of the Populations,  
INERA: Institute of the environment and Agricultural Research  
MJE: Ministry of Youth and the employment,  
AJPDAB: Association of the Young Professionals for the Agricultural Development of Burkina

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## SURVIVAL OF HIGH RISK, MULTIRESISTANT BACTERIAL STRAINS IN ABIOTIC ENVIRONMENT

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### ABSTRACT

In hospitals the biodiversity of pathogens decreases compared to wild populations because of the selection pressure of the extreme environment created by humans. Serious infections and epidemics are caused by a few bacterial clones, which are able to survive on abiotic surfaces and have the effective genetic equipment against antibiotics and disinfectants. Surfaces finished with antimicrobial agents may help in the elimination of microorganisms. We believe that the practical efficiency of antimicrobial agents should be assessed using previously tested, well surviving, multidrug-resistant pathogens. Our goal is to find such bacterial strains. In this article we examined the survivability and the biofilm production of the multidrug-resistant, aerobic bacteria which cause nosocomial infections in Hungary. 5-5 strains of multidrug-resistant *Enterococcus faecium* (VRE), *Staphylococcus aureus* (MRSA), *Acinetobacter baumannii* (MACI) and *Klebsiella pneumoniae* were selected on the basis of genetic diversity and type of the origin. Surviving ability of bacteria was investigated on glass and cotton surfaces. Microtiter plates were used to evaluate biofilm formation. Gram-negative strains tolerated desiccation and 7 days of incubation significantly worse on glass than Gram-positive ones. On average, MACI strains survived better than MRSA on fabric. According to expectations VRE bacteria proved to be the most resistant on dry surfaces. *Acinetobacter* and *Klebsiella* isolates survived better on fabric, but MRSA strains proved to be significantly more resistant on slide. We did not find a difference between the survivals of VRE strains belonging to the two most frequent PFGE (Pulsed Field Gel Electrophoresis) types. The sporadic MRSA isolate was not culturable from swatches after 7 days, but on slides produced similar results as the epidemic ones. The only *K. pneumoniae* strain that was viable after a week on slides has the most resistance markers from the examined *Klebsiella* isolates. We found no connection with biofilm forming and surviving ability on dry surfaces. Our results may be important in relation to survivability on plastic materials.

**Keywords:** nosocomial pathogens, abiotic surfaces, biofilm

### INTRODUCTION

Changes in biodiversity of disease causing organisms are an example of human evolutionary impact. Even in special, artificial environments (e.g., in a hospital), natural selection controls evolutionary processes. Natural bacterial populations contain large-scale variations in their genetic material. The appropriate antibiotics and disinfectants are able to destroy the wild type bacteria, but some possess genetic tools that make them resistant. These few strains can survive in the extreme environment of hospitals, and with effective genetic equipment they are able to multiply quickly, and spread even globally. Bacteria can become resistant to an antimicrobial drug either through mutation or via horizontal gene transfer. Multiresistant, virulent bacteria, which are able to survive for shorter or longer periods outside the human body can cause serious nosocomial pandemic.



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Hospital acquired infections – which present a global public health problem – are mainly caused by only a few successful bacterial clones. A clone is a group of bacterial strains, whose common ancestry may be presumed because of their pheno- and genotyping similarity, even if they are isolated from dissimilar sources in different time. According to investigations performed by ECDC (European Centre for Disease prevention and Control) each day, 80.000 patients (i.e., every 18<sup>th</sup>) contract at least one Healthcare Associated Infection (HAI) in European hospitals. (Latour et al. 2014) Infections due to multidrug-resistant bacteria in the EU result in enormous human suffering, about 25.000 patient's death, extra healthcare costs and productivity losses of at least EUR 1.5 billion each year. (ECDC 2009) A large number of bacteria are capable of generating biofilms, which may increase their resistance against antibiotics, disinfectants, dehydration and immune defenses. (Dunne 2002) Biofilms are structured communities of bacterial cells enclosed in a self-produced polymeric matrix and adherent to inert or living surfaces. (Costerton et al. 1999) Biofilm forming strains can colonize implants (e.g., catheters, artificial cardiac valves) (Donlan 2002; Donlan and Costerton 2002) efficiently, thus they may cause chronic diseases. Therefore, the ability to produce biofilms might give relevant, complementary information about surviving on plastics.

Infections can be avoided by destructing pathogens or by preventing their growth. Surfaces finished with antimicrobial agents (for examples bedclothes, clothes, workbenches, door handles, medical instruments etc.) may help in the elimination of microorganisms. (Gauger et al. 2003; Borkow and Gabbay 2004; Sondi and Salopek-Sondi 2004) This would be particularly important in public health institutions, where lots of immunocompromised patients are exposed to many kinds of hazardous microbes. (Casey et al. 2010; Mikolay et al. 2010; Karpanen et al. 2012; O'Gorman and Humphreys 2012)

### **AIMS**



Efficiency measurements of antibacterial agents are often carried out only with standard reference microorganisms, or with a few randomly selected strains of unknown origin and genetic background. We believe that investigations of antimicrobial agents designed for hospital use should be performed with previously tested, well surviving, multidrug-resistant pathogens. If a substance proves to be effectual under these conditions, then it is probably able to destroy the other microbes, too.

Therefore our goal is to examine the survival of aerobic, multiresistant bacterial strains on abiotic surfaces, and to find the most suitable microbes for the subsequent efficiency measurement of antimicrobial agents.

### **MATERIALS AND METHODS**

We examined 5-5 strains of VRE (i.e., vancomycin-resistant *Enterococcus faecium*), MRSA (i.e., methicillin-resistant *Staphylococcus aureus*), MACI (i.e., multidrug-resistant *Acinetobacter baumannii*), and multidrug-resistant *Klebsiella pneumoniae*. Diversity in genetics and type of the origin (surfaces, clinical samples) were the main considerations during the selection of strains. The pheno- and genotyped pathogens are important epidemic clones in Hungary. The isolates were collected from different areas of the country between 1998 and 2013. Some of them are invasive strains, which originated from otherwise sterile body sites (e.g. blood, liquor etc.), others originated from non-invasive samples (e.g. nose, throat etc.) or artificial surfaces (e.g., cannula, drain, toilet bowl). Detailed information about strains are shown in the Appendix 1.



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### **Survival experiment:**

Suspensions were prepared from fresh, overnight cultures, then 20-20 µl was inoculated onto 6.25 cm<sup>2</sup> (2.5\*2.5 cm) surfaces of glass slides and swatches made from 100% bleached cotton fabric (190 g/m<sup>2</sup>). Swatches were cut from used, hospital bed sheets. The morphology of the cotton samples was analyzed using optical and scanning electron microscopy.

Actual bacterial counts (approximately 2\*10<sup>5</sup> CFU/sample) in each inoculum were determined by dilution series on agar plates (Columbia agar with 5% sheep blood, National Centre for Epidemiology, Hungary). The inoculated samples were incubated in sterile petri dishes or test tubes, at 25°C and 52% relative humidity (maintained using saturated Mg(NO<sub>3</sub>)<sub>2</sub> solution). (Rankin 2009) Bacterial cells were removed after inoculation (immediately, after drying (about 10 minutes in laboratory circumstances), after 1 hour, 1 day and 1 week), using 2-2 ml 0.9% w/v saline solution and sterile swab (in case of slides) or vortexing for 15 seconds (textile). The number of surviving bacteria were established by the serial diluting and plating method.

Results were calculated as the mean bacterial CFU (Colony-Forming Unit) per strain, incubation time, and surface material. The recoverable proportion was analyzed as the percentage of the inoculated colony counts. Reduction factor of desiccation was calculated as:  $\log_{10} C_0 - \log_{10} C_D$ , where  $C_0$  is the number of CFUs immediately after inoculation and  $C_D$  is the number of CFUs after desiccation. We used IBM SPSS Statistics Data Editor and One-Way ANOVA models to perform the statistical tests.

### **Biofilm assay:**

We examined the biofilm forming ability of every strain used in the surviving experiments, along with one positive (good biofilm forming: *Staphylococcus aureus* - ATCC 12600) and one negative (not biofilm forming: *Staphylococcus epidermidis* - ATCC 12228) controls.

We developed our own protocol for biofilm assay combining advantageous attributes of several procedures. (Kristich et al. 2004; Upadhyaya et al. 2010; Suzuki et al. 2011; Frank et al. 2013) Bacteria were multiplied in 3 ml TSB (Trypticase Soy Broth) with continuous agitation overnight, then cultures were diluted 1:200 in TSB containing 0.25% v/v glucose. Finally 200-200 µl of each strain was pipetted into 6 wells of a 96-well, U-bottom polystyrene microplate.

Culture optical density (OD) was assessed at 620 nm with microplate reader before and after incubation. Then the medium was pipetted out and wells were washed three times with 100-100 µl saline to remove all of the planktonic cells. Adherent biofilms were fixed with 200 µl 96% ethanol for 5 minutes, then stained with 100 µl 0.1% safranin for 2 minutes. After rinsing (200-100-100 µl saline) the superfluous stains, we dissolved the safranin (100 µl 96% ethanol, 10 minutes) bound in the biofilms, and measured the absorbance of the 50 µl solution at 492 nm.

## **RESULTS AND DISCUSSION**

### **Survival experiment**

The microscopic photographs are shown in Figure 1. Damage to the fabric is visible on the pictures, which is probably caused by daily use (the fabric was originally used as a bed sheet in a hospital ward). The structure of the fabric is uneven: due to yarn migration, the distances between two yarns are different. (Figure 1/A) Many elementary fibres have partially left the yarn. The surfaces of the yarns are fuzzy, due to many repeated washing and possible tumble drying cycles (Figure 1/B). All fibres are strongly fibrillated. The elementary fibres are mostly flattened by calendaring. (Figure 1/C) The increased surface of the fabric and the presence of very fine fibrils might support the adhesion of microbes.





## Textile

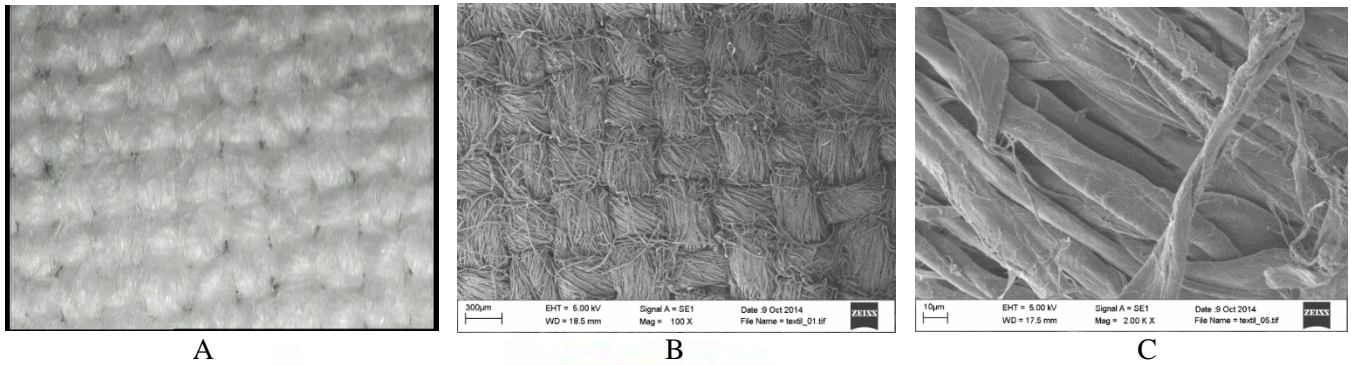


Figure 1

A: Optical Microscope image of cotton fabric B, C: Scanning Electron Microscope photographs of cotton fabric.

### Recoverable proportion:

During the survival experiment, we removed the bacterial cells immediately after inoculation to measure the proportion of cells adhered to the surfaces. The recoverable proportion varied largely on glass slide and also on cotton swatch, ranging 17.47 % – 97.52 %, and 15.69 % – 67.88 %, respectively. The average recoverable proportion was 53.26 %. Wendt *et al.* obtained a similar result in their study of four other surfaces (Wendt *et al.* 1997). We compared the recoverable proportions from the two kinds of surfaces by all species. *Klebsiella pneumoniae* strains are significantly more recoverable from glass than from textile ( $P < 0.01$ ). Adhesion reduced the recoverable bacterial counts by 0.01  $\log_{10}$  steps (MRSA on glass slides) to 0.8  $\log_{10}$  steps (MRSA, *Klebsiella p.* and VRE strains on textile). According to Wendt *et al.* strains isolated from the environment adhere better to the surface than bacteria derived from patients. (Wendt *et al.* 1998) Our results do not show any relation between recoverable proportion and source of strains. Although a VRE strain (2013-045039) isolated from an intravascular device adhered very strong to the glass slide (mean recoverable proportion: 17.4%), but at the same time it was the most retrievable VRE strain from swatch (mean 52.75%). Moreover, *Acinetobacter baumannii* strain 2013-010034, collected from a drain, was found to be 91.5% recoverable from glass.

### Reduction by desiccation:

Desiccation reduced the colony counts on average by 1.30  $\log_{10}$  and 0.45  $\log_{10}$  steps on glass and on fabric, respectively. The reduction of colony counts during desiccation varied ranging 42.69 % (*Enterococcus sp.*) – 99.33% (*Klebsiella p.*), and 26.25 % (MRSA) – 69.08 % (*Klebsiella p.*) on glass and on textile, respectively.

### *Enterococcus sp.*:

All five strains remained viable on glass slide and also on cotton swatch and they were recoverable in magnitudes of  $10^2$  and  $10^3$  after seven days. VRE strains proved to be resistant in other survival experiments, too. (Noskin *et al.* 1995; Otter and French 2009) Comparing the survival of VRE strains on the two surfaces, we did not find appreciable differences (Figure 2). The examined strains belong to the two most frequent PFGE types (Berta *et al.* 2013), we did not find a difference between their survivals. Deviation between standard reference strains and isolates from invasive samples is a debated question in scientific literature. According to some authors there is a significant difference (Jawad *et al.* 1998), while others do not find evidence about this. (Otter and French 2009) For comparison we tested the surviving ability of a sensitive *Enterococcus faecalis* strain (ATCC 29212). The recoverable CFU already decreased greatly after one day on textile, and after seven days we did



not find any living bacteria. The sensitive strain was less viable than multiresistant ones on glass surface, too, but the difference was less obvious.

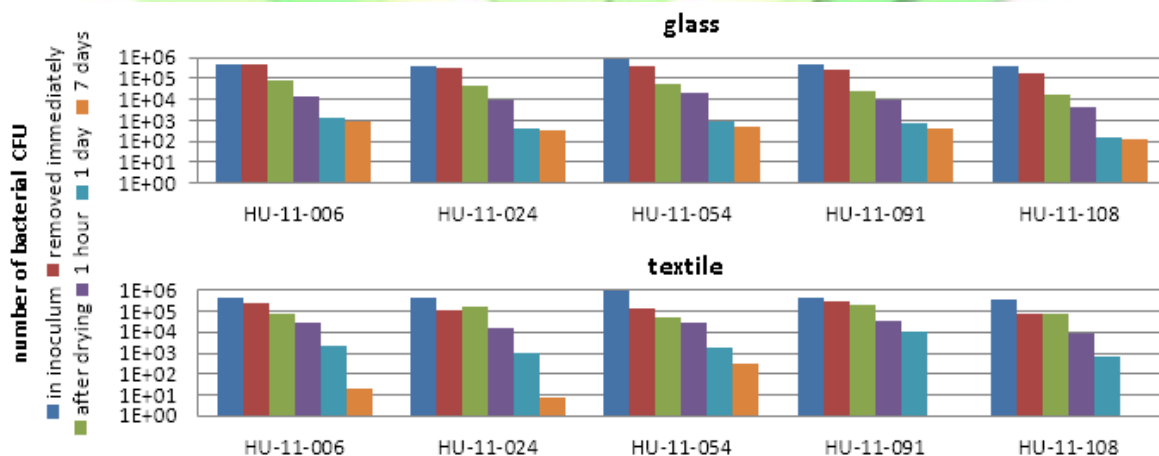


**Figure 2**  
*Surviving ability of Enterococcus spp. strains (x-axis) on dry surfaces*

**Methicillin-resistant Staphylococcus aureus (MRSA):**

After a week of incubation MRSA strains proved to be significantly more resistant on slide than on cotton ( $P < 0.05$ ), although these strains were the least sensitive to desiccation on textile. Two MRSA strains (sporadic HU-11-108, and HU-11-091), which belongs to the t002, one of the most frequent *spa*-type in Hungary (Ungvári et al. 2012)) were not culturable from swatches after 7 days (Figure 3). Neely *et al.* also experienced (Neely and Maley 2000) that MRSA strains are less viable on 100% cotton fabric, but according to their article these pathogens are able to survive longer on polyester and on polyethylene swatches. On glass surface MRSA strains did not show any differences in survival ability. The sporadic (isolatedly appearing) HU-11-108 strain and the epidemic pathogens produced similar results. It is possible that differences experienced in other researches can be detected only in long-term investigations. (Beard-Pegler et al. 1988; Wagenvoort et al. 2000)

We did not notice any differences between hospital and community-acquired MRSA strains.

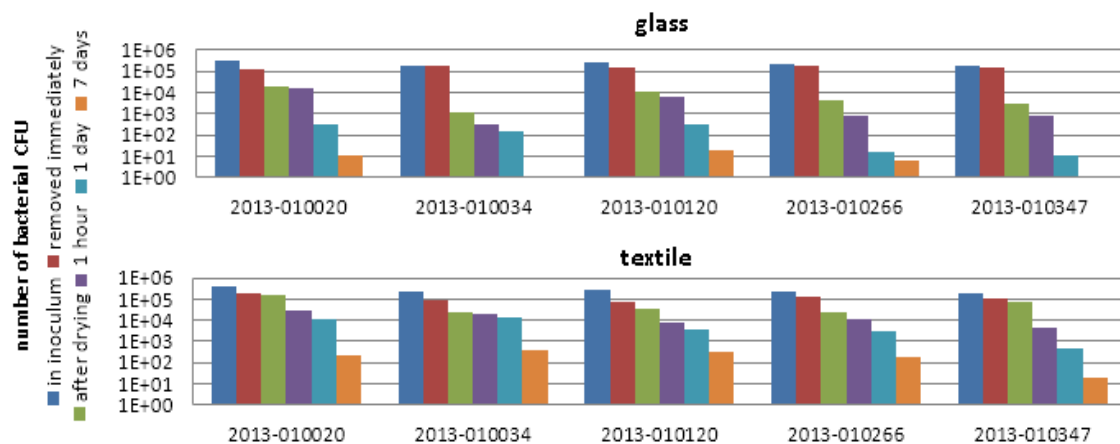


**Figure 3**  
*Surviving ability of Staphylococcus aureus strains (x-axis) on dry surfaces*



#### Multidrug-resistant *Acinetobacter baumannii* (MACI):

The gram-negative, multiresistant *A. baumannii* strains were very resistant on dry textile swatches. They showed similar behavior to the Gram-positive isolates (VRE, MRSA) based on the results of the one week examination. On glass two strains perished in less than a week (Figure 4), and the other three ones survived only in a few numbers, contrary to expectations. In another research (Jawad, Seifert et al. 1998) it was measured 23-32 days of surviving time, albeit from a larger inoculum ( $10^7$  CFUs). While Wendt *et al.* (Wendt, Dietze et al. 1997) found no difference regarding the material qualities of the surfaces, *Acinetobacter b.* strains survived significantly ( $P < 0.025$ ) better on textile according to our investigation.



**Figure 4**  
Surviving ability of *Acinetobacter baumannii* strains (x-axis) on dry surfaces

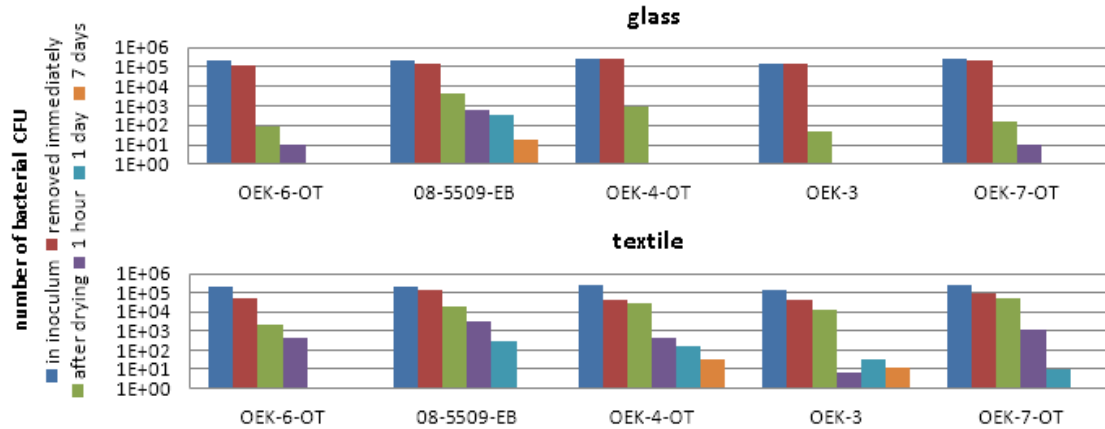
#### Multidrug-resistant *Klebsiella pneumoniae*:

From the four species, *Klebsiella pneumoniae* strains were the least viable on dry surfaces. Other authors reported similar results. (Otter and French 2009) They were significantly ( $P < 0.05$ ) less recoverable than the other species after desiccation, after 1 hour, 1 day, and 1 week, too.

*Klebsiella p.* isolates survive better on cotton: after a day and a week, four and two strains showed growth, respectively (Figure 5).

On slides, two from the five strains were not culturable after an hour. The only strain (08-5509-EB), that was viable after a week, has the most resistance markers from the examined *K. pneumoniae* isolates. It produces extended-spectrum beta-lactamase (SHV-12 type ESBL) and carbapenemase enzyme (KPC-2), which make it resistant to almost all beta-lactame antibiotics. The same strain perished in less than a week on fabric.

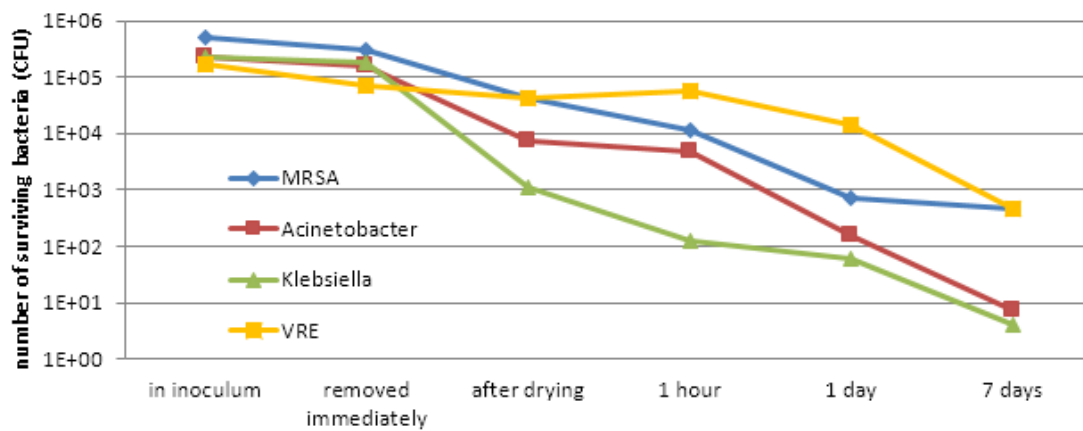




**Figure 5**  
Surviving ability of *Klebsiella pneumoniae* strains (x-axis) on dry surfaces

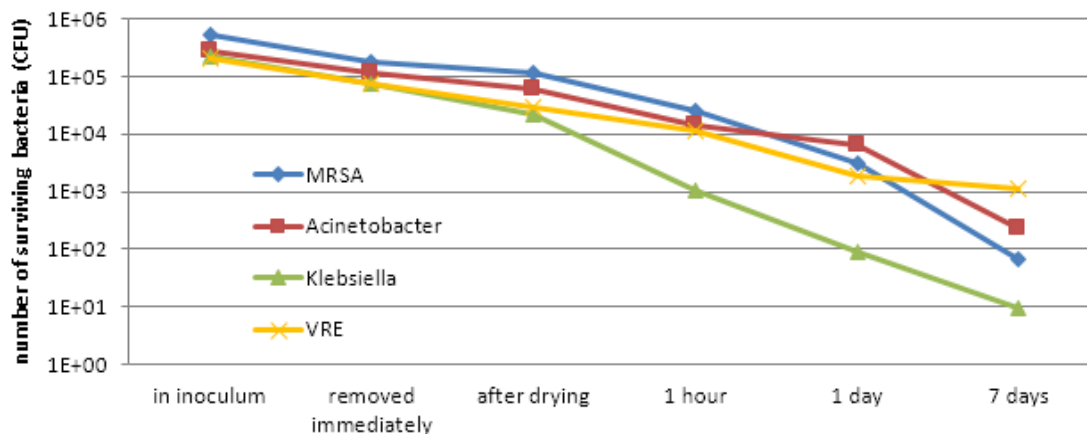
**Gram-negative vs. Gram-positive bacteria:**

Gram-negative strains (*Klebsiella pneumoniae* and *Acinetobacter baumannii*) tolerated desiccation significantly ( $P < 0.01$ ) worse on glass than Gram-positive ones (VRE and MRSA). The difference was significant ( $P < 0.01$ ) after seven days, too. (Figure 6)



**Figure 6**  
The average surviving ability of the four bacterial species on glass slide

On textile, no significant difference was found between the two groups. (Figure 7) The *A. baumannii* strains were as survivable as Gram-positives. On average, they were better recoverable than MRSA, but this result is not significant. Otter et al. also reported high survivability of *Acinetobacter b.* strains on steel discs. (Otter and French 2009)



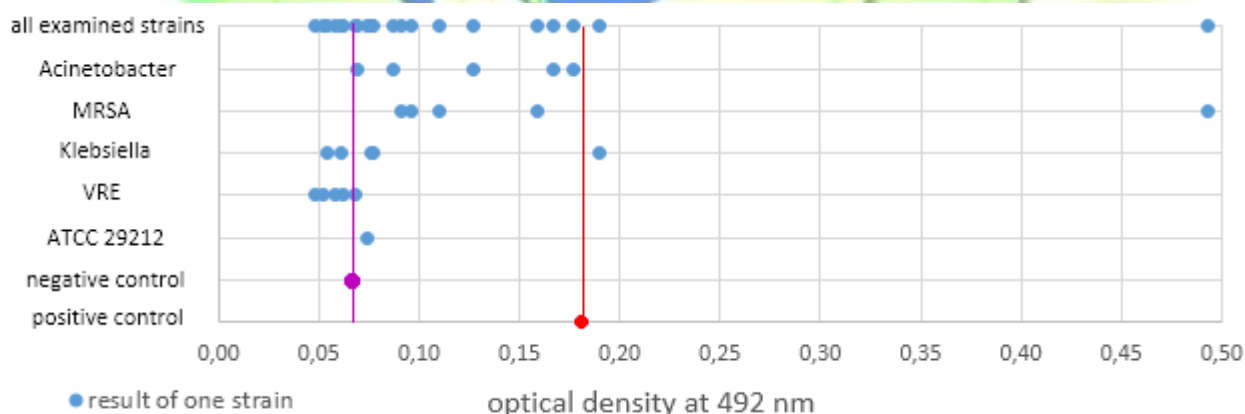
**Figure 7**  
*The average surviving ability of the four bacterial species on fabric*

### Biofilm assay:

We carried out six parallel tests for every bacterial strain. The mean biofilm forming ability is shown on Figure 8. We found no connection with biofilm forming and surviving ability on dry surfaces. Our results may be important in relation to survivability on plastic materials.

Even though VRE isolates showed good survival abilities, they are all very weak biofilm producers, some of them fell short of even the negative control. *Klebsiella p.* isolates showed similarly low biofilm forming abilities, except one strain (OEK-4-OT), which reached the result of the positive control.

We found one exceptionally good biofilm producer MRSA strain (HU-11-108), which showed more than 2.5 times the optical density of the positive control. There are two *Acinetobacter b.* isolates (2013-010034 and 2013-010120), whose results approached the positive control. Interestingly, these were the same two strains that did not survive a week on glass.



**Figure 8**  
*The biofilm forming ability of bacterial strains*

## CONCLUSION

In this article we examined the survivability and the biofilm production of the multidrug-resistant, aerobic bacteria, which cause nosocomial infections in Hungary. In hospitals the biodiversity of



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pathogens decrease compared to wild populations because of the selection pressure of the extreme environment created by humans. Serious infections and epidemics are caused by a few bacterial clones, which are able to survive on abiotic surfaces and have the effective genetic equipment against antibiotics and disinfectants. Our goal is to find these successful bacteria, which may be suitable for testing antibacterial agents made for hospital use.

Our results demand confirmation because of the small number of examined strains, but indicate the further direction of our research. This investigation corroborates the ability of high risk, nosocomial bacteria to survive many days on abiotic surfaces even in large numbers. Such surfaces may be the source of infections or transmission.

The majority of the strains showed better survivability on textile than on glass. This may be important because fabrics (nightclothes, sheets): *i.* are in direct contact with the body even for longer periods (days), *ii.* may be disinfected with only complex processes (washing), *iii.* may keep alive the pathogens longer next to the skin, owing to the body temperature, and the presence of humidity and nutrients.

Biofilm forming bacteria can adhere to plastic medical devices used within the body, and can cause serious acute or chronic infections. It is difficult to defend against such pathogens even with antibacterial agents. It may be worth examining the survivability of good biofilm producing strains on plastic surfaces. Surface characterization and description of bacterial cell walls could help find the explanation to the different survivability of the strains.

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### APPENDIX 1

species	number of the strain	year of isolation	source of the sample	town, hospital ward	important resistance marker	typing		
						spa	PFGE	clonality
<i>Acinetobacter baumannii</i>	2013010020	2013	cannula	Cegléd	OXA-23		AC020	EU-II
<i>Acinetobacter baumannii</i>	2013010034	2013	drain	Budapest	OXA-58		AC020	EU-II
<i>Acinetobacter baumannii</i>	2013010266	2013	decubitus	Budapest	OXA-23		AC042	EU-I
<i>Acinetobacter baumannii</i>	2013010347	2013	liquor	Budapest, neurosurgery	OXA-23		AC042	EU-I
<i>Acinetobacter baumannii</i>	2013010120	2013	bronchus	Debrecen	OXA-23		AC057	
<i>Enterococcus faecium</i>	2012045015	2012	inside of toilet bowl	Pécs	vanA		ENTCO-002	
<i>Enterococcus faecium</i>	2012045086	2012	sanies	Budapest, intensive care unit (ICU)	vanB		ENTCO-016	
<i>Enterococcus faecium</i>	2013045039	2013	intravascular device	Budapest, ICU	vanA		ENTCO-002c	
<i>Enterococcus faecium</i>	2013045043	2013	sanies	Szolnok, depart. of internal medicine	vanB		ENTCO-016	
<i>Enterococcus faecium</i>	2013045183	2013	urine from long term catheterisation	Zalaegerszeg, emergency depart.	vanA		ENTCO-002	
<i>Klebsiella pneumoniae</i>	OEK4-OT	1998	throat	Kecskemét, neonatal intensive care unit (NICU)	SHV-2a			ST25
<i>Klebsiella pneumoniae</i>	OEK3	2005	blood culture	Budapest, ICU	CTX-M-15			ST15
<i>Klebsiella pneumoniae</i>	OEK6-OT	2006	blood culture	Budapest, neurosurgery	CTX-M-15			ST274
<i>Klebsiella pneumoniae</i>	OEK7-OT	2008	blood culture	Vác, pediatrics	SHV-2a			ST274
<i>Klebsiella pneumoniae</i>	08-5509-EB	2008	nasal	Miskolc, neurosurgery	SHV-12, KPC-2			ST258
<i>Staphylococcus aureus</i>	HU-11-006	2011	blood culture	Budapest, other bad-patient depart.	mecA	t011	NT	
<i>Staphylococcus aureus</i>	HU-11-024	2011	blood culture	Székesfehérvár, emergency depart.	mecA	t032	D6	
<i>Staphylococcus aureus</i>	HU-11-054	2011	blood culture	Szeged, other bad-patient depart.	mecA	t022	D6	
<i>Staphylococcus aureus</i>	HU-11-091	2011	blood culture	Kecskemét, ICU	mecA	t002	A1	
<i>Staphylococcus aureus</i>	HU-11-108	2011	blood culture	Szombathely, bad-patient depart.	mecA	t121	sporadic	

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## **MONITORING OF DIFFERENT HEAVY METALS IN SOIL SAMPLES DERIVED FROM VALLEY SAJÓ AND NEAR LAKE “VERESMART”**

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Several pollutants threaten our environment. Some of the harmful materials are the heavy metals, which are a risk for soil-, plant-, water- and air systems. For each heavy metal it can be said to occur in nature without anthropogenic influences. However, human exposure often drastically changes the amount of these substances mainly along the industrial plants, mines and densely populated areas. Naturally, they are present in amounts, which can be harmful in some cases, and today there is hardly possible to find a place on earth where one can not detect any contamination from the human activity induced by a harmful process. For the above reasons, valley Sajó (Hungary) and near Veresmart Lake were chosen for monitoring of heavy metal concentrations. Samples were digested by Milestone 1200 Mega microwave oven. Heavy metal concentrations were measured by ICP-OES and atomic absorption spectrometry. In several soil sampling places the heavy metal concentrations were higher, than contamination limit values.

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***Keywords:** pollutants; monitoring of heavy metal concentrations*

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## **PANORAMIC ENVIRONMENTAL HABITATS OF (PLIOCENE – RECENT) AS-SAHABI AREA, NORTHERN LIBYA**

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As-Sahabi area is located to the south of Ajdabiyah city in Sirt Basin, Libya. This area considered as a spectacular open Museum of vertebrate remains (i.e. teeth, bones, skulls and skeletons) of mammals, reptiles, aves and Fish. This paper will presents the methods used during the excavation and lists most of the documented taxa and finally compare these paleo-habitats with the corresponding present day habitat of As-Sahabi.

The As-Sahabi fossils played important role in delineating the paleoenvironment and in understanding the migration routes as well as in tracing their evolutionary trends. These remains are preserved in continental deposits (mainly sands and clays) since 5 million years ago. Seven habitats have been suggested “Desert, Savannah-like forest, river, lake-swamp, lacustrine and shallow sea”.

As-Sahabi vertebrates (e.g. crocodiles, hippos, hyena, etc.) are considered to be the ancestral taxa of the descendant vertebrates exist today in other parts of the world. However, some are found to be indigenous taxa due to migration failure such as gigantic size, Mastodon (*Stegotetrabeledon lybicus*) and shovel-tusker proposcidean (*Amebelodon cyrenaicus*) or medium-sized with short-legged Anthracothere (*Libycosaurus petrocchii*).

**Keywords:** *Environmental habitats; Sirt Basin; Sahabi; Sahabi vertebrates*

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## **CU AND ZN IMPACTS THE BIOLOGICAL ACTIVITY AND PLANT GROWTH IN SOIL AMENDED WITH COMPOST**

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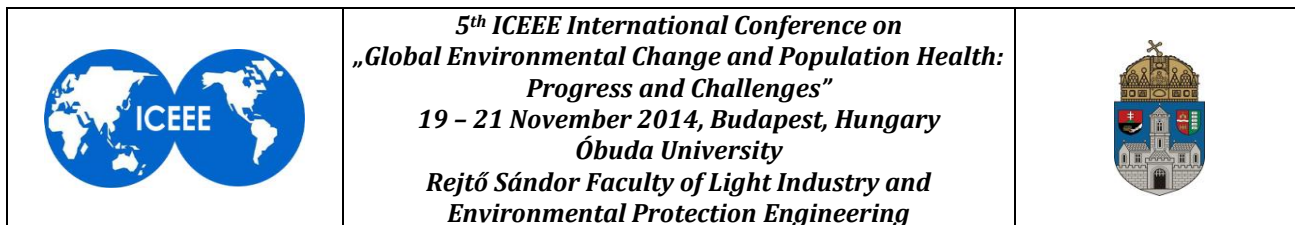
### **Abstract**

Reducing solubility and bioavailability of heavy metal in contaminated soil without removing them is common practice in decreasing the negative impacts on the environment and improving the soil quality. Increasingly, composting is becoming an environmentally and economically alternative technique for applying organic waste materials to soil. The objective of this study is to evaluate the effects of compost applied at different rates in the presence or absence of Cu or Zn on plant biomass, microbial and enzymatic activities in clay loam brown forest soil. The compost-soil system was cultivated with mustard plant for 30 days. The result showed that the Cu or Zn at 100 or 300 mg/kg, respectively contaminated compost-soil system improve the plant growth and soil microbial and enzymatic activities but not at with 150 and 400 mg/kg, respectively. Overall, the results suggest that addition of compost could enhance the soil fertility, improved the soil hydrolytic enzymatic activities compared with control soil (Cu and Zn free and without compost material) and promote plant growth. The addition of OM may be considered as a good strategy for remediating HM contaminated soil. For stabilizing Cu and Zn contamination in soil, large amount of compost of high organic matter should be added.

**Keywords:** *Compost; copper; zinc; enzyme activities; mustard plant growth*

### **INTRODUCTION**

Reducing solubility and bioavailability of heavy metal (HM) in contaminated soil without removing them is common practice in decreasing their negative impacts on the environment and improving the soil quality. Soil quality is a complex characteristic, and is determined by the physical, chemical, and biological components of the soil (Johansson et al., 1999). Changes in soil biochemical characteristics may be good indicators of soil quality, since they are more dynamic and often more sensitive than physical or chemical soil properties (Friedel et al., 2000). Such information is required to detect any possible toxicities resulting from the use of organic fertilizers and as an indicator of soil rehabilitation. The behaviour of Cu in organic wastes shows similarities to Zn, Wen et al. (2001) demonstrated that Cu produces more severe quenching of ATP bioluminescence than Zn. This implies that the Cu potential toxicity to soil microorganisms could be more severe than Zn. Copper is known to have high affinity for various organic compounds (McBride, 1989) and several studies have shown that Cu has a stronger tendency to form organic complexes than Zn (Bell et al., 1991). Increasingly, composting is becoming an



environmentally and economically alternative technique for applying organic waste materials to soil. Through composting, organic matter (OM) is converted into nutrients for plant growth and soil conditioner for improving soil physicochemical properties which are adversely affected by high levels of HMs. The mobility, bioavailability and ecotoxicity of HMs are depending on their specific chemical forms, way of binding and nature of soil introduced in it.

For remediation of HMs contaminated soil, it important to applying compost of significant amount of humic substances that could adsorb HMs temporarily by stable complexes formation and adsorb them for long time interval. This practice is useful for increases the biomass and microbial activity and improving the nutrient recycling and soil physical properties too.

Many enzymes response immediately to changes in soil fertility can be used as early indicators of biological changes and potential to sustain of microbial activity. Hazardous organic and metallic residues or by-products can enter into plants and soils from processes associated with domestic, municipal, agricultural, industrial, and military activities. One method of stabilizing degraded areas is to add OM in order to improve physical, chemical, and biological characteristics (Ros et al., 2003). The soil microbial community should be a sensitive indicator of metal contamination effect on bioavailability and biogeochemical processes. The ultimate goal is to enhance biogeochemical nutrient cycles and increase the soil productivity. However, it has been shown that with time organic amendments lose their effectiveness; therefore, making recovery of HM contaminated sites difficult (Pierzynski et al., 2002). Mild white mustard plant (*Sinapis hirta*) is used in phytoremediation to remove HMs from the soil in hazardous waste sites because it has a higher tolerance for these substances and stores the HMs in its cells. This method is easier and less expensive than traditional methods for the removal of HMs and prevents erosion of soil.

The objective of this study is to evaluate the effects of compost applied at different rates in the presence or absence of Cu or Zn on plant biomass, microbial and enzymatic activities in clay loam brown forest soil.

## **MATERIALS AND METHODS**

Large glass test tube (220 mm x 30 mm in size) experiments were established to study the impacts of compost at 0, 2.5, 5 and 10% that was contaminated with Cu (0, 50, 75, 100, 150) or Zn (0, 100, 200, 300, 400) in mg/kg soil on microbial biomass C (MBC,  $\mu\text{g/g}$  soil) was determined by chloroform fumigation extraction method (Vance *et al.*, 1987)., dehydrogenase (Dh,  $\mu\text{g INTF/g}$  soil) activity using the method of García *et al.* (1993).  $\beta$ -glucosidase (Glu,  $\mu\text{mol PNP/g}$  soil/h) was measured according to Masciandaro *et al.* (1994). Protease (Prot,  $\mu\text{gmol NH}_4^+\text{-N/g}$  soil/h) activity was measured by the method of Nannipieri *et al.* (1980). aryl-sulphatase (AryIS,  $\mu\text{mol PNP/g}$  soil/h) activity was determined as proposed by Tabatabai and Bremmer (1970), phosphatase (Phos,  $\mu\text{mol PNP/g}$  soil/h) activity was estimated according to Tabatabai and Bremmer (1969), soil organic carbon (SOC, g/kg soil) and soluble organic carbon (HWSOC) using hot water method according to the methods of Walkley and Black (1934) and Haynes *et al.* (1991), respectively, in clay loam brown forest soil (originated from Gödöllő, Hungary) as well as plant dry weight (PDW, dried at 60°C, g/tube).

Aerobe heterotroph mesophile bacteria (AHMB,  $\times 10^6$ ), actinomycetes (ACT,  $\times 10^5$ ) and fungal populations (FUNG,  $\times 10^4$ ) were counted according to Szegi (1979). Fifty gram of amended soil was placed in large glass test tube. Treatments were replicated three times for each treatment and randomized within each replicate. The control tube contained untreated soil. The compost-soil system was cultivated with mustard plant. Soil was sampled at 30 days after sowing and



stored at 4°C then sieved and analyzed for microbial properties and enzymatic activities as well as the plant growth.

## RESULTS

Treatments lower and higher 100 mg Cu /kg and 300 mg Zn /kg soil doses with different rates of compost content had no significant differences higher than the control. Table 1 gives different biological measurements in mustard rhizosphere after 30 days of incubation under different amendments. For All investigated parameters, Zn contaminated compost treatments were significantly higher than Cu contaminated compost samples, while all high compost additions had significantly higher enzymatic activities than control. This indicates that high compost additions are still effectively maintaining microbial populations at 30 days after treatments.

Table 1. Monitoring the impacts of Cu (100 mg/kg) or Zn (300 mg/kg) contaminated compost amended to clay loam brown forest soil cultivated with mustard plant on microbial and enzymatic activities and plant dry weight after 30 days of incubation

Amendments of HM (mg/kg)	Tested Parameters	Compost rates (%) amendments			
		0	2.5	5	10
0	AHMB	5.6	6.2	6.9	7.6
	ACT	3.6	3.9	4.4	4.9
	FUNG	5.1	5.8	6.5	7.1
	MBC	256.1	274.3	284.7	314.7
	Dh	123	154	167	199
	Glu	115	128	151	192
	Phos	91	124	157	179
	Aryl-S	82	97	122	165
	Prot	1.7	2.2	2.6	3.1
	HWSOC	65.2	91.1	122.8	154.3
	SOC	5.44	5.98	6.64	7.1
PDW	0.23	0.27	0.35	0.41	
Cu	AHMB	5.7	6.8	7.8	8.8
	ACT	4.1	5.4	6.6	7.3
	FUNG	5.7	5.9	6.8	7.1
	MBC	263.8	321.7	354.8	398.2
	Dh	128	141	189	237
	Glu	119	137	188	207

	Phos	97	128	163	191
	Aryl-S	87	105	138	178
	Prot	1.8	2.1	2.5	3.6
	HWSOC	69.7	98.4	134.5	161.1
	SOC	6.03	7.97	8.33	9.45
	PDW	0.26	0.32	0.39	0.44
Zn	AHMB	6.4	8.2	10.27	12.4
	ACT	4.7	5.91	7.02	8.1
	FUNG	6.3	6.9	8.12	9.27
	MBC	279.4	351.6	371.2	421.1
	Dh	128	144	211	243
	Glu	121	156	204	229
	Phos	98	129	178	214
	Aryl-S	87	143	201	253
	Prot	1.8	2.2	2.8	3.9
	HWSOC	69.8	100.7	145.6	173.6
	SOC	6.89	8.56	9.33	10.79
	PDW	0.27	0.35	0.42	0.48

The compost containing Cu more inhibited the enzymatic activity than Zn. Almost all soil hydrolytic enzymatic activities were significantly ( $P < 0.05$ ) affected by amendment doses. A significant increase of all the measured activities was observed after 30 days at all doses except highest doses. Also, the results indicate that soil enzymatic activities decreased with increasing the concentrations of Cu and Zn over 100 and 300 mg/kg, respectively.

The treatment of Zn compost was significantly able to increase the microbial content than Cu compost treatment. The aerobe heterotroph mesophile bacteria, actinomycetes and fungal count were high at these treatments in comparison with the control. Additionally, tubes with increased plant growth had significantly higher levels of microbial biomass, suggesting a rhizosphere effect.

The result shows that Cu or Zn contaminated compost-soil system improve the plant growth and the microbial functioning and MBC at lower levels of 150 and 400 mg/kg, respectively. Almost all soil hydrolytic enzymatic activities were significantly (at  $P < 0.05$ ) affected by amendment doses lower than 150 and 400 mg/kg soil, respectively. Also, it was found that Cu and Zn immobilization is greater in soil of high organic matter content (at 10%) in comparison with control soil. Amount of total organic carbon and soluble organic carbon content decreased by increasing the concentrations of Cu than Zn over 100 and 300 mg/kg respectively.

## DISCUSSION

Bioavailability of metals can be decreased by the addition of organic matter to soil by formation of insoluble metal organic complexes with humic acids, thereby lessening risk of metal toxicity to plants and microbes (Kirkham, 1985). In our study, the addition of compost led to higher values of MBC as compared to control soils. By contrast, in the presence of compost, dehydrogenase values were higher. Compost as organic fertilizers and HMs may create environmental problems and the possibility of soil pollution should be taken into consideration. The present study provides further evidence of the positive effects that organic amendments have on the biological activity of HM contaminated soils. The OM material provides a mechanism for metal retention, improves soil chemical properties, and provides a nutrient/energy source for plants and microbes. Soil enzyme activity was used to test the biochemical status of the soil-plant system. High applications of compost were able to stimulate enzyme activities, increase microbial content and biomass, and increase microbial community structure. Results suggest that a high application of Zn compost improved the soil biological status over the Cu contaminated compost and control soil, in particular restoring soil microbiological properties and/or function to a higher level. It is important that these tubes continued to be monitored to see if the level of organic fertilizer amendments added can sustain this production for an extended period of time and large scale.

Overall, the results suggest that addition of compost could enhance the soil fertility, improved the soil biological activities compared with control soil and promote plant growth. Addition of OM may be considered as a good strategy for remediating the HM contaminated soil. For stabilizing Cu and Zn contamination in soil, large amount of compost of high organic matter content should be added.

Since many enzymes and microbial biomass respond immediately to changes in soil fertility, they can be used as potential indicators of soil quality (Garcia et al., 2000). Bhattacharyya et al. (2010) mentioned that understanding of the dynamics of SOC as affected by farming practices is imperative for maintaining soil productivity and also for restraining global warming by CO<sub>2</sub> evolution, and increased SOC contents. These results are confirmed by our observations. This practice is useful for increases the biomass and microbial activity and improving the nutrient recycling and soil properties too. Tested enzymes are sensitive indicators of management-induced changes in soil properties because of their strong relationship with quantity and quality of SOM.

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## **INVESTIGATION OF GAS EMISSION IN FOOD CHAIN REACTOR SYSTEM**

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Due to industrial development greenhouse gas (GHG) emission pollution causes global problems all over the world. In this context over the last few years environmental monitoring and prevention of pollution are becoming increasingly important. The production of the clear drinking water became especially important. In the known technologies are examined very often e.g. heavy metals, but very rarely the greenhouse gas emissions.

In sewage treating processes, waste water cleaning in wetlands promote the beneficial activity of sludge, plants and associated microbial communities. There is a lot of potential in optimisation of wetlands for different goals. However, it is an important issue how to facilitate the process of cleaning gas emission change occurs.

The aim of our project was to develop the sewage treating cascade technology of the Food Chain Reactor (FCR) system at Organica increasing the cleaning effect and increases the speed the purification process. During the research the investigated plant and artificial media improved the cleaning efficiency, but increases gas emissions in the process.

The most important element of the developed system was the microbe carrier. To our best knowledge the selected plant (*Miscanthus*) has not been used as a natural carrier yet.

**Keywords:** *gas emission; Food Chain Reactor system*

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## **ARAB FOOD SECURITY CHALLENGES AND OPPORTUNITIES**

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### **ABSTRACT**

Live Arab State of food deficit increasing severity, day after day the volume of food is not enough to cover consumption, which requires resort to import to cover the shortfall, resulting in many of the economic problems, where the weakening balances of foreign exchange and promote indebtedness and dependency political and economic major states.

This study attempts to specify the elements, factors and policies which affecting the food security in the Arab countries. In this study, we argued that the most important causes of food-deficit lies in the uneven distribution of resources between countries and energies necessary for agricultural development, natural resources, human and financial, and that poverty is a major cause of food insecurity.

Arab food gap is characterized by Arab food gaps to fluctuate from year to year due to changes in agricultural production and the volume of consumption and fluctuations in world prices for food commodities. The growing food gap and the degradation rates of self-sufficiency in the Arab world allows saying that food security is still a dream not realized until this moment, and requires to achieve in the future to take a set of attitudes and actions consolidated and integrated to remove the problems that hinder development in general and agricultural development in particular. The paper concludes that it is clear the food gap in the Arab world that have reached critical levels, is the result of a higher level of growth in demand for food production growth rates. This is due to several factors lead to increased demand and / or slowing production. Finally, the interaction between the scarcity of agricultural resources and the abundance of oil and its revenues in the Arab world is one of the key pillars that define the future of the Arab economic integration.

**Keywords:** Food security, Agricultural production, Food gap, Food policy.

### **INTRODUCTION**

Maintaining crop production to feed a growing population during a period of climate change is the greatest challenge we face as a species. The increasing crop yields during the Green Revolution in the last century were brought about mostly through the application of chemical fertilisers and pesticides (and during an uncommon period of climate stability). Yield increases have slowed and may go into decline as the world runs out of sources of phosphate and fossil energy used to produce nitrate fertilisers. New approaches to yield improvement are desperately needed to produce more climate resilient crops.

There are a number of economic and political conditions that control the destiny of Arab states and can say bin those circumstances is not born only today but for centuries home to the Arab world from a number of economic and political crises which we can say that the beginning was with the liberation of the Arab homeland and follow the new policies, especially those assigned to economic policies of each country.



With the beginning of the twenty-first century were the Arab states may have merged fully in the global markets. As evidenced by the region at the beginning of the second decade of this century, a number of changes at the level of Arab States and the Arab regimes and policies.

Live Arab state of food deficit increasing severity, the volume of food is not enough to cover consumption, which requires resort to import to cover the shortfall, resulting in many of the economic problems, where the weakening balances of foreign exchange and promote indebtedness and dependency political and economic major states.

Was obsessed with getting food highlighted the problems faced by the human throughout its history, still the crisis list to now where the process is a secure food the most prominent aspects of the economic situation of the new, and the most prominent manifestations of the economic crisis of deficit food and get food gap sharp and widespread hunger and malnutrition in some countries, in light of the failure of its economic policies and development, while most of these countries, particularly Arab countries are primarily agricultural, and is able to achieve self-sufficiency and even export food if they took advantage of the possibilities available and put development plans and follow up their implementation has.

Not everyone agrees that the increase in production is the best way to address food insecurity, and the argument that the world already produces enough food to feed all its inhabitants, but only needs to distribute more efficiently, and with minimal wastage. And consumer habits play an important role in food security, because of the impact on the types of food that is produced, and the resources needed to cultivate, and the production alone is not enough.

Because of the nessserious of the crisis is no longer just a problem of food deficit problem, but agricultural economic exceeded it to become a political issue. The food became a strategic weapon in the hands of countries producing and exporting grain pushing him to the importing countries to achieve political goals, which led to that there will be global attention to this growing problem representing the Millennium Development Goals (MDGs), which was the first of the elimination of extreme poverty, which is one of the results of the high prices and lack of food, leading to a rise in the proportion of hungry and food insecure.

Table (1) Hunger Index in Different Regions of the World (1990 - 2013)



<b>Territory</b>	<b>1990</b>	<b>2013</b>
South Asia	31.5	20.7
Africa South Desert	25.0	19.2
East and South East Asia	15.9	7.6
East Near and North Africa	8.1	5.8
America Latin and the Area Sea Caribbean	9.5	4.8
Europe East Countries Commonwealth Independent	5.3	2.7
<b>World</b>	<b>20.8</b>	<b>13.8</b>

Source: International Institute for Food Policy Research (2013): Global hunger index.

Table (1) show the hunger index in different regions of the world which recorded rate of 20.7, 19.2, 7.6 and 5.8 in the South Asia, Africa South Desert, East and South East Asia and East Near and North Africa respectively, meanwhile the total rate of the hunger index was decrease to 4.8 and 2.7 in America Latin and the Area Sea Caribbean and in the Europe East Countries Commonwealth Independent respectively, in 2013.

### **ELEMENTS OF FOOD SECURITY**

The most important elements of food security in the following:

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1. Climate
2. Terrain
3. Water resources
4. Agricultural land
5. Forests and natural pastures
6. Livestock
7. Human resources
8. Modern technology and agricultural research

### **FOOD SECURITY INDICATORS**

1. Index per capita food production, which is the average per capita amount of food produced annually in the country is attributed to the base year
2. Daily calorie supply
3. Ratio dependence on food imports
4. Cereal food aid

### **FACTORS AFFECTING THE FOOD SECURITY IN THE ARAB WORLD**

#### **1. Demographics**

The growing population of justifications that are formulated for the food problem in the region, if the size of the population has seen a noticeable acceleration at a rate higher than average rates of growth in agricultural production in the same period, will lead to imbalances on the level of supply and demand for food. Moreover, this increase quantitative population may accompanied by a fundamental change in the population distribution between urban and rural areas, where the result of rural migration to the cities within the same country or/and between countries (the student for employment), to a significant increase of the urban population and depriving the agricultural sector in the rural areas of labour, leading to a decline in the performance of the agricultural sector in these regions.

It also resulted in improvement in the overall economic situation in most countries in the past decade, to high levels of per capita incomes and changing food consumption pattern accordingly, and to a decline in the proportion of the agricultural population to the total population as a result brought about by other sectors. And the attendant economic growth changes in population distribution between urban and rural areas, so that the rural population dribbles low and increasing urban population. This leads to the modification of urban expansion at the expense of agricultural land and therefore the rural migration leads to the fluctuation of agricultural production unless offset by a marked improvement in the productivity of farmers. Despite the enormous potential like large area suitable for agriculture in the Arab countries they don't use them well to satisfying the needs of its citizens in the productions.

#### **2. Natural factors**

Attributed failure of agricultural production in general for food needs to satisfy a number of factors, including:

- Desertification and erosion and climate shifts that are known
- Low percentage of arable land, compared with the total area
- Inadequate water sources and poor and exploited the tendency to move from rain-fed agriculture to irrigated agriculture
- Adoption of most crops to climatic factors, which are characterized by volatility

### 3. Development options college

Development process usually involves the transformation of the economy from the development of the agriculture-dominated economy to the growing role of other economic sectors, and in many of the development strategies of Agriculture does not only play a secondary role supportive. And were often overlook the importance of positive interactions between agriculture and other sectors, and is not given great attention to the promotion of research and investment in agriculture. Many development economists have not indicated the importance of the agricultural sector, but relatively small.

The neglect of the agricultural sector in the development directions of public - and in the early stages of the emergence of the food crisis - one of the most important factors behind the deepening food deficit, in addition to the lack of success of agricultural policies in place to reduce food dependency to the outside and to achieve self-sufficiency at the national level or national.

#### ARAB FOOD GAP



Arab food gap is characterized by fluctuating from year to year due to changes in agricultural production (plant and animal) and the volume of consumption and fluctuations in world prices for food commodities [1]. The Arab world is suffering from a severe food gap is increasing with time. And became finance the import of food reeling under the burden and the brunt of most of the financial budgets of most Arab countries, and drains a significant part of the national income is heading towards the Arab world markets to meet the escalating need for food in the Arab world [2].

There is a shortage of food commodities in most Arab countries, is dropped, especially grain of wheat are the most important food commodities imported, accounting for the proportion of its imports about 50% of food imports as imports two-thirds of the Arab world needs of sugar and more than half of its oil, grease, and about one-third of its requirements of milk and legumes. The proportion of self-sufficiency in vegetables and fruits is about 100%, and this rises to allow the production of a surplus for export for fish.

Table (2) The Contribution of the Arab States in the Value of the Food Gap (%)

State	2011 (%)	2012 (%)	2013 (%)	Average Period 2011-2013 Million Dollar	Ratio Contribution In Gap (%)
Egypt	20.4	20.4	20.4	7248.0	20.4
Saudi Arabia	20.0	19.6	19.6	6994.2	19.7
Algeria	12.9	12.8	12.8	4544.5	12.8
Emirates	10.1	10.6	10.6	3706.9	10.4
Morocco	5.5	6.9	6.9	2276.7	6.4
Yemen	4.0	5.1	5.1	1672.4	4.7
Iraq	4.2	4.2	4.2	1505.0	4.2
Libya	4.1	4.0	4.0	1430.6	4.0
Syria	2.8	2.8	2.8	996.0	2.8
Sudan	2.2	2.5	2.5	866.1	2.4
Qatar	1.8	2.6	2.6	815.2	2.3
Kuwait	2.0	2.0	2.0	698.2	2.0



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Lebanon	3.0	0.9	0.9	571.5	1.6
Oman	1.6	1.2	1.2	459.5	1.3
Tunisia	1.2	1.2	1.2	437.3	1.2
Bahrain	1.1	1.0	1.0	371.4	1.1
Somalia	0.7	0.6	0.6	229.5	0.7
Jordan	1.2	0.2	0.2	194.8	0.6
Djibouti	0.5	0.5	0.5	176.0	0.5
Palestine	0.5	0.4	0.4	156.1	0.4
Mauritania	0.4	0.4	0.4	152.8	0.4
<b>Total</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>35502.5</b>	<b>100.0</b>

Source: Arab Organization for Agricultural Development (2013): the Arab Yearbook of Agricultural Statistics. Vol. 33.

Vary the Arab states in the amount of their contribution to the value of the Arab food gap as shown in Table (2), according to the number of population and consumption patterns, income level and agricultural potentials capabilities. An estimated about 74.48% of the total value of the Arab food gap as the average for the period 2011-2013, were contributes namely in Egypt, Saudi Arabia, Algeria, United Arab Emirates, Morocco and Yemen.

#### ARAB SELF-SUFFICIENCY

Tended self-sufficiency ratio in the Arab world of food since the beginning of the seventies to deteriorate, and in recent years has become very low, and the result that the Arab region, considered one of the most regions of the world importers of food.

The deterioration rates of self-sufficiency of the Arab threat to food security, which represents one of the basic components of the national security of the Arab economic perspective. Food security, which means the ability of the community to ensure the needs of the consumer of basic food commodities produced locally or imported from abroad [3] is not the achievement of self-sufficiency, which often means the production of all basic food needs locally, but also to secure sources of getting food locally and / or internationally.

The Arab states at the present time depend on imports from abroad to cover the deficit in its food requirements, and here it should be noted some of the facts related to this situation.

And requires the food out of the impasse Arab serious efforts on the road to integration, particularly at the farm. However, the efforts of Arab integration is still lacking the political will and the governments responsible and active forces to achieve this goal, which has become the only way out of the Arab nation of crises that afflict economically, politically and socially. [4]

Achieving food security of any nation and the Arab nation, in particular, a central issue should not be left to the changing circumstances [5] not external factors to control it, but it must be pursued with all seriousness to ensure the security of sustained through increased attention to the agricultural sector and expand the base of productive work and improve productivity.

Table (3) Economic and Technical Indicators in the Arab Countries Compared with their Counterparts in the World in 2012

Statement	Unity	Arab countries (1)	World (2)	Percentage (2/1)
The value of GDP (A)	Billion Dollar	2579.0	72490.0	3.6
Per capita GDP	Dollar /	6962.0	10318.0	67.5

	person			
The value of the agricultural gross domestic product (B)	Billion Dollar	139.1	3076.0	4.5
(B) / (A)	%	5.4	4.2	..
Per capita agricultural GDP	Dollar / person	375.5	284.2	132.1
The index for food production	%	122.0	118.0	
The use of agricultural mechanization rate*	Tractor / 1000 Hectares	11.0	20.0	55.0
The use of chemical fertilizers rate*	Kg / ha	54.1	95.5	56.6
The productivity of cereal crops	T / ha	1.6	3.6	44.4

\*Data for the world in 2011.

Source: Arab Organization for Agricultural Development (2013): the Arab Yearbook of Agricultural Statistics. Vol. 33.  
World Bank (2014): Development and the World Development Indicators Report, the Bank's Website, Food and Agriculture Organization of the United Nations, the Organization's Website.



Table (3) show the total value of the agricultural GDP in Arab countries, was approximately 139.1 Billion Dollar in 2012, meanwhile the total value of the agricultural GDP in the world was represent of 3076.0 Billion Dollar in 2012.

### **POLICIES TO ACHIEVE ARAB FOOD SECURITY**

Achieving food security of any nation, a central issue should not be left to the changing circumstances, not external factors to control it, but it must be pursued with all seriousness and to ensure sustainable security through increased attention to the agricultural sector and expand the base of productive work and improve productivity to achieve Arab food security must work to achieve that:

1. work on the development of the agricultural sector as this sector is on the achievement of food security.
2. Any development strategy to achieve food security in the country must be taken of sustainable agricultural development is very, determining this end stems from the knowledge of the underlying causes of the problem of food security and the desire to find a radical solution and a permanent and can be summed up this end in the "strengthening of efforts to modernize agriculture and the development of its productive capacity and competitiveness, and the development and conservation of natural resources and preservation of the environment so as to ensure the achievement of the objectives of the current generation and future generations in an integrated framework to achieve the interests of all countries, and this is what can be expressed to achieving sustainable agricultural development.
3. Optimal exploitation of natural resources, human and financial to increase productivity in agriculture to the development of the agricultural sector and achieving this requires enhanced capacity through the integration and coordination of development policies in countries, especially in the agricultural field.
4. Equal distribution of agricultural resources must find and promote the economic integration of agricultural and particularly the economic integration of Arab agricultural,



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especially that the Arab world has the necessary conditions to achieve this integration (integration of resources in agricultural productivity, lack of varying levels of economic growth, and unity of language, history and religion). This is in addition to what would achieve this integration of features significant economic benefit to the economic development in the Arab countries.

5. Strengthen the capacity of the acquisition of agricultural technology through attention to scientific progress and opens the broad prospects for the development of agricultural techniques used in the production of crops.

## RESULTS

1. Were not the food crisis in the Arab world to a large extent the problem of lack or scarcity of the resources available and population growth accelerating or deficit in the financial possibilities, but is primarily a matter of the failure or malfunction in agricultural policies and abuse of what is available to the Arab homeland.
2. At the level of Arab food gap we find the growing gap due to a higher level of growth in demand for food production growth rates as a result of many factors, natural and demographic options beside developmental Arab College and also the global financial crisis.
3. Despite the failure of the reforms and the various agricultural policies in achieving Arab food security and the passage of development and reforms Arabic, which passed through various stages of socialist reforms to liberal reforms show that the main reasons for the failure of reforms nature of the socialist antecedents in the mismanagement suffered by farms, which oversees by the state, as well as agricultural cooperatives.
4. Establishes the economic transformations international world order is required from the Arab world, the merger which, whether out of conviction or reluctantly is suffering from it. The contemporary Arab Economy contemporary remain largely marginalized voluntarily not the Arab countries was guided to exploit its vast resources for development nor is qualified itself to storm changes sweeping the global challenges.
5. The Arab countries so far - even though it possesses the elements of integration and economic unity - could not get away from the control of the national character of the economic development plans, which prevent the Arab world from the full exploitation of available natural and human resources, financial and led to the weakness of the productive efficiency of these resources and to increase the food gap in most Arab countries.

## RECOMMENDATIONS

1. Is economic integration Arabian agricultural most important means of achieving the objectives of sustainable agricultural development and solving the problem of food in the, where will the reallocation of economic resources and increase agricultural production elements of flexibility, which will allow production to increase the size in demand for agricultural commodities.
2. Need to work on improving the competitiveness of agricultural products Arabic in the local and international markets and will not be done only through a strategy makes it among its objectives to achieve production efficiency and requires it to cut costs and that competitiveness is not based solely on cost reduction, but also to raise the level of quality.
3. As regards the agricultural policies of Saudi obstacles to overcome agricultural policies and to find practical solutions we suggest. At the level of agricultural lending need to







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## CONCLUSION

Were not the food crisis in the Arab world to a large extent problem of lack or scarcity of available resources, and population growth accelerating or deficit in financial resources, but it is primarily a matter of the failure or malfunction in agricultural policies and abuse of what is available to the homeland Arab resources, it is part of the issue of development in the Arab essence, the modes of production and distribution of consumer and at the country level and national security. It is clear from the previous view that the food gap in the Arab world that have reached critical levels, is the result of a higher level of growth in demand for food production growth rates. This is due to several factors lead to increased demand and/or slowing production, and can be summarized in the following points:



- High rates of demographic growth
- Improvement in income levels
- Low proportion of land actually cultivated and elimination of the desertification
- The importance of rain compared natural land water resources where the first depends mainly on climatic conditions
- Consumption pattern as it constitutes the most important commodity grain food consumption in many Arab countries
- Asymmetric distribution of agricultural resources
- Water scarcity and misuse of disposable ones
- Low agricultural productivity and the failure of agricultural policies.

Despite the suffering of the Arab world food problem is widening, it has the potential of ingredients and objective enough not only to fill their needs of food, but also to achieve a surplus issued to the outside world.

The interaction between the scarcity of agricultural resources (water, arable land) and the abundance of oil and its revenues in the Arab world is one of the key pillars that define the future of the Arab economic integration. It has become clear that the Arabs should not work only to overcome the crises situational and short-term, but they are required to take positions and decisive strategy is to merge their forces in the strength of the real one will enable them to build a mass of economic actors in the age of conglomerates creeping, ensure the exploitation and protection of their resources better to ensure the standard of living and the dignity of their fellow citizens better, and ensure the provision of food needs Arab locally (nationally) in an area where food may be a lethal weapon for the liberation of food dependency and dragged them from political and economic pressures.

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Other sources have been used as well: FAO, Arab Organization for Agriculture and Development



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## **ISOLATION OF INDIGENOUS *STREPTOMYCES* SPP. FROM ARID AREA AND EVALUATION OF THEIR ANTIFUNGAL ACTIVITY**

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### **ABSTRACT**



Actinomycetes are the main sources of secondary metabolites reflecting an anti-cellular activity, species belonging to the genus *Streptomyces* constitute 50% of the total population of soil actinomycetes and 75% of molecules with antibiotic activity are produced by this genus. In addition, rare Actinomycetales bacteria are a potentially important source of unexplored new secondary metabolites with antibacterial and antifungal activity. This study was conducted from thirteen samples in total of which the majority were collected in arid regions. Some have undergone treatments to allow enrichment of bacteria in the initial sample, such as a thermal shock for a week. Methods for decimal dilution in physiological water to 0.9% NaCl with an incubation of 28°C for three days led to the isolation. Most selective media used in this work are as follows: Starch modified casein (pH 7.0), Bennette (pH 7.3) and ISP2 (PH 7.3). The modified starch-casein medium proved to be the most suitable for the selective isolation of actinomycetes. The isolated strains were screened for their macroscopic appearance on solid medium and their filamentous appearance under an optical microscope. A total of 54 strains were selected and stored in LB broth medium supplemented with 20% glycerol and stored at -20°C. Stirred broth cultures were performed on GLM medium at room temperature, the strain 1P made a highly viscous medium, the strain 15 G determined the formation of an ovoid gel structure, these two strains are certainly responsible for the formation of exopolysaccharides. In addition, three other strains (5L, 15R and 9R) disseminate yellow pigments, red and purple. Interactions were performed with respect to three genera of fungi (*Mucor sp.*, *Penicillium sp.* and *Aspergillus Niger*). The results showed antifungal activity as follows: ten strains of *Streptomyces* neutralized one fungus, eight had an inhibitory effect on both fungi and finally two neutralization exerted on the growth of three fungi. Finally, 15 *Streptomyces* strains showed no antifungal inhibition.

**Keywords:** arid area, *Streptomyces sp.*, starch-casein modified, *Mucor sp.*, antifungal activity

### **INTRODUCTION**

Man has always used microorganisms (bacteria, yeasts, molds) for making various products such as bread, beer, cheese. These microorganisms are ubiquitous in our environment (air, water, soil) and in food we consume. They occupy a more and more important place in several fields and industries (food, pharmaceutical, etc). However, despite their advantages, some are pathogenic for living beings and cause major problems.

Several works are oriented to solve these problems through the continuous search for bioactive molecules (antibiotics, antifungals, bacteriocins, etc). Actinomycetes are the main sources of secondary metabolites anti-cell activity (Finance et al., 1985). These bacteria are subject to great

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attention because of their production of various biologically active metabolites including antibiotics, enzymes and enzyme inhibitors. The best antifungal agents on the medical market products are fermentation of Actinomycetes.

More than 25000 bioactive secondary metabolites (including antibiotics) were published in the scientific and patent literature; half of them are produced by actinomycetes. Nowadays about 150 antibiotics are used in human therapeutic, 100 to 120 of them are produced by actinomycetes (Perez et al., 2002).

Actinomycetes are subject to great attention due to their production of various bioactive metabolites: immunostimulating substances, fungal, enzyme inhibitors, anti-tumor substances, pesticides, immunosuppressive substances, herbicides, insecticides, enzymes, antibiotics. They offer new compounds (antibiotics, antifungals) able to deal with the phenomena of resistance constantly growing (Fielder et al., 1993).

The continuing search for new actinomycetes strains may lead to the discovery of some able to offer interesting and unknown substances previously (Larpen et al., 1989). Species belonging to the genus *Streptomyces* constitute 50% of the total population of actinomycetes in soil and 75% of molecules producing bacteria activity antibiotic (Jiang et al., 2013). The continuing search for new strains among this group can lead to the discovery of some able to offer valuable substances and hitherto unknown (Larpen et al., 1989).

However, the development of new drugs from actinomycetes is increasingly difficult around the world, due to a too large number of known compounds. To overcome these challenges, new concepts based on the genome have been described, including the "new habitats, new methods, new species, new group of genes, new products and new use (Jiang et al., 2013). Their selective isolation from various ecosystems has led to the discovery of interesting new substances from the genera of *Micromonospora*, *Actinomadura* and *Streptosporangium* (Shearer et al., 1997; Lamari et al., 2002). Many companies and laboratories focused on new resources of actinomycetes, new habitats, such as oceans, extreme environments, plants and animals, to develop new drugs. In recent years, research on uncultivable microorganisms was carried out in many laboratories (Joseph et al., 2003).

## **MATERIALS AND METHODS**

### **1. Sampling site**

Soil samples are collected using a large sterile spatula. Five first centimeters of topsoil are removed (Pochon and Tardieux, 1962), take 100 g of soil with a small sterile spatula into the underlying layer (between 5 and 15 cm deep), make the sample on an aluminum paper and make a first sorting away like a large debris (rocks, roots), than make the sample in a sterile container and transported to the laboratory for analysis. Thirteen soil samples were collected from different regions in Algeria (arid, fertile, and semi-arid).

### **2. Pretreatment of soil samples**

**2.1. Pre-enrichment of soil:** treatment by the addition of calcium carbonate ( $\text{CaCO}_3$ ) (Kavala, 1994). 1 g of a soil sample was mixed with 0.1 g of  $\text{CaCO}_3$  and incubated at 26°C for 7 days.

**2.2. Thermal treatment:** the samples were subjected to different types of heat treatment: a few grams of soil are heated at 110°C for 10 minutes (Agate and Bath. 1963), this type of treatment reduces Gram-negative bacteria (Jeffrey., 2008).

The sample was dried at room temperature for 7 days. This treatment induces a significant increase in the number of *Streptomyces*. A few grams of soil were heated at 45°C for 2 to 16



hours. This treatment reduces the number of bacteria contained in the soil sample without affect that of *Streptomyces*. Some samples do not undergo any pre-enrichment.

### 3. Dilution and inoculations on different medium

Decimal dilutions were performed by taking 1g of each treated and untreated soil, added to 9 mL of sterile 0.9% saline. Shake using the vortex for a few minutes (to allow good dispersion microbial load in the tube). The solution obtained is of the order of  $10^{-1}$  and represents the solution stock (SM). Take in aseptic conditions, 1 ml of the stock solution, we put into 9 ml of saline water to have dilution of  $10^{-2}$  and  $10^{-3}$ . Collect 100  $\mu$ l of dilution  $10^{-3}$  of each sample, and inoculate on plates Petri containing: ISP2 media or Bennett or strach-casein modified. Than incubated at 28°C in aerobic conditions for 7 days (Boudemagh, 2007).

### 4. Isolation of *Streptomyces*

After 7 days of incubation, the colonies suspected to be *Streptomyces* were isolated by:

- The macroscopic characteristics: their characteristic morphological appearance of genus, they appear dry, rough, colored or not, adhered to the agar and with vegetative and aerial mycelium. There is the presence or absence of soluble pigments and production of melanin.
- Microscopic characteristics: The filamentous *Streptomyces* is determined by microscopic observation after Gram coloration.

Colonies suspected of being *Streptomyces* were purified with successive subcultures necessary to obtain pure strains. Different obtained colonies were subcultured on the same medium used for isolation by the method streaks on a Petri. Incubate at 28°C for 5 days. It is recommended that the least possible subcultures to maintain the genetic stability of the strains (Boudemagh et al., 2005).

### 5. Conservation of strains

All colonies which have the characteristics of *Streptomyces* were conserved by making a suspension of spores. It was prepared by scraping the surface of the culture then stored in freezer at -20°C in LB medium in the presence of glycerol at 20% (Jeffrey, 2008).

### 6. Isolation of fungi

Samples were taken from different habitats for the isolation of three groups of fungi (Table 1). To determine the kind of isolated fungi, a phenotypic-identification was performed based on the appearance and fresh microscopic observation and comparing with literature (Larpent, 1997).

**Table 1: Biotopes of isolated fungi**

Samples	Biotopes	Isolated fungi
A	Contaminated Camembert	<i>Mucor sp.</i>
B	A moldy orange	<i>Penicillium sp.</i>
C	Few grams of soil collected from Es-Senia (Oran)	<i>Aspergillus sp.</i>

### 7. Selection of strains producing metabolites antifungal activity



All strains isolated and suspected to belong to the genus *Streptomyces* were tested with three fungi to evaluate their antifungal activity against these bacteria.

### **7.1. Primary screen**

All isolates were tested in the presence of three isolated fungi from different biotopes to determine the presence or absence of an antifungal activity. Several methods have been used for the detection of inhibitory potency.

**Method 01:** Take using the handle a few drops of the spore suspension of actinomycetes, than inoculate like spots two strains which are tested in each end of a Petri plate containing PDA medium (Potato Dextrose Agar). Incubate at 28°C for three days. In another plate containing the same medium than streaked fungi tested. Incubate at 28°C for 48 hours. Using a Pasteur pipette make a disk of agar 5mm from the fungal culture and inoculated the plate containing the tested actinomycetes. Remove the disk so that it stays on each side between it and the strain 60 mm (shema not shown).

**Method 02:** Another method of inoculation of the fungus was tested to evaluate the fungal activity of strains. It consists in seeding *Streptomyces* on spots as for the previous method only difference was fungus is seeded in central line (shema not shown).

### **7.2. Secondary screen**

**7.2.1. Viscosity tests:** this test has been undertaken for all strains selected for their inhibition against the selected fungi are carried in liquid culture. The strains were grown on medium GLM on agitation at 150 rpm for 7 days at 28°C. Microbial growth is manifested by the appearance of pellets visible disorders and deposits.

**7.2.2. Disk method** (Lemriss et al., 2003): After obtaining culture on the GLM medium, the culture was filtered with sterile Whatman paper to have the active filtrate. Prepare sterile disks paper of 6 mm in diameter impregnated with 5µl of filtrate. Another disk was impregnated like a negative control with sterile distilled water. Leaving disks dry and place them in a Petri plate containing fungi to test previously inoculated on PDA. The plates were incubated at 4°C for 4 hours for a good spread of antifungal metabolite. Incubate plates at 28°C for 48 hours (shema not shown).

## **RESULTS**

### **1. Effect of pre-treatment of soil**

Pretreatment samples used in different programs of screening the actinomycetes producing antimicrobial attempt to promote growth by two methods of the actinomycetales.

**1.1. Enrichment with CaCO<sub>3</sub>:** The addition of CaCO<sub>3</sub> in the soil sample leads to a reduction in the number of bacteria Gram negative (Jeffrey, 2008) and a 100-fold increase colonies of *Streptomyces* isolated in plate compared with the untreated control. Occurs at the same time a decrease in the fungal flora (El-Nakeeb and Lechevalier, 1963). The addition of CaCO<sub>3</sub> to samples has obtained good results compared with the untreated samples. Average number of actinomycetes was 7.10<sup>4</sup> UFC/ml in sample supplemented with CaCO<sub>3</sub> and 4.10<sup>4</sup> in sample no treated.

**1.2. Pretreatment of samples by heat:** The heat pretreatment of samples in fertile area, is one of most commonly used in screening processing techniques in actinomycetes, when the isolates were selected, a significant reduction in the number of undesirable bacteria were obtained (Agate and Bath, 1963. Pisano et al, 1987). Heating the samples at temperature from 55°C to 100°C for 1 h, reduced considerably the number of bacteria without affecting the actinomycetes (El and Nakeeb Lechevalier, 1963).





**2. Isolation of actinomycetes**

Differentiation between strains isolated was primarily based on the place of sampling, colony color (white, gray, pink, etc) and appearance (powdery smooth, embedded in agar, etc). To do this, one medium was used, it affects the appearance of colonies (Boudemagh, 2007). The medium used for this study is the modified starch-casein medium.

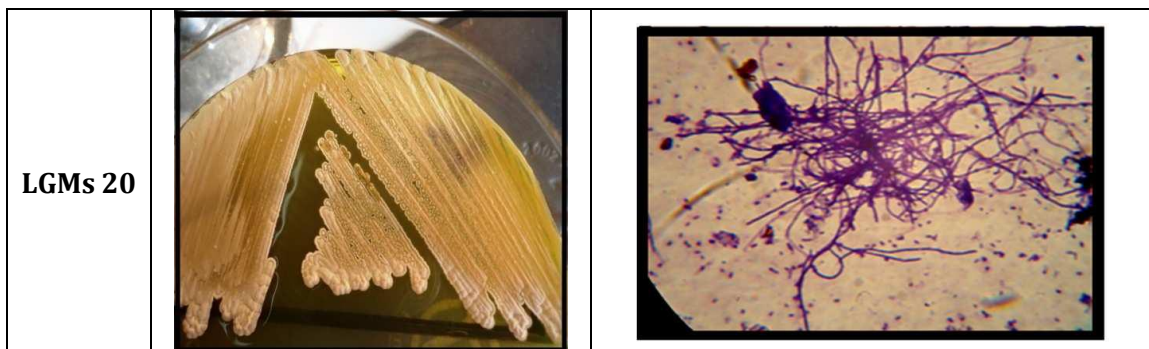
After, variety of selective media was used for isolation of *Streptomyces* from different habitats. The presence of chitin, starch, glycerol, arginine, asparagine, casein or nitrates in the isolation medium, leads to selective isolation of actinomycetes while bacteria and fungi grow weakly (Williams and Davies, 1965). The actinomycetes colonies are recognized by their characteristic morphology and confirmed by microscopic observations. They are differentiated them in this function these characteristics and their habitat.

This pre-identification allowed us to retain 54 strains with macroscopic characteristic appearance and microscopic filamentous appearance (Table 2). The isolation of actinomycetes from soil in different regions has to obtain at least 4 actinomycetes per sample. Based on these results, actinomycetes are present in all types of soil (sand, forestry, agriculture).

**Table 2: Macroscopic and microscopic observation of the collection strain of actinomycetes**

Strain	Macroscopic aspect	Microscopic aspect
LGMs 23		
LGMs 14		






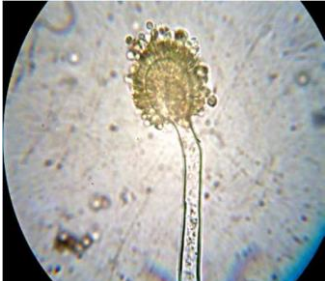




### 3. Isolation of fungi

Three different kinds of fungi were isolated from three habitats and phenotypic identification was performed by macroscopic and microscopic appearance (Table 3) and comparing with the literature (Larpent, 1997).

**Table 3: Macroscopic and microscopic observation of selected fungi from different biotopes**

Samples	Macroscopic aspect	Microscopic aspect	Phenotypic-identification
<b>A</b>			<i>Mucor sp.</i>
<b>B</b>			<i>Penicillium sp.</i>
<b>C</b>			<i>Aspergillus sp.</i>



#### 4. Evaluation of antifungal activity of isolated strains of actinomycetes

All strains were screened to determine the presence or absence of antifungal activity. Interactions were made with selected fungi *Mucor sp.*, *Penicillium sp.*, *Aspergillus sp.* The results of the primary screen were calculated by diameters inhibitions against the fungi (mm, data not shown).

From the results of the primary screen, the results were summarized in Figure 1, only two strains exhibit an antifungal activity against the selected fungi (*Mucor sp.*, *Penicillium sp.*, and *Aspergillus sp.*). This is equivalent to 3.70% of total strains. These bacteria were isolated from samples collected in arid regions (Beni Abbes). It has already been shown that arid and semi-arid soils of southern Algeria are populated of actinomycetales bacteria (Boudemagh, 2007). What makes these areas an excellent site of study, research and isolation of new strains of actinomycetales. Some strains showed strong inhibition against the *Penicillium sp.* like LGMS9 strain LGMS15 LGMS34 with very interesting inhibition diameters. The strain LGMs13 inhibited strongly *Mucor sp.* This fungus is the enemy number one of cheese industries, which makes this strain a potential solution to the problems encountered in this type of industry.

40, 74% of isolated actinomycetes strains showed no antifungal activity, and 25.93% inhibit two selected fungi. 29.63% inhibit one that is higher than 10% have been demonstrated in the work of Boudemagh et al. (2007) and closer at 20.7 to 33.0% shown by Ranjbariyan et al. (2011). *Mucor sp.* was inhibited by 40.47% of *Streptomyces* isolated, then *Aspergillus sp.* by 27.77% and *Penicillium sp.* by 25.93%. The percentages obtained agree with the work of Ranjbariyan et al., 2011, 33% of *Streptomyces* inhibit *A. niger* and 21.4% *P. marneffeii*.

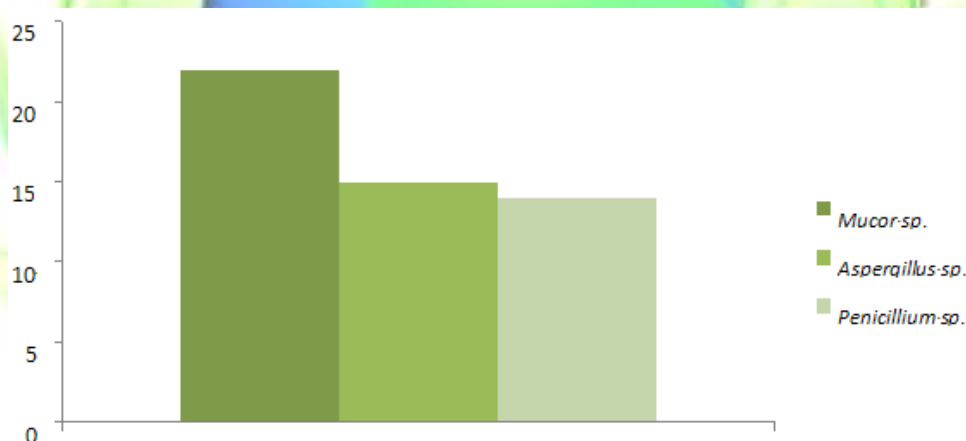


Figure 1: Histogram showing the number of active strains against selected fungi

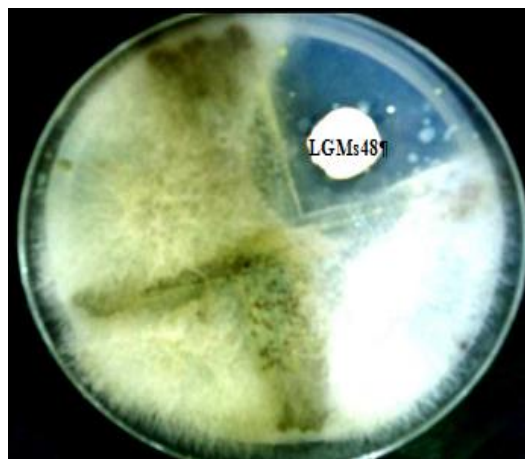


Figure 2: Interactions between *Mucor* sp. and LGMs48 on PDA.

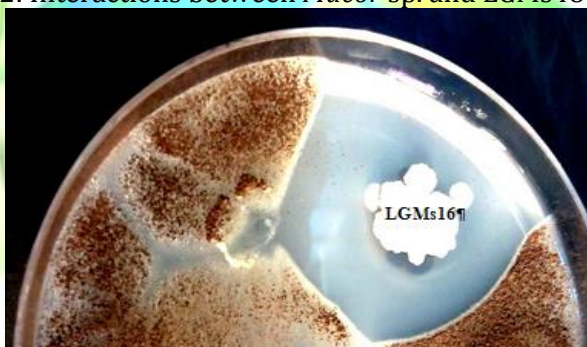


Figure 3: Interactions between *Aspergillus* sp. and LGMs16 on PDA

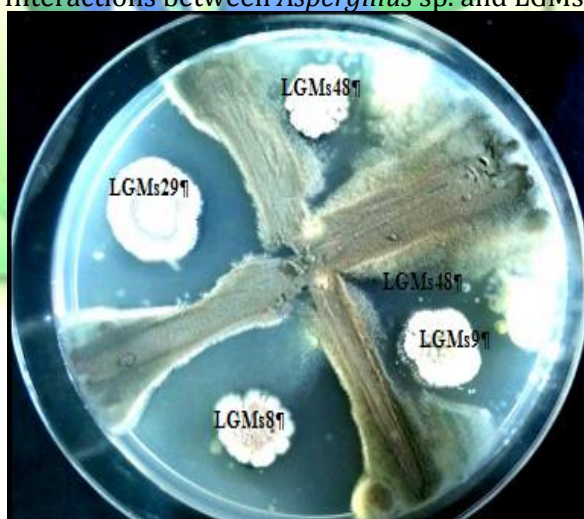


Figure 4: Interactions between *Penicillium* sp. and LGMs8, LGMs48, LGMs29 and LGMs 9 on PDA

## 2.2. Secondary screen

Strains LGMS43 and LGMs48 were inoculated on GLM medium, agitation at 150 rpm for 7 days at 28°C and filtered. Sterile disks were soaked in the filtrate as described in Materials and Methods and tested against *Mucor* sp., *Penicillium* sp. and *Aspergillus* sp.



Figure 5: Culture of strain LGMs43 on liquid medium GLM

After a few days of culture LGMs43 strain on liquid medium GLM. The growth occurs by clarification of the medium and an increase in viscosity (Figure 5) against the negative control.

**Table 4: Results of the secondary screen**

Filtrat of strains	Diameters of inhibition (mm)		
	<i>Mucor sp.</i>	<i>Penicillium sp.</i>	<i>Aspergillus sp.</i>
<b>LGMs43</b>	8 mm	20 mm	-
<b>LGMs48</b>	8 mm	18 mm	-

During the secondary screen, the filtrate tested by the method of the disks permit inhibition of two selected fungi *Mucor sp.* and *Penicillium sp.* However any of the two filtrates inhibited *Aspergillus sp.* For better inhibitions it is advisable to extract and concentrate the active ingredient in order to assess the antifungal activity of the tested strains.

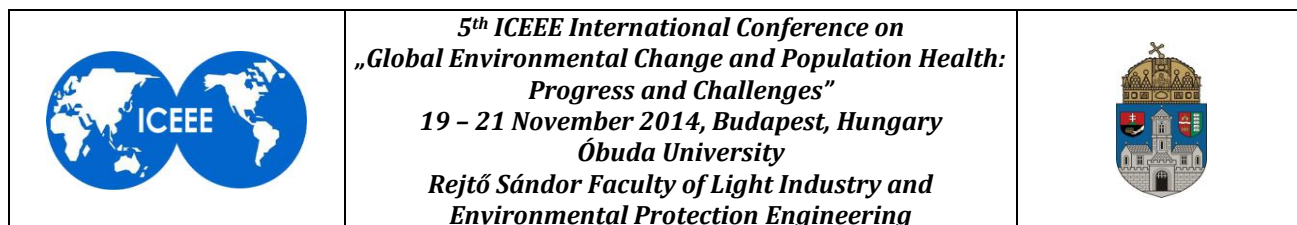


Figure 6: Antifungal activity of the filtrate of LGMs48 LGMs43 strains against *Penicillium sp.* on PDA

## DISCUSSION

Selected bacteria that have grown are mostly Gram positive stains. The number of actinomycetes is not particularly high with these pretreatments. However, the number of non-filamentous bacteria and yeast was reduced compared to untreated samples. Furthermore, Fungi seem not





sensitive to this type of treatment. Heating soil samples thus affect the development of non-filamentous yeasts and no effect fungi. Agate and Bhat (1963) said that a pretreatment of the soil at 110°C for 10 min were used for the selective isolation of actinomycetes (Nonomura and Ohara, 1969). These techniques used the arthrospores resistance under the harsh conditions and high temperature (Prinzis, 1990).

The heat treatment at 110°C for 10 minutes reduced more than 50% the number of isolated selected actinomycetes. It appears in this work that the heat treatment decrease halves unwanted bacteria is but also, it act the similarly against the actinomycetes. These results agree well with those obtained by Nonomura and Ohara, 1969, which show that treatment of soil samples by heat was used for the selective isolation of some genera of actinomycetes, while other genres such as *Streptomyces* didn't resist this kind of treatment. It is due to the fact that most of the spores of *Streptomyces* don't resist at temperature above 50°C in wet heat and at 70°C in dry heat temperature (Larpen, 1997). In addition, the actinomycete in growth mycelial phase can not resist at heat conditions imposed during the heat treatment of the samples (Takizawa al., 1993). The actinomycetes isolated were performed on three selected medium in the literature: ISP 2 medium, Bennett and starch casein modified.

The medium favorites more the isolation of an important number of actinomycetes from soils of different regions of Algeria is the medium of starch casein modified. This complex medium is composed of starch as a source of carbon, which allows the selective isolation of actinomycetes (*Streptomyces* are able of hydrolyse starch). The composition differs from other areas by the presence of KNO<sub>3</sub>, K<sub>2</sub>HPO<sub>4</sub>, NaCl and the presence of a trace element-containing magnesium sulfate, calcium carbonate and the ferrous sulfate solution. The modified starch-casein medium favors the isolation of actinomycetes and fungi are slow in their growth on this medium. The three types of selected fungi are often found on food, mainly cereals and derivatives, dairy products, meat and meat products, oilseeds, fruits and vegetables, dried fruits, jams and beverages. Some species are toxigenic, they produce mycotoxins which ingestion in an amount sufficient cause poisoning to the consumer (Maria et al., 2004).

During the culture of the strain LGMS 48 liquid media, there has been an emergence of ovoid structure called pelotte. This is a typical phenomenon of *Streptomyces* in liquid medium and this is due to their filamentous appearance. The appearance of the pelotte is problem during fermentation processes for the production of bioactive substances. The balls limit oxygen transfer and nutrients from the culture medium to the bacteria (Papagianni, 2004).

According to some authors, resources of molecules in pharmaceutical interest from *Streptomyces* have been exploited and they say it must be directed towards the isolation of rare actinomycetes in order to supply new substances (Lamari et al, 2002; Zakharova., 2003). In parallel, several laboratories have engaged on the screening of the entire flora of actinomycetales without discarding the *Streptomyces*. Their work gives very satisfactory results for obtaining several interesting molecules from *Streptomyces* (Lee et al., 2002). So it seems that the genus *Streptomyces* has not yet exhausted its resources and continues to offer the same antibiotics and other pharmaceutical substances.

## CONCLUSION

This study demonstrates that Algerian soil is populated with Actinomycetales bacteria. The work consist to isolate a maximum strains using different culture media and based on the macroscopic and microscopic appearance of colonies. The selective isolation of actinomycetes from soil samples is favoured by the pre-enrichment by addition of CaCO<sub>3</sub>. The choice of medium for the



selection of actinomycetes is the starch-casein modified medium. A total of 54 Actinomycetales strains was isolated and purified from 13 samples. 59.26% of this population showed antifungal activity against at least one target fungus. This percentage is higher than other work prior screening.

Two strains LGMs43 and LGMs48 showed significant antifungal activity against all filamentous fungi used in this study. Filtrates of liquid cultures on GLM of LGMs43 and LGMs48 also showed a very significant antifungal activity against *Penicillium sp.* Weak inhibition against *Mucor sp.* and none against *Aspergillus sp.* The search for new antifungal molecules is a component of research and unlimited turn to what nature provides is crucial. The strains isolated in this study presented satisfactory and applicable antifungal activity in several areas where development of fungus is a problem.

Among the perspectives to be drawn from this study, exploit diverse ecosystems and especially the extreme southern Algeria, undertake a complementary approach to the antibacterial activity of interesting strains, use a variety of methods and solvents for the extraction of the active substances, and identification of the chemical components of the extracts by the use of methods such as HPLC, GC/MS and finally make a molecular identification by PCR based on detection and optionally genes of interest.

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## **SAVING SOIL AND WATER USING DIFFERENT REMEDIATION TECHNIQUES AT THE LEADER'S TERRITORY OF RAILWAY STATION**

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Contamination of gas oil, engine oil, and lube oil occurred at a leader's territory of Hungarian Railway Station was examined. The aim was to determine whether the area was cleaned during a project, and if it was what the process was. The project started in 2008; we joined in 2012. Soil and groundwater were sampled in working-pits, raiser and observing pumps. According to our results, the area is not cleaned properly, although the technology was effective, i.e.: the TPH-GC values of each soil sample in prisms and work-pits were reduced to below the target (D remediation, 3000 mg/kg), and in average too. During remediation, 93 samples originated from the prisms of biodegrade handling (bacterial inoculation, stirring) were analysed. We found that increasing pollution occurred only when new polluted soil was placed into the prisms after carrying out the work-pits. This short-term increase was followed by reduction in each case. Combination of ex situ-on site method and the intensified breakdown of bacteria facilitated our work substantially, not just because of its high budget but it can be carried out at the territory of the area. By this method, significant expense could be saved, and further pollution occurring during long distance transportation could be prevented. Additionally we could reuse the soil - after reducing its content below the limit of D remediation - for refilling the work-pits. Cleaning of groundwater was also efficient, i.e.: finally cleaned entirely. Samples analysed by the first author and monitored by Saubermacher-Magyarország Kft. in 2012 had no contaminants above the limit of D remediation in the groundwater. No polluted underground water was found in pumps and in clarifiers. Clarifiers filled with active carbon-zeolite worked properly based on samples taken yearly. At most of the remediated areas - where budget did not set a limit to the process - polluted soil was exploited, and work pits were filled in by soil containing pollutant below the limit. Torn down articles of virtue were replaced and polluted water in the pumps was purified by pumping. Financial constraints can be blamed for finishing the remediation works, which proved clearly very expensive. However nowadays the Hungarian Remediation Programme in its third party act on „National Environmental Programme”, most of the suppliers and other organizations consider that protection of environment and this type of remediation are important and their duty.

**Keywords:** *contamination of oil, limit of D remediation; polluted soil and ground water, remediation technologies; TPH-GC values, Hungarian Remediation Program*

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## **COMPARATIVE ANALYSIS OF TIMBER QUALITY OF SPRUCE AND PINE PLANTATION**

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### **Abstract**

With respect to the wood supply of Hungary it is particularly important to improve the wood quality of the plantation of the tree species that grow quickly. The study of the relations between the anatomic and technical characteristics of plantation wood material can significantly increase the efficiency of wood utilization in the future. The tissue structure of the tree planted in a network differs from the structure of trees growing in natural or natural-like forests. The choice of the planting distance, that is to say the size of network enables the change of the growth circumstances of the tree. The problem of the first narrow networks justified the growth of planting distances and the study of the wood material resulting from these network experiments. I intend to give information to professional in the field of forest planting on the topic of which networks produce wood materials that have the best characteristics with respect to wood processing. Out of the coniferous trees in our country Scotch pine, black pine and spruce have economic significance. With my investigation I give information to professionals in wood utilization about the wood characteristics of Scotch pine and spruce trees.

**Keywords:** *Wood supply of Hungary; anatomic and technical characteristics; wood utilization*

### **INTRODUCTION**

With respect to the wood supply of Hungary it is particularly important to improve the wood quality of the plantation of the tree species that grow quickly. The study of the relations between the anatomic and technical characteristics of plantation wood material can significantly increase the efficiency of wood utilization in the future.

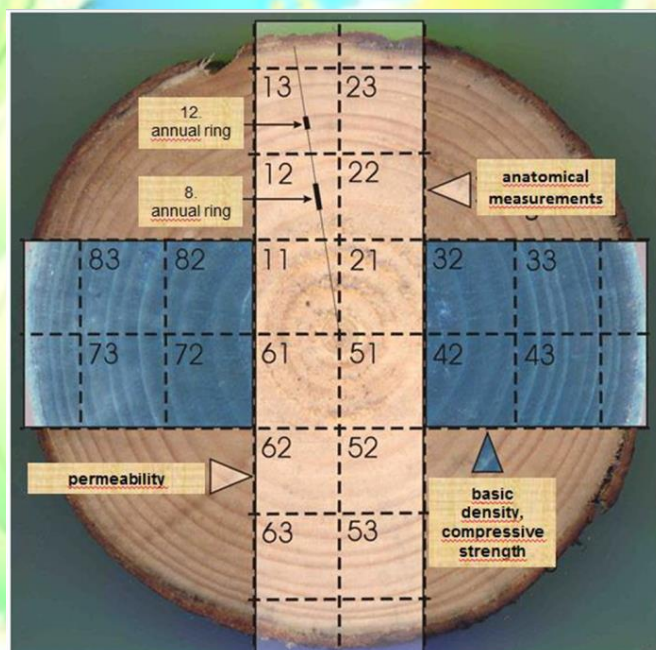
The tissue structure of the tree planted in a network differs from the structure of trees growing in natural or natural-like forests. The choice of the planting distance, that is to say the size of network enables the change of the growth circumstances of the tree. The problem of the first narrow networks justified the growth of planting distances and the study of the wood material resulting from these network experiments. I intend to give information to professional in the field of forest planting on the topic of which networks produce wood materials that have the best characteristics with respect to wood processing.

Out of the coniferous trees in our country Scotch pine, black pine and spruce have economic significance. With my investigation I give information to professionals in wood utilization about the wood characteristics of Scotch pine and spruce trees.

## MATERIALS AND METHODS

Within the framework of research I have studied 157 trunks of 41 clones in case of spruce and the wood material characteristics of 23 trunks of 3 clones in case of Scotch pine. In case of the latter the three clones came from four different networks (2x2; 8x2; 8x6; 8x16).

On the material of both trees, that is to say the sample trunks of spruce and Scotch pine, the macroscopic, microscopic tissue and physical features were examined. When planning the inquiries, I had to take into account the moisture condition of wood and the fact that for each trunk I had at my disposal a disc with a thickness of 2,5-3 cm. My primary goal was to secure the measure of as many wood features as it is possible on the discs for the sake of complexity. For this I established a scheme, in which I divided the discs into parts. On the wood material divided into parts, test bodies of 2x2 cm were created along two axes vertical to each other. With this method it was possible to trace wood characteristics on a radial direction.



**Figure 1.-** Cutting of specimens for compression strength test, basic density and for anatomical measurement from the sample disks.

The following examinations were conducted on the discs:

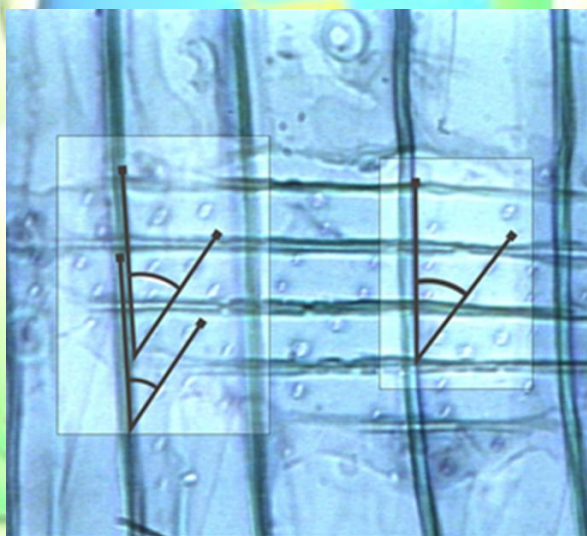
- To determine the diameter of trunk
- To determine external precision
- To measure annual ring width
- To measure the length of tracheids
- To determine the cell wall-lumen ratio
- To measure the angle of micro fibers
- To measure basic density
- To measure the shrinking of volume
- Permeability examination



- To determine compressive strength

In practice, the preservative saturation of spruce has a very important role. Saturation is closely related to permeability. According to the result of permeability examinations, the 80 % diluted solution of ethyl alcohol (C<sub>2</sub>H<sub>6</sub>O) proved to be the best permeable liquid. The reason for this is the fact that it hardly swells the wood, and it damages wood structure to lesser degree than other dissolvent. On the basis of measures I concluded that the average permeability grade of spruce is  $7,61 \cdot 10^{-6}$  darcy ( $0,776 \cdot 10^{-10}$  m<sup>3</sup>/m·Pa·s), which is very low, and proves the heavy saturation of spruce. Furthermore, the result of examinations between clones has shown that the scale of aspiration of pits can change even within one trunk, which largely influences the results of measurement.

I measure the decurrent direction of micro fibers located in the cell wall of the tracheids with the “method based on the direction of the pit opening of the intersecting field”, which is familiar to foreign researchers. I concluded that this method is very suitable for the determination of the compression wood in coniferous wood material, which is sometimes difficult to locate because it can happen that the wood containing compression wood shows no change of colour. For the wood industry the wood containing compression wood is less interesting since their technical features are largely determined by its presence.





**Figure 2.** – An example for measuring microfibril angle in a radial section.

## Results

As a result of the examinations conducted in the framework of the project that out of the examined Scotch pine networks (2x2; 8x2; 8x6; 8x16) the individuals growing in the network of 2x2 have the best wood material features.

That the genetic improvement of spruce significantly influences wood quality, and out of the 41 spruce clones I chose the ones that have advantageous features with respect to wood processing and paper industry. Therefore I recommend the plantation of the following 6 clones: ‘2454’, ‘25177’, ‘25194’, ‘27140’, ‘28114’, ‘28396’. Based on the analysis revealed that the quality of Scotch pine wood body is less influenced by improvement because I found no significant

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differences between the 3 Scotch pine clones examined in the project with respect to their anatomic, physical and mechanical features. To increase the natural protection of wood material during the various saturation processes and to use hydrothermal treatment we have to know the permeability features of the wood. The result of the investigations, we got the average of  $7,61 \cdot 10^{-6}$  darcy for the whole population, which proves the difficult saturation of spruce. Established that the “method based on the direction of the pit opening of the intersecting field” useful to determine compression wood.

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## **PERICONCEPTIONAL MEDICINE: A KEY FACTOR TO OUR CHILD'S HEALTH?**

Attila VERECZKEY, Eva MARGITTAI

Versys Clinics Human Reproduction Institute, Budapest, Hungary

### **Abstract**

The periconceptional period is believed to play an important role in programming offspring's physiological functions. This period is sensitive to several insults, e.g. to nutritional state, which might be crucial regarding to both mother's and offspring's health before and during pregnancy. Even moderate weight loss before pregnancy was found to be beneficial, but the potential risks – i.e. under nutrition – should be kept in mind. Offsprings conceived during a time of maternal nutritional restriction showed changes in hypothalamic-pituitary-adrenal axis function, body composition, glucose metabolism, and cardiovascular function. Maternal obesity and aberrations in maternal glucose metabolism was shown to have adverse effects on the oocyte and preimplantation embryo stage which may contribute to lasting morbidity in offspring, underscoring the importance of optimal maternal weight and nutrition before conception. Periconceptional antioxidant rich diet – especially with the inclusion of vitamin C – might help to influence glucose tolerance and prevent gestational diabetes.

Periconceptional nutritional supplementation strategies focus mainly on iron and folic acid. Folic acid supplementation administered in the periconceptional period has been established having preventive effects on neural tube defects and on some cardiovascular anomalies, and may reduce the risk of certain childhood cancers; while iron fortification is necessary to prevent anaemia and related disastrous consequences in the mother and fetus. Vitamin B-12 has also been suggested to contribute to neural tube defect prevention.



The multiple micronutrients often, taken by pregnant women but with limited proven benefits. Environmental factors (e.g. pesticides, arsenic, BPA, phthalate, fragrances, plastics, cosmetics, antibiotics) may also have special importance during the periconceptional period. Prenatal exposure to environmental chemicals is linked to various adverse health consequences and sometimes with delayed conception. Increased phthalate levels in men for example were shown to be associated with longer preconception period. Prolonged BPA exposure may also increase the risk of infertility. Extensive research shows that many pollutants are capable of modifying physiological systems in mammals. Lead and persistent organic pollutants have been associated with decreases in measures of sperm quality and changes in the character of menses, thus causing a delay in pregnancy. Increased exposure to pollutants might alter fetal development as well, e.g. preconceptional maternal and paternal concentrations of several persistent organic pollutants were associated with statistically significant differences in birth size among offspring. Maternal – and paternal – lifestyle factors during periconceptional period are associated with embryonic growth and fetal development as well. Maternal active smoking and exposure to passive cigarette smoke emerged as a potential teratogen that affects for example limb and digit formation and was associated with an increased risk for cleft lip with or without cleft palate in offspring. Even periconceptional paternal smoking increased the risk of certain cardiovascular heart defects, e.g. isolated conotruncal heart defects, septal defects and left ventricular outflow tract obstructions. In summary, more research is necessary to unravel the underlying mechanisms of the above effects and to assess the implications for preconception and early pregnancy care, such as the development and implementation of effective lifestyle interventions.

**Keywords:** *periconceptional medicine; lifestyle factors; nutritional supplements; pollutants*

### **INTRODUCTION**

The periconceptional period was a rather neglected stage of early human development, but gained larger attention in the past few years. It usually refers to the time frame before



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conception till early pregnancy, and embraces oocyte maturation, follicular development, fertilization, embryo formation and development. It is considered to finish with the implantation, but since the initial weeks following implantation are crucial in fetal growth, others regard to terminate periconceptual period on week 10<sup>th</sup> of gestation, coinciding with the closure of the secondary palate in the embryo.



The periconceptual period is believed to play critical role in programming offspring's physiological functions. This period is sensitive to several insults, e.g. to maternal nutritional state, metabolism and lifestyle, which might be crucial regarding to both mother's and offspring's health before, during and after pregnancy. Environmental exposures before conception and during early fetal development are considered to be responsible for a large part of human disease risk and they are believed to program the predisposition for certain illnesses. The so called 'fetal programming' is thought to be related to epigenetic modifications, i.e. to acquired chemical changes in DNA (methylation), histones (acetylation and methylation), and the role of non-coding micro RNAs inducing chromatin remodelling is assumable as well. These permanent modifications work in concert to regulate gene expression and provide a link between environmental stimuli at early development and susceptibility to adult illnesses, and they may be transferred to other generations as well.

## **PERICONCEPTUAL PERIOD AND NUTRITION**

Among environmental factors, maternal nutrition has probably the most important role in the development of fetal programming. Important to emphasize that nutrition is the most easily modifiable environmental factor, so detrimental impacts of perturbed nutritional state would be easily prevented. The frequent prevalence of malnutrition both in developing and developed countries places it on a substantial place of the map of environmental agents. It is known to disturb several metabolic pathways, and such, disturbances in parental nutrition state may modify fertility, early fetal development and the evolution of intrauterine growth restriction, preterm birth and stillbirth, and offspring's health in long-term as well. Both the immediate and long-term consequences of the alteration of reproductive milieu are crucial in terms of the offspring's health. The sensors for parental nutritional status are metabolic co-substrates, which are involved in the molecular process of epigenetic modification, so they might be able to 'translate' nutritional status to epigenetical changes.

Many animal studies prove that perturbation of maternal nutritional state may act as an early mechanism of embryonal and fetal programming. The ongoing metabolic stress inhibits embryonic cell proliferation and the generation of appropriately sized stem-cell pools. In long term, certain disease prevalences, abnormal nurture state of offspring's and altered growth of fetus can also be observed, which are governed by epigenetic modifications (Jang et al. 2014). Offsprings conceived to mothers expressing severe malnutrition showed changes in hypothalamic-pituitary-adrenal axis function, which has long term implications to health – i.e. may be attendant with altered body composition, glucose metabolism, and cardiovascular function, and may predispose the individual for the development of metabolic syndrome (Matusiak et al. 2014). Maternal endocrine profiles independent from hypothalamic-pituitary-adrenal axis and hepatic gene expressions are also modified, for example IFG family and adipokin receptors are varied.

Maternal obesity and aberrations in maternal glucose metabolism is an increasing concern in developed communities and is accompanied with severe complications both in pregnant women and in fetus/newborns. It is often associated with impaired liver functions and insulin

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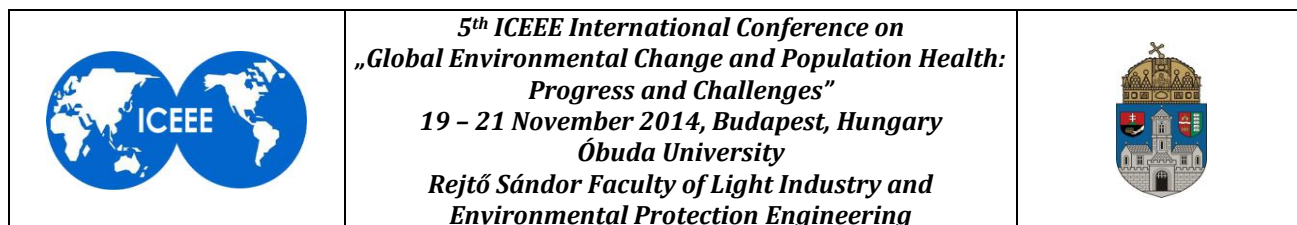
resistance, which was shown to decrease fertility and having adverse effects on the oocyte and preimplantation embryo stage (Sinclair et al, 2013), worsening the quality of these. Overweight women participating in infertility treatment have higher risk for spontaneous pregnancy termination and unsuccessful treatment. During pregnancy, obesity may promote the development of gestational diabetes, which in turn increases the risk of fetal diabetes and overweight. Furthermore, it increases the risk of maternal hypertension, pre-eclampsia and thromboembolism, underscoring the importance of optimal maternal weight and nutrition before conception (Matusiak et al. 2014). Non-communicable diseases – such as diabetes or obesity – were attributed to unhealthy lifestyle for a long time, which idea was later challenged and intrauterine environment was stated to play a crucial role in their development. Maternal obesity and diabetes have made an increasing contribution to childhood obesity and diabetes at a young age. Besides the adverse effects on long-distance, overweight during pregnancy increases the risk of stillbirth, preterm birth and neonatal mortality (Hadar et al. 2014).

Even moderate weight loss before pregnancy was found to be beneficial, but the potential risks – i.e. under nutrition – should be kept in mind. Moderate weight loss among mothers before pregnancy decreased the chance for developing gestational diabetes and pre-eclampsia. Offsprings born to women underwent weight-reducing surgery had better cardiometabolic profiles compared with their sibling born before the surgery. The interrelation between low maternal weight at conception and low birth weight has been described 25 years ago (Kramer 1987), but human studies on the subject are severely missing. It was clearly shown in the most famous study of its kind – the so called Dutch Famine cohort study, which was investigating offsprings of mothers underwent serious under nutrition in the second World War during their pregnancy– that descendants had greater risk of metabolic disorders, e.g. obesity and glucose intolerance, increased prevalence of cardiovascular diseases, breast cancer and for certain psychiatric disorders even several decades later and the effects may be transmitted to other generation as well (Jang et al, 2014). Important to note that regarding the outcomes of these adult diseases, the first trimester of maternal pregnancy was proven to be the most significant period. Another human study examining the offsprings conceived to mothers during starvation in The Gambia showed increased rate of preterm birth and elevated number of morbidity and mortality in young adult offsprings. Differences in epigenetic patterns between the control group and the one conceived during starvation could have been shown as well.

Besides over- or under nutrition, specific dietary patterns may cause detrimental effects in offsprings. Disturbances in maternal protein metabolism results in the elevation of ammonium levels in tissues and affect embryonic and fetal development (Sinclair et al. 2013). Perturbation of one-carbon metabolism - besides contributing to reproductive failure of women - may cause insulin resistance and hypertension in the offspring (Stegers-Theunissen et al. 2013). A study involving human pregnancies showed that a dietary pattern containing several protein-rich food, fruits and whole grains is associated with reduced rate of preterm delivery, while a diet mainly consisting of arbitrary components is associated with preterm delivery, shorter birth length, and earlier gestation (Grieger et al. 2014). Maternal hypercholesterinaemia during pregnancy increases the risk atherosclerosis in the offspring. Intake of long-chain polyunsaturated (omega 3) fatty acids during pregnancy reduces the risk of allergic sensitisation, allergic diseases and cardiovascular risk of fetal. A human case-control study showed that cleft lip or cleft palate was two fold more frequent in offsprings of mothers' on Western diet (rich in potatoes, meat, and low in fruit, Vujkovic et al. 2007).

The presence or absence of certain vitamins and micronutrient supplements in the periconceptual period are also of crucial importance. Their absence may accompany both over- and under nutritional state in mothers. In general, pre-or periconceptual intake of





vitamins and micronutrients suggest to increase fertility (Grajecki et al. 2012) and reduce the risk of pregnancy complications, such as preterm birth or small birth weight of the neonate (Ramakrishnan et al. 2012). Periconceptional nutritional supplementation strategies focus mainly on iron and folic acid. Folic acid supplementation administered in the periconceptional period has been established having preventive effects on neural tube defects and on some cardiovascular anomalies, and may reduce the risk of certain childhood cancers; while iron fortification is necessary to prevent anaemia and related disastrous consequences in the mother and fetus. Vitamin B-12 has also been suggested to contribute to neural tube defect prevention. Multiple micronutrients often taken by pregnant women but with limited proven benefits. Periconceptional antioxidant rich diet – especially with the inclusion of vitamin C – might help to influence glucose tolerance and prevent gestational diabetes (Cetin et al. 2010). Higher dietary intake of antioxidants or antioxidant rich foods during pregnancy reduces the risk of wheezing, asthma and eczema in the offspring. Maternal D vitamin status is also associated with allergic diseases (Palmer 2011).

#### **PERICONCEPTIONAL PERIOD AND LIFESTYLE FACTORS**

Couples consciously planning pregnancy usually maintain healthier lifestyle but still many women could improve their habits in connection to pregnancy. According to a Danish study, the extent of alcohol consumption in affected couples is higher than recommended for best pregnancy outcome (Backhausen et al. 2014), but other lifestyle factors should be paid attention to and the behaviour change should be recommended from several aspects. Besides the control of nutritional state and adequate vitamin/micronutrient supplementation or fortification, which are detailed above, pre-or periconceptional parental smoking and alcohol interventions are the most effective factors to prevent pregnancy complications and birth defects. Furthermore, addictive parental behaviour – e.g. towards alcohol or nicotine – has trans-generational consequences as well; i.e. preconceptional exposure to the addictive drugs – probably via epigenetic modifications – promotes the development of addictive phenotypes in the offspring (Vassoler et al. 2014).

Fetal alcohol exposure is the leading preventable cause of birth and developmental defects in the United States. Despite a growing body of evidence and the awareness of the anomalies resulting from fetal alcohol exposure, 1 in 9 pregnant women continues to drink alcohol during pregnancy, and a small percentage of pregnant women continues excessive alcohol consumption (Waterman et al. 2013). Besides abnormal brain development – which results in cognitive and behavioural disabilities – fetal alcohol exposure may cause preterm birth, growth retardation and facial dysmorphism. It causes deficits in both gross and fine motor functions. The most sensitive period to alcohol is the first trimester of pregnancy, but the relevance of preconceptional alcohol intake should also be emphasized. Reduced birth weight and increased number of malformations in the infant can be observed in preconceptional paternal alcohol drinking habits too (Ramsay 2010). Maternal alcohol intake in the periconceptional period – besides the above enumerated anomalies - was shown to be associated with higher risk of several congenital diseases, e.g. d-transposition of great arteries, neural tube defects and cleft lip with or without cleft palate in the offspring (Grewal et al. 2008). Conotruncal defects of the heart was described to have only mild association with alcohol consumption during periconceptional period. Though the risk was elevated with increasing amount of consumed alcohol, the risk assessments were imprecise and the chance could not be ruled out as an explanation of the findings (Carmichael et al. 2003).





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Maternal smoking is an increasing concern among women planning pregnancy in near future. It has been clearly showed in cohort studies that smoking has a negative effect on fertility; this issue needs to be addressed carefully since fertility is continuously dropping in developed countries. Offsprings born to smoking mothers have a higher incidence for congenital anomalies, specially limb abnormalities and defects in central nervous system (Merritt et al. 2013). Maternal active smoking and exposure to passive cigarette smoke emerged as a potential teratogen that affects furthermore digit formation and was associated with an increased risk for cleft lip with or without cleft palate in offspring. It shows a positive association with cardiovascular anomalies and musculoskeletal defects, craniosynostosis, clubfoot, facial defects, eye defects, gastrointestinal defects, gastroschisis, hernia and anal atresia. Even periconceptional paternal smoking increased the risk of certain cardiovascular heart defects in the infant, e.g. isolated conotruncal heart defects, septal defects and left ventricular outflow tract obstructions. An early epidemiologic study examined the effect of certain parental lifestyle factors in the development of offspring's mental retardation, and found positive association with paternal smoking (and maternal alcohol consumption) before and during pregnancy (Roeleveld et al. 1997). Maternal smoking during pregnancy is significantly associated with low birth weight according to several analysis. In contrast, smoking is associated with a lower risk for neural tube defects and conotruncal heart defects (Grewal et al. 2008). A negative association was shown between maternal smoking and hypospadias and skin defects in the offspring (Hackshaw et al. 2011).



The role of periconceptional stressful life events has been established in many adverse birth outcomes. It has been described that stressful life events prior to conception were strongly associated with very low birth weight of neonates (Witt et al. 2014). Major maternal stress in the first trimester is also accompanied with elevated risk for gastrischisis, a severe anomaly with increasing incidence worldwide (Palmer et al. 2013).

## **PERICONCEPTIONAL PERIOD AND ENVIRONMENTAL FACTORS**

Environmental factors (e.g. pesticides, arsenic, bisphenol A – BPA, phthalate, fragrances, plastics, cosmetics, antibiotics) may also have special importance during the periconceptional period. Preconceptional exposure to environmental chemicals is linked to delayed conception, while prenatal exposure results in various adverse health consequences of the infant.

Increased phthalate levels in men for example were shown to be associated with longer preconceptional period. Phthalate exposure negatively influenced the level of reproductive hormones in both genders (Jurewicz et al. 2011) and some studies indicate its adverse effects on sperm quality in terms of morphology, motility and concentration. Extensive research shows that many pollutants are capable of modifying physiological systems in mammals. Lead and persistent organic pollutants have been associated with decreases in measures of sperm quality and changes in the character of menses, thus causing a delay in pregnancy. Prolonged BPA exposure may also increase the risk of infertility in women. Human studies are scarce on the subject, but *in vitro* and animal models suggested a correlation between BPA exposition and adverse reproductive health. Women undergoing *in vitro* fertilization cycles were examined to urinary BPA content, and higher concentrations were linked to decreased ovarian response for stimulation - reflected in lowered estradiol peak and oocyte count at the time of retrieval -, reduced number of fertilized oocytes, and blastocyst formation was also lowered (Ehrlich et al. 2012).

Elevated exposure to pollutants might alter fetal development as well, e.g. preconceptional maternal and paternal concentrations of several persistent organic pollutant were associated

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with statistically significant differences in birth size among offspring. Occupational exposure of prospective fathers in the preconceptional period to pesticides, solvents or welding fumes increased the prevalence of congenital anomalies among their offsprings (El-Helaly et al. 2011). Maternal exposure to pesticides increased the occurrence of neural tube defects according to a study in Mexican Americans (Brender et al. 2010); but exposition to agricultural work (pesticides) of both mothers- or fathers-to-be was associated with elevated number of anencephalic children (Lacasana et al. 2006) in other populations as well. Permanent intake of low dose pollutants (including BPA and phthalate) starting from the periconceptional period resulted severe – gender specific - metabolic alterations in the descendants of a mouse model. In males, target genes of cholesterol homeostasis were influenced, while in females glucose tolerance and estrogen-response related genes were extremely affected (Neville et al. 2013).

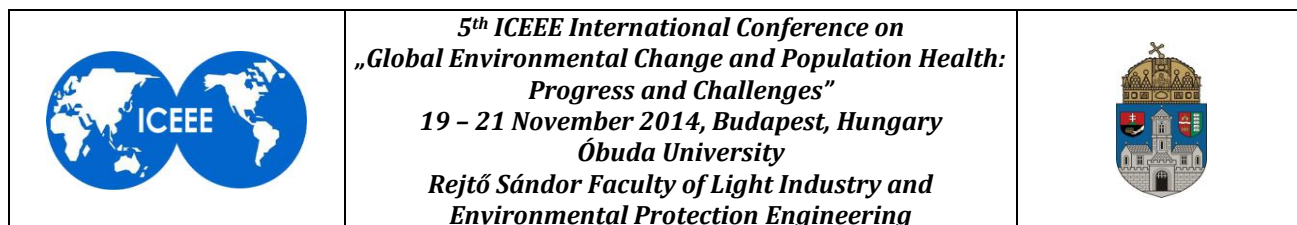
## CONCLUSIONS

Besides its important role in the pregnancy outcome, periconceptional period is considered to be a critical time to prevent 'fetal programming' and related future diseases or anomalies of the offsprings. Since periconceptional period starts before the conception, conscious pregnancy planning accompanied with behaviour change and healthier lifestyle of parents-to-be are of crucial importance. Improving the nutrition and the health of young girls could therefore make a significant contribution to reducing the rapidly rising number of obesity and diabetes – the primary components of metabolic syndrome - worldwide. This *in utero* prevention is referred to as primordial or primary prophylaxis of these diseases (Yajnik, 2014). Besides its beneficial effects on offspring and other generations, maternal hazards may be also reduced during pregnancy.

Keeping offsprings' long-term health in mind, obstetric clinics should offer a periconceptional weight management program and should extensively educate prospective mothers for the risks of malnutrition and unhealthy lifestyle. Since unhealthy dietary patterns are usually associated with other lifestyle factors negatively influence pregnancy outcome, their effects may be accumulated and even more detrimental for the infant. The most important aim is to keep maternal BMI in a normal range -even before conception. To achieve this, dietary modifications and increased physical activity in the preconceptional period is recommended. However, both potential benefits and risks of weight loss prior pregnancy should be kept in mind in the population attending obstetrics clinics in the preconception period. However, till now evidence-based guidelines do not exist for the management of obesity. This is partly due to the fact that human studies are lacking in studying the effects of periconceptional weight loss, which encumber the elaboration of optimal timing and mechanism of weight reduction. The exact mechanisms by which nutritional insults result in long-term change in programming infants are still to be elucidated, however, epigenetics is thought to play a key a role in the process. In future, it might be of importance to evaluate the most critical periods during periconceptional time frame to enhance effectiveness of the prevention, but till now it seems that the whole period of periconception is of crucial relevance.

Despite a high level of pregnancy planning, awareness of preconception health among women and health professionals is low, and responsibility for providing preconception care is unclear. Besides the attendance of antenatal care, consulting prior to conception is also highly advised, and recommendations, examination should be extended to the preconceptional period as well. Important to emphasize that both partners should be involved in preconception counselling, since many adverse outcomes are associated with paternal health and lifestyle





factors. In long term, awareness of pre- and periconceptional risk factors foresee wider benefits for public health care, including reduced burden of patients with congenital anomalies and non-communicable diseases.

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## **ECODESIGN AS A PART OF PRODUCTION**

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### **ABSTRACT**

Ecodesign is an environmental management tool, which is suitable for optimizing the production of the product. It is determined by the pre-production phase of the product life cycle. It is known that the total impact of a product on the environment shall be decided in the design phase of the product life cycle. It provides an ideal eco-design tool for optimal design of the product in relation to its life cycle. This paper informs about the importance of combining of the tool, not only in relation to the environment but also in relation to safety and quality.

*Keywords: Ecodesign, environment, safety, quality*

### **INTRODUCTION**

A DfE program cannot be implemented in isolation from other programs within a product-development organization. The program needs to be integrated with other programs that fall under the corporate responsibility umbrella and carry the same weight. Typical corporate responsibility programs include giving back to the community, promoting diversity awareness. These programs have detailed plans and goals that are disseminated to all employees through a substantial medium such as a communications meeting. The employees then begin “living” these programs, which results in a corporate culture.



Most product-development organizations environmental awareness initiatives are based at the manufacturing level rather than the product level. A new DfE program will most likely be integrated with this preexisting portion of environmental awareness. Upon implementation, the program objectives and specific process need to be clearly presented to employees. The commitment from the upper management within the organization should be enough to get the program rolling. If there is resistance, the organization may need to implement a system that rewards those who participate. Only after seeing the organizations commitment and receiving direction can the engineers do their jobs and determine how to meet the goals [6].

### **IDENTIFYING THE STAKEHOLDERS**

The first step in creating a DfE program is to identify and understand the environmental stakeholders. Stakeholders ultimately define the objectives and resulting environmental metrics of the DfE program. Between the typical stakeholders for product development organizations are:

- board members,
- socially responsible investors,
- non-government organizations,
- government organizations,
- customers,
- competitors,



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- community.

Each stakeholder has different environmental interests, which leaves the organization with a considerable amount of environmental demands to meet. Since product development organizations operate with limited resources, the stakeholders will need to be prioritized based on their influence on the organization.

### **CREATING ENVIRONMENTAL OBJECTIVES**

After a thorough analysis of the stakeholders, it is possible to create environmental objectives for the DfE program. The environmental objectives will need to align with as many of the environmental demands of the stakeholders as possible. The objectives will also need to align with the values and culture of the corporation.

Since it is necessary for an employee to adapt to the values that will align with employee values and should be successfully implemented. When creating environmental objectives, it is important to use the correct level of specificity.

The objectives should be broad enough that they do not have to be frequently updated but specific enough that they provide consistent direction for the DfE program. An environmental objective of “protect the Earth” would be too broad, while “eliminate the use of lead” would be too specific. Environmental objectives should have lower-level targets associated with them so the company can assess its progress toward objectives. For example “eliminate the use of lead” could be a lower-level target for the environmental objective “reduce the use of hazardous materials” [3].

### **IMPLEMENTING A DfE PROCESS**

In this chapter is defined a DfE process that naturally integrates environmental issues into the existing product-development process with little extra effort or time. Every stage requires certain tasks to be completed before management signs off, giving permission to proceed to next stage. Safety reviews are meetings intended for reviewers to evaluate the assessment, actions, and process of the design team in addressing product safety. The DfE process adds an environmental review to the agenda of the safety reviews held during stages 2, 4 and 5. A separate environmental review will be held during stage 3, an important design stage, in order to focus specifically on the environmental issues for the particular product. The environmental reviews will require design team to review the checklist of key requirements and to consider guidelines for reducing environmental impact. When the DfE process is first implemented, design teams will have to fill out the environmental scorecard only during stage 5 after the product design is complete. Doing this begins the process of recording environmental data and allows design teams to adapt gradually to the new process. When design teams become more familiar with the process, the scorecard will be completed two or more times during the stage-gate process in order to track design changes that affect environmental metrics during the development process. Environmental targets will be set during stage 1 as goals for the new product. The design team will write a lessons-learned summary during stage 8 to highlight innovative environmental design changes. The lesson-learned summary will provide the innovation statement metric. Figure 1 shows the Safety Review Process and Environmental Review Process running parallel [2], [4], [5].

The first environmental review is coupled with a safety review. During this meeting, the design team should discuss current environmental regulations, design guidelines and environmental metrics. The environmental metrics can be found in the guidelines and checklist document.



The second environmental review is held separately from the safety hazard review. During this meeting, the project team will check compliance regulations, fill in the guidelines and checklist document, discuss the metrics in the scorecard and review opportunities and additional environmental issues.

The third environmental review is coupled with a safety review. During this meeting, the project team should ensure that all environmental compliance issues are resolved. There should be no further changes to the design due to environmental reasons after this meeting. The lead engineer will update the scorecard for the next meeting.

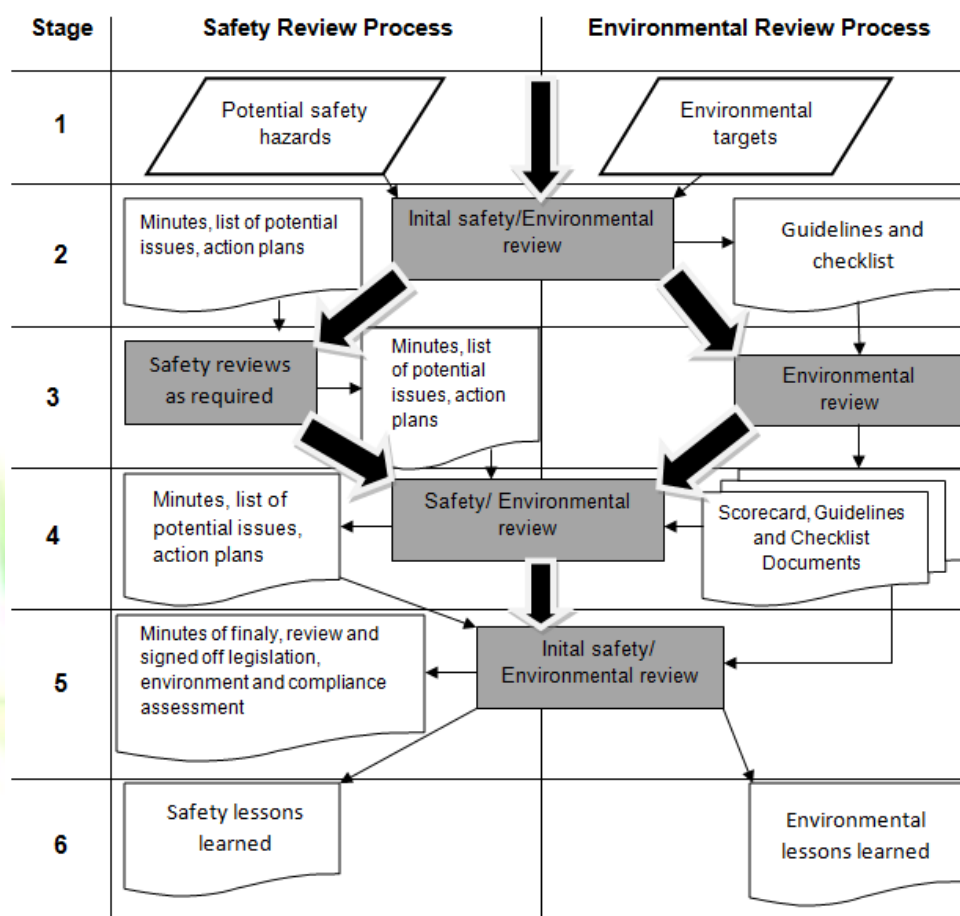








Figure 1 combined safety and environmental review process

legend:

-  = deliverable
-  = input
-  = process
-  = path of main processes

The fourth and final environmental review is coupled with a safety review. During this meeting, all environmental compliance issues must be resolved. Optimally, no design changes due to environmental reasons would have been made between the last meeting and this meeting. The result of the meeting is a final guidelines and checklist document and meeting minutes. The

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reliability representative will finalize the guidelines and checklist document and write the minutes. The lead engineer will finalize the scorecard and create a material declaration statement packet for the product.

## CONCLUSION

The completed guidelines and checklist documents and lessons-learned summaries create a feedback loop for the DfE process. Design engineers working on similar products can use this information to make better decisions immediately, and the information is also valuable when the next generation of the product is designed years down the road. Design engineers will decision information, scorecards, and comments on the guidelines document will be archived permanently. The goal is to save the right things so the information is there in the future when more feedback activities, such as a product tear-down to verify scorecard metrics, can be introduced.

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## **CROSS-BORDER WATER STREAMS QUALITY IN THE BANAT REGION**

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### **ABSTRACT**

This paper represents results of surface water monitoring of watercourses in Banat region that includes the largest and most important rivers that are the part of Danube basin. The monitoring was performed as part of the project Romania-Republic of Serbia IPA Cross-border Cooperation Programme. After analyzing the data resulted from the surface water monitoring campaign of main Banat Rivers it becomes clearly that is difficult to draw a clear conclusion. It is difficult to analyze this data especially due to untypical weather conditions during May 2014, with unusual cold temperatures and frequent rain episodes. However, the analysis of water generally showed that water from selected localities at watercourses of Banat region are loaded with nutrients, especially nitrites and phosphorus, which causes relatively low concentrations of dissolved oxygen.

**Keywords:** *water quality, stream, Banat, monitoring*

### **INTRODUCTION**

Banat is geographically referred to as a part of the Pannonian Basin bordered by the River Danube to the south, the River Tisa to the west, the River Mureş to the north, and the Southern Carpathian Mountains to the east. Banat region is divided among three countries (30.680 km<sup>2</sup>): the eastern part lies in western Romania, the western part in northeastern Serbia (mostly included in Vojvodina) and small northern part lies within southeastern Hungary (<http://www.zrenjanin.rs/1-92-19-0/banat>).

Serbian part of Banat is divided into three administrative districts: North, Central and South Banat, with seventeen municipalities and two communities with the status of a town, Pancevo and Zrenjanin. The Serbian part of Banat region is a plain with Deliblatska pescara and Vrsac mountains (elevation 641m) in the south, bordered with the natural waterways, Danube and Tisa, to the south and west respectively. The most important economic branch is the agriculture, still the industrial facilities are rather present. These facilities are oriented mostly to the food industry, ceramic manufacturing industry and the oil and gas production and processing industry.

Romanian part of Banat, with 18966 km<sup>2</sup> is divided between four counties: Tamis, Caras-Severin only, Mehedinti (only small area in South-West) and Arad (small area south of Mureş River). The main cities are: Timișoara, Caransebet, Lugoj, Retita and Orsova. The Romanian Banat region is mainly formed by plain (Timiș County) and wild mountains and forests (Caraș County). There are numerous and important natural reservations in the area, most of them in Caraș county, such as: Buhui cave, Beușnița waterfall, Viroaga waterfall, Cheile Nere national park, Cheile Carasului, national park, Iron gates, nation park, Ochiul Beilului lake, a.o.





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The Danube is greatest and the most important river in region. The greatest and the most important Danube influent river in Banat region are Tisza river (for Serbian part), as well as Bega, Tamis Nera and Karas.



Picture 1: Map of Banat region

One of the features of the Banat watercourses is that they all have their source in Romania, and confluence in Serbia. All the rivers get and carry water coming from the Romanian Carpathians and in their upper parts have extremely torrential character. The river flows through Romania for 241 km, and 118 km through Serbia. In its lower course, the river is regulated, and for the last 53 km it is navigable. The most important port is the heavily industrialized Pancevo.

Course of the river Tamis is mostly lowland with intensive agricultural production which presents the most significant diffuse source of pollution. Also, significant pressures in urban and rural areas are sewage effusions and wild dump.

A pollutant register is made for the river Tamis in Serbian part of Banat which has identified all significant point and diffuses sources of watercourses pollution. Pollution register covers 17 villages located in 5 local governments that lie by the watercourse of the Tamis. Pollution register has detected 18 activities divided into 6 sectors, i.e. 69 polluting substances which are discharged from point and diffuse sources of pollution. One of the most significant pressure on the Tamis river by Romanian side is city Lugoj which besides food processing industry (dairy, mlin) has also an textile and leather industry, wood, ceramic and industry of building metal construction production (Aleksic et al, 2010).

The Bega channel represents a landmark both for the Banat region. Next to the Danube and the Tisza, Bega is the most important river in Banat and the largest tributary of the Tisza in Serbia. From the source to the confluence length of the Bega is 244 km of which 67 km in Romania and 168 km in our country.



As well as Tamis, Bega River flows through agricultural area, as well as few industrially developed centers. Point sources are various industrial sectors (chemical, construction, machinery, animal husbandry industry) located at the entire part of watercourse at Romanian side, while on Serbian part of watercourse dominant industrial pollution sources are various: from food and chemical industry to metal industry.

Pollutant register was made for the Serbian Bega river which identified all significant point and diffuse sources of pollution of watercourses (JVP „Vode Vojvodine“, 2010).

Despite the fact that Banat is agricultural area which makes it a convenient base for the development of food industry, there is also a wide range of other industry sectors. Both sides, Serbian and Romanian Banat part has a long industry tradition, which is reflecting on rivers water quality.

## MATERIALS AND METHODS

One of the defined activities of the IPA project was the monitoring of surface water quality in the region of Banat performed by both Serbia and Romania side. Monitoring was performed in order to define the surface water quality as well as it's degradation by industrial, urban and other relevant pollution sources typical for this region. Selection of parameters and location for sampling was performed according to standards and recommendations for surface water monitoring and it was based on detail analyses of the present point and diffuse sources, as well as the previous results of surface water monitoring. The Surface water monitoring considered 41 sampling points – 22 in Serbia and 19 in Romania, on total seven watercourses (Tamis, Bega, Tisza, Danube, Nera, Karas, HS Nadela) (Figure 1). Only results of Bega and Tamis water analysis will be shown in this paper.

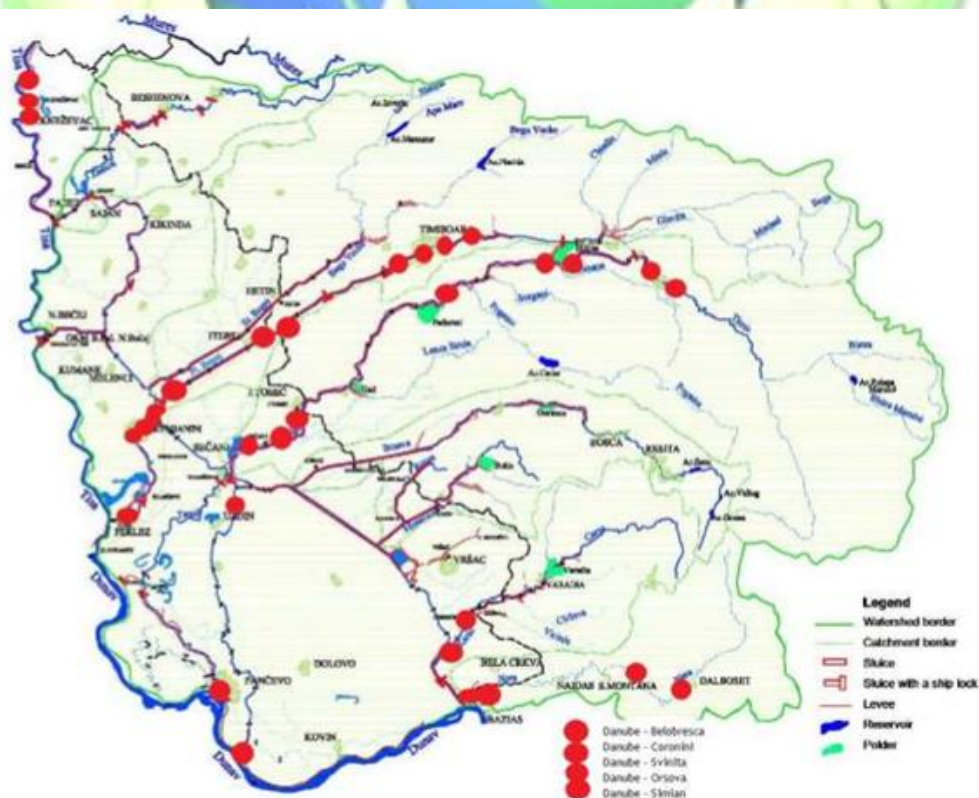




Figure 1: Map of Bega canal measurement site location

After a sampling organoleptic analysis, presence of visible matter water temperature, pH value and dissolved oxygen concentration were done on site. Concentrations of nitrate nitrogen, nitrite nitrogen, total phosphorus, suspended solids, COD and BOD<sub>5</sub> were done in laboratory using spectrophotometry within the 48 hour from sampling time. Methods that were used in analysis of individual parameters are shown in *Table 1*.

Table 1: Methods used for analysis of water samples

Parameters	Methods
Ph	Potenciometry
Dissolved oxygen	Voltametry
Suspended matter	Spektophotometry
Bod5	Manometry
Cod	Dichromate method/ spektofotometry
No3-n [nitrates]	Spektophotometry
No2-n [nitrites]	Spektophotometry
P [phosphorus]	Spektophotometry

### LIMIT VALUES OF MEASURED PARAMETERS

According to Ordinance on limit values of pollutants in surface and ground water and sediment, and the deadlines for their achievement (*“Official gazette RS” No 50/2012*), Banat rivers are classified in following groups: Type 1 - large lowland rivers, the dominance of fine sediment (Bega, Tisza, Tamis, Danube), Type 2- the great river, the dominance of the middle sediments (Nera), and Type 5- streams of the Pannonia basin (Karas).

Limit values for measured parameters prescribed in Rulebook on parameters of ecological chemical status of surface waters and parameters of ecological, chemical and quantitative status of ground waters (*“Official gazette RS” No 74/2011*) are shown in *Table 2*.

Table 2: Limit values for measured parameters in surface water

Parameters	Unit	Limit value				
		I class*	II class*	III class*	IV class*	V class*
<b>pH</b> (Type I, II and V)		6,5-8,5	6,5	8,5	6,5	>6,5 or >8,
<b>Dissolved oxygen</b> (Type I, II) (Type V)	mgO <sub>2</sub> /l	8,5 8	7 6	5 5	4 4	>4 >4
<b>Suspended matter</b> (Type I, II and V)	mg/l	25	25	-	-	-



<b>Nitrates (Type I) (Type II and V)</b>	mg/l	1 1,5	3 3	6 6	15 15	>15 >15
<b>Nitrites</b>	mg/l	0,01	0,03	0,12	0,3	>0,3
<b>Total phosphorus (Type I and II) (Type V)</b>	mg/l	0,05 0,15	0,2 0,3	0,4 0,4	1 1	>1 >1
<b>BOD5 (Type I) (Type II) (Type V)</b>	mgO <sub>2</sub> /l	2 1,8 2,5	5 4,5 5	7 7 7	25 25 25	>25 >25 >25
<b>COD</b>	mgO <sub>2</sub> /l	10	15	30	125	>125

**I class** - Water in this class corresponds to **great ecological status**. Surface water in this class, based on limit values of quality elements, provide conditions for functioning of ecosystems and survival and protection of fishes (salmonides and ciprinides) and it can be used in the following purposes: as a drinking water after pre-treatment that includes filtration and disinfection, for swimming and recreation, irrigation, industrial use (process and cooling water).

**II class** - Water in this class corresponds to **good ecological status**. Surface water in this class, based on limit values of quality elements, provide conditions for functioning of ecosystems and survival and protection of fishes (ciprinides) and it can be used in same purposes as I class water.

**III class** - Water in this class corresponds to **moderate ecological status**. Surface water in this class, based on limit values of quality elements, provide conditions for functioning of ecosystems and survival and protection of fishes (ciprinides) and it can be used in the following purposes: as a drinking water after pre-treatment with coagulation and flocculation, for swimming and recreation, irrigation, industrial use (process and cooling water).

**IV class** - Water in this class corresponds to **poor ecological status**. Surface water in this class, based on limit values of quality elements, can be used in the following purposes: as a drinking water after combination of treatments above and improved methods, irrigation, industrial use (process and cooling water).

**V class** - Water in this class corresponds to **bad ecological status**. Water in this class can not be use in an purpose.

## RESULTS

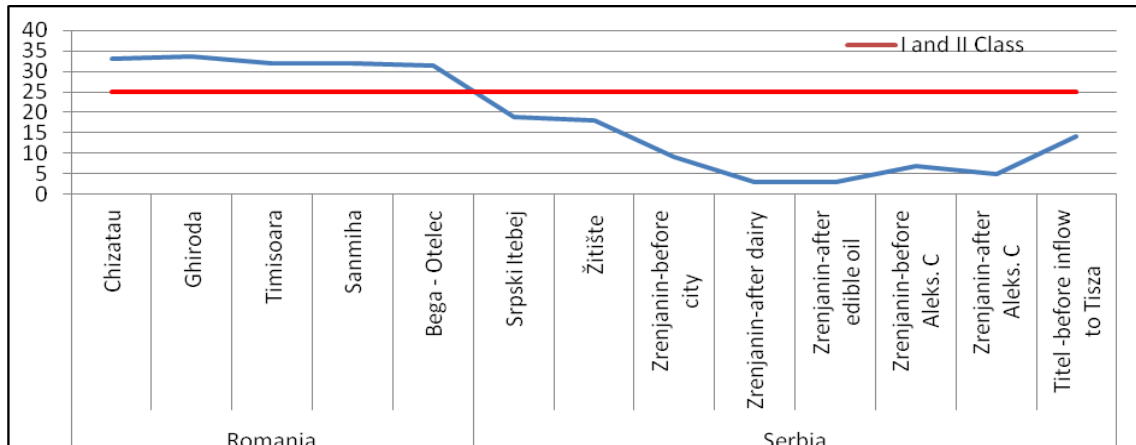
### pH values

pH value of aquatic ecosystems which are not under anthropogenic influence is on the range from 6.2 to 8 (Maletic, 2012). Acidity and alkalinity of water depend on geomorphological characteristics of soil, but also on human activities. Major anthropogenic influence on pH of aquatic system is discharge of nutrients (fertilizers) which leads to rapid growth of algae and increase of pH value. During the analysis of Bega and Tamis water samples the pH values were in range defined for I and II class of water and are considered as having a great and good ecological status, respectively (Bega-7.3 to 8.22; Timis 7.65-8.44).

### Suspended matter

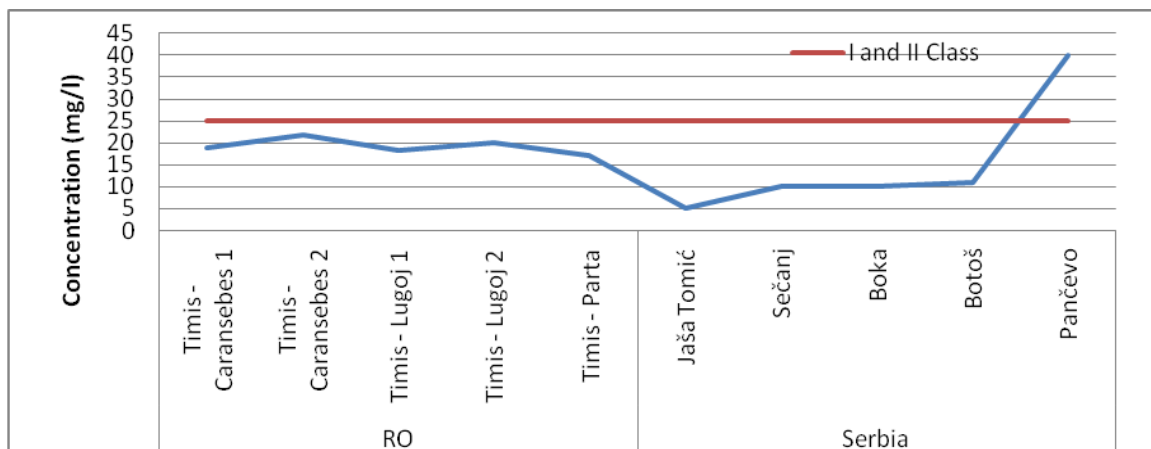
Suspended soils in surface water usually arrive by soil's washing away, erosion or sediment resuspension (Becelic and Tamas, 2004). Chemical composition may vary and it is one of it's most undesired characteristics that can have a bad impact on surface water.

Measured values for suspended soils in Bega river were between 3mg/l and 33,7mg/l (Graph 1). Measured values are higher in Romanian than in Serbian part. This can be caused by sampling in diferent part of year when meteorological conditions were difereint. In fact, samples from Romania were taken in May 2014, when there were a lot of rainfalls, that can cause higher concentrations of suspended soils.



Graph 1- Concentration of suspended matter (mg/l) in Bega river (mg/l)

Measured values in Tamis river were between 5 mg/l do 40mg/l. All measured values were classified as I and II class of water, except sample of the Tamis river taken after inlet of chemical industry (production of soaps and detergents) near Pancevo, that one is out of class.

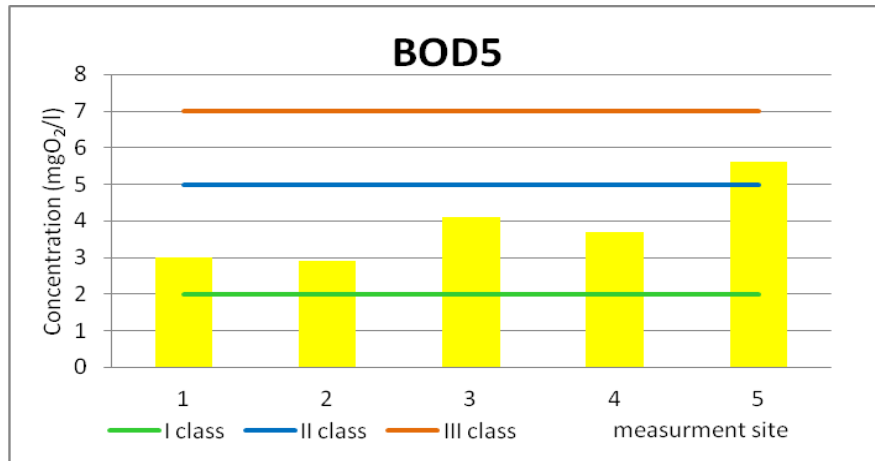


Graph 2: Concentration of suspended matter in Tamis river (mg/l)

### Biological oxygen demand (BOD)

BOD is an important parameter for usage conditions of surface waters. It is an approximate measure of the amount of biochemical degradable organic matter present in a water sample. It is defined by the amount of oxygen required for the aerobic microorganisms by the amount of oxygen required for the aerobic microorganisms (Dogan et al., 2009).

Measurement of BOD<sub>5</sub> was done only for Bega river samples, at the part that flows true Zrenjanin. Values for BOD<sub>5</sub> were in the range from 3.0 to 5.6 mg O<sub>2</sub>/l. Obtained results shown that, according to 4 samples, the Bega river may be classified as II class (good ecological status). However, sample taken after inlet of Aleksandrovacki canal shows values that classify it as III class (moderate ecological status), which confirmed that strong influence of this canal on the quality of the Bega water (Graph 3).

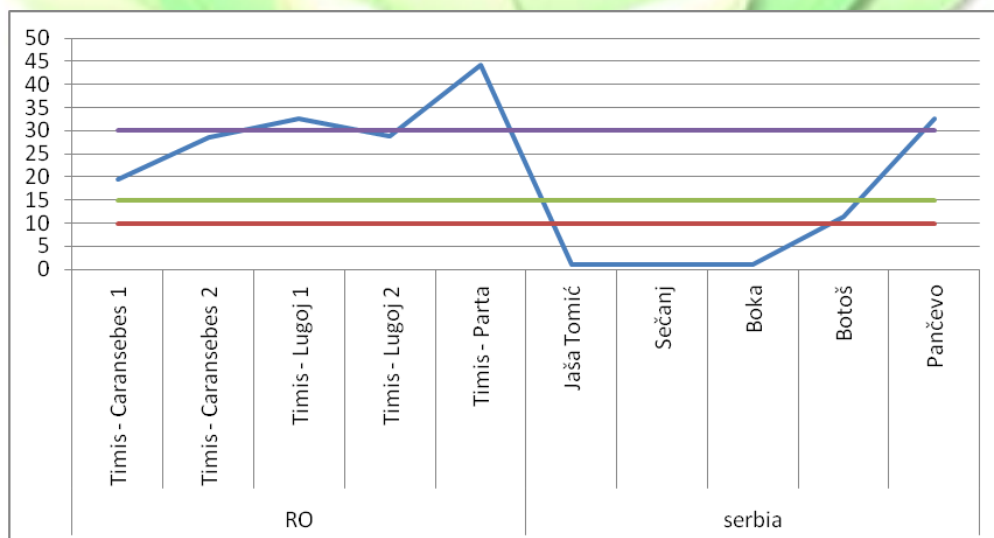


*Graph 3: BOD in samples from Bega channel (mgO<sub>2</sub>/l)*

### Chemical oxygen demand (COD)

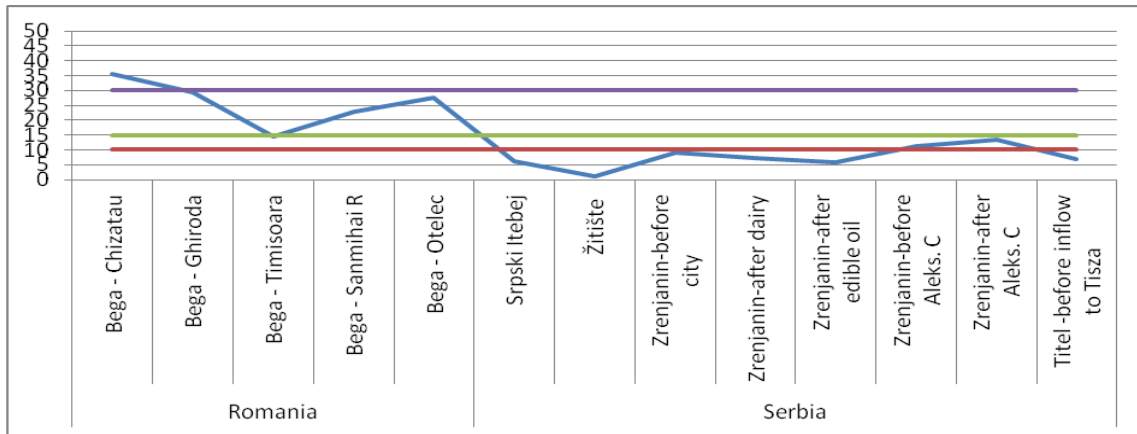
COD presents the necessary level of oxygen for oxidation of both organic and inorganic matters and it is expressed in mgO<sub>2</sub>/l. This indicator, as well as others, can be used for water pollution assessment, especially for industrial wastewater (Sawyer *et al.*, 2003).

According to results of Bega water samples analysis, COD values were in range from 1 to 29.5 mgO<sub>2</sub>/l. Samples taken from Romania side showed higher COD concentration (14.5 - 35.6 mgO<sub>2</sub>/l) compared to the water samples taken from Serbian part of Bega river (1-13.4 mgO<sub>2</sub>/l) (Graph 5). Measured COD values in Timis water samples were in range from 1.0 - 44.3 mgO<sub>2</sub>/l. High concentration which was detected after the village Parta near Timisoara could be explained by vicinity of the recently closed Timisoara's dump/waste field. Most probably the very high values recorded on Timis River (near Parta) are caused by infiltration from the dump field. Other recorded relatively high concentration of COD values on Timis river are expected concerning the fact that Timis flows some trough highly industrialised settlements (Caransebes, Lugoj in Romania and Pancevo in Serbia) (Graph 4).



*Graph 4: Measured COD values for Timis river samples (mg/l)*





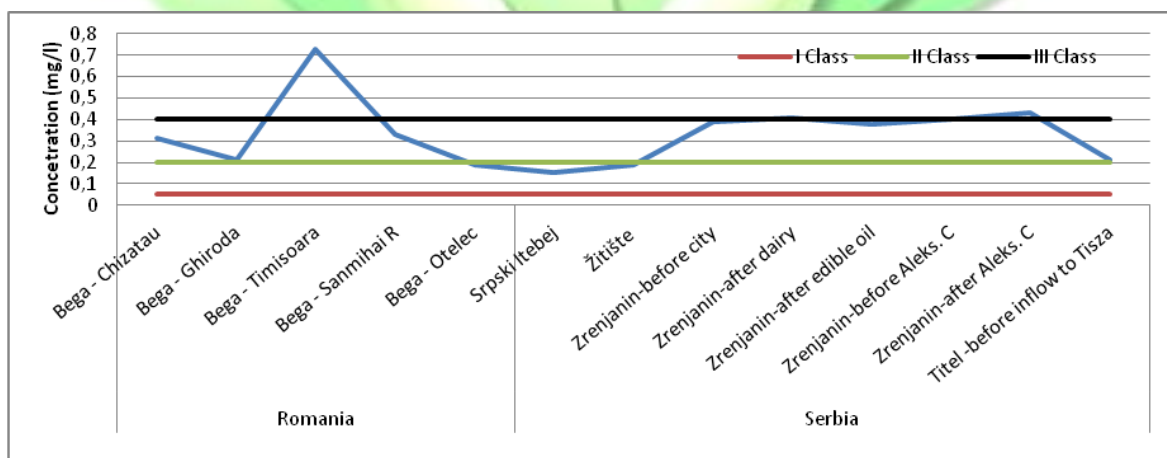
*Graph 5: Measured COD values for Bega river samples (mg/l)*

### Nutrients

Nitrogen (in form of nitrite and nitrate) and phosphorus, are chemical elements that are essential for growth of plants and animals. High concentrations of nutrients can cause a rapid growth of algae, which can reduce the concentration of oxygen in water, as well as occurrence of unpleasant smell and taste. This rapid growth of plants induced by the high concentration of nutrients is called eutrofication (*Badruzzaman et al., 2012*). A lot of groceries contain phosphorus and its loss leads to increase of its concentration in water.

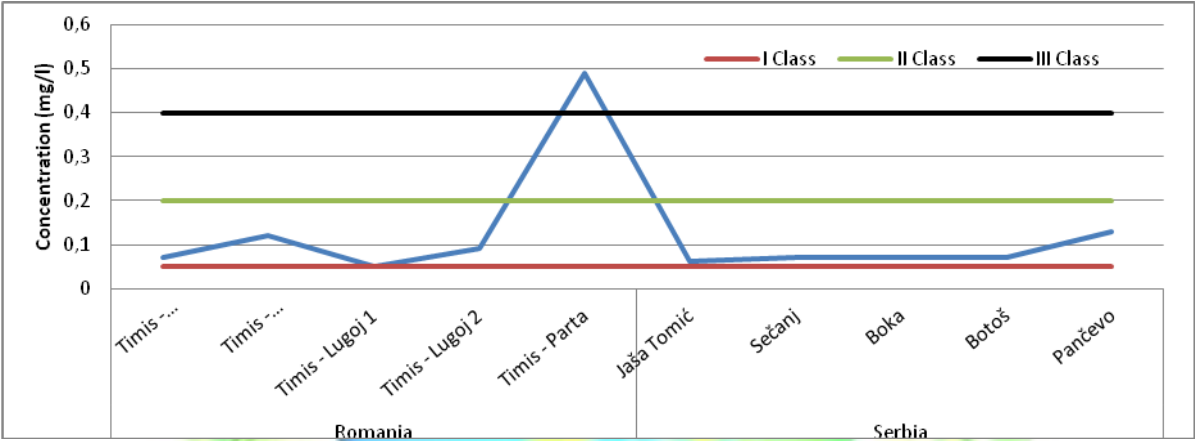
### Phosphorus

Urban and industrial waste water as well as a agricultural areas could be reason for higher concentration of phosphorus in aquatic waters. A lot of everyday groceries contain phosphorus. Phosphorus is also part of hygiene products used in food industry. The concentration of total phosphorus taken in Bega water samples were in the range from 0,16 to 0,73 mg/l. Concentrations of phosphorus in some samples taken in Timisoara and Zrenjanin reaches values that classify the samples as IV class (bad ecological status) (*Graph 6*), which confirms strong influence of urban area on water quality concerning this pollutant.



*Graph 6: Concentration of total phosphorus measured in Bega water samples (mg/l)*

Phosphorus concentrations measured on Tamis river were relatively low, in range of I and II Class of water, except sample taken near village Parta near Timisoara which showed concentration of 0,48 mg/l (IV Class of water or bad ecological status). As well as in the case of COD, the vicinity of the old dupm site could be the reason for high concentration of this pollutant (Graph 7).

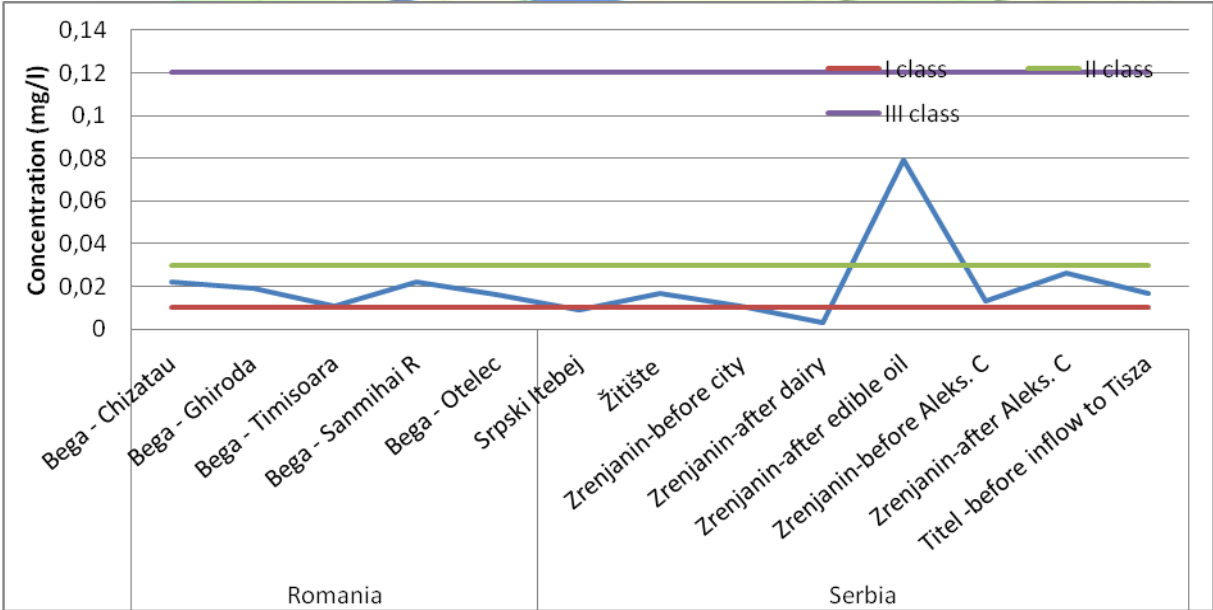


Graph 7: Concentration of total phosphorus measured in Tamis water samples (mg/l)

**Nitrites**

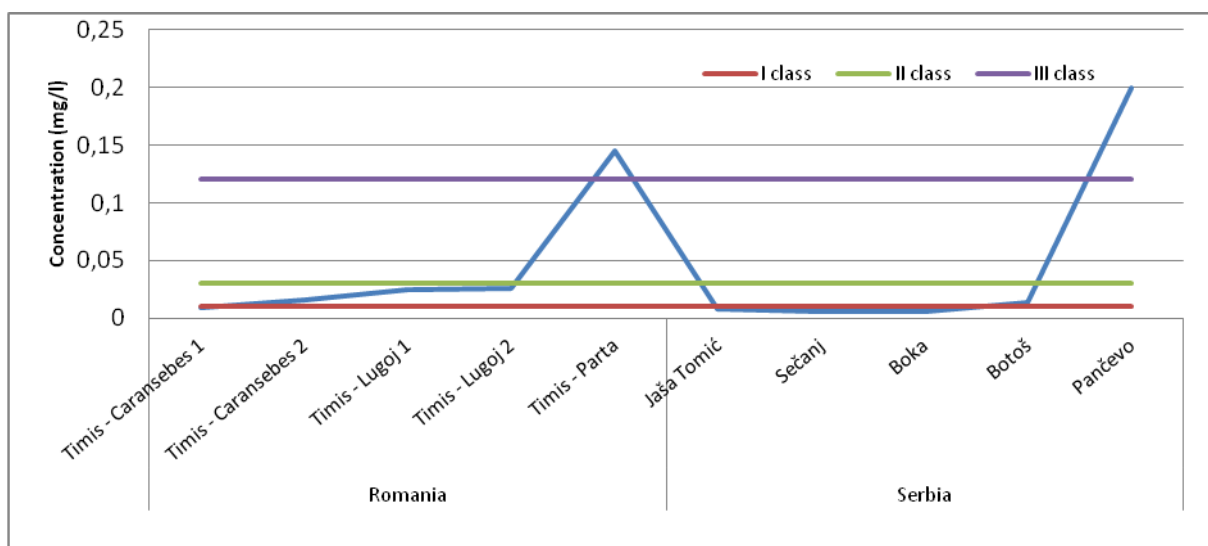
Elevated concentrations of nitrate in surface and ground waters, as a result of firstly, excessive use of nitrogenous fertilisers, and secondly, disposal of untreated municipal and industrial wastes, are a serious global environmental problem (Loganathan et al., 2013).

Bega river samples showed concentrations of nitrites in range for II Class of water, except sample taken after the edible oil industry where recorded value was 0.079 mg/l which is classified as a sample with III Class of water (Graph 8).



Graph 8: Measured concentrations of nitrites in Bega river samples (mg/l)

Total phosphorus concentrations in samples of Tamiş river were between 0,2 and 0,006 mg/l. Maximum values were noticed downstream from village Parta in Romania and after chemical industrial complex in Pancevo in Serbia. These samples may be classified as IV class of water.



Graph 9: Concentrations of total phosphorus measured in Tamiş river (mg/l)

### Nitrates

Measured concentrations of nitrates were in the range from 0,7 to 2,6 mg/l for Bega Channel and from 0.14 to 1.98 mg/l for Tamiş river. According to these results watercourses belong to I and II class.

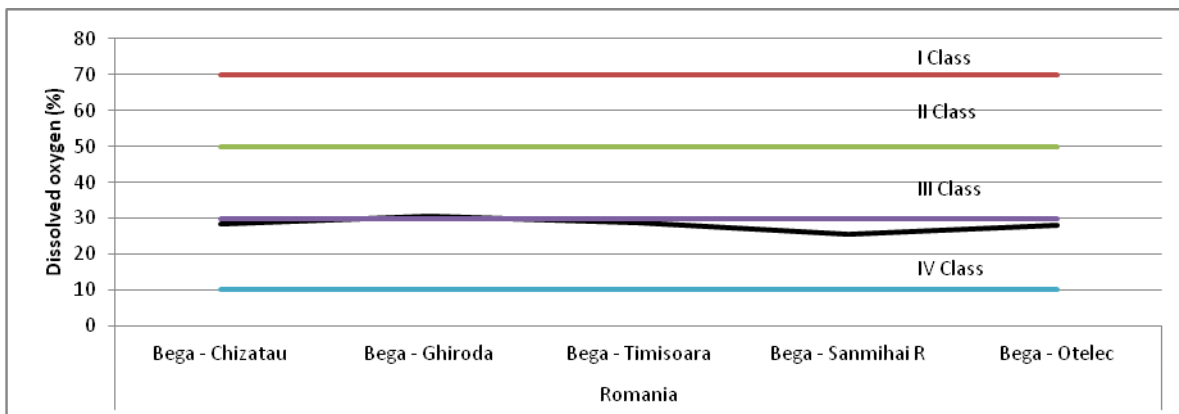
### Dissolved oxygen

Dissolved oxygen is one of the most significant features of all aquatic ecosystems because it is essential for the existence of all aquatic organisms. If the concentration of dissolved oxygen is higher, the water quality is better (minimal concentration for I class is 8,5 mgO<sub>2</sub>/l (70-90%).

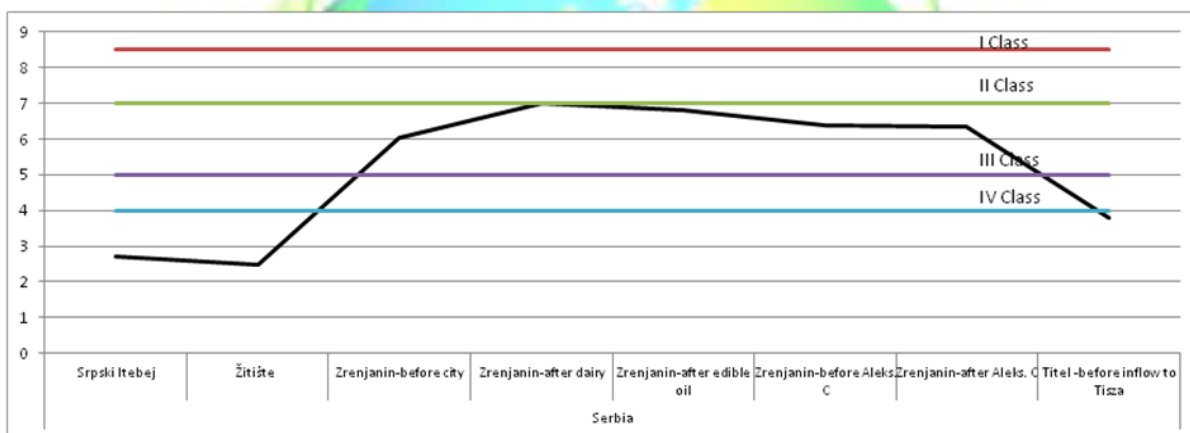
At the part of watercourses of Bega in Serbia were measured concentrations of dissolved oxygen (mgO<sub>2</sub>/l) while at the other watercourses was measured oxygen saturation (%). However, measured concentrations of dissolved oxygen were relatively low, showing values which classifies water in III Class, or water with moderate ecological status on Romanian side of the river. The recorded range of oxygen concentration were from 27,5 to 30,5 % (Graph 10). Regarding the concentration of Serbian Part of Bega the most of the samples could be classified into III Class (well ecological status) except water sampled at the cross border profile and after settlement Zitište where water may be classified as IV class. The recorded range of oxygen concentration were from 2,5 to 7,07 mgO<sub>2</sub>/l (Graph 11).

Unfortunately, this problem is present and well-known long ago. Since 1957 this issue is the subject of debate in all the Serbian - Romanian hydro Commission. A large part of organic materials decompose in the place of discharge of wastewater (downstream of Timișoara) and to profile the border. Because of decomposition of organic substances in the upstream border result pollution problems due to oxygen deficiency. Oxygen regime was seriously threatened. Complete lack of oxygen was recorded from 15% to 46% of cases were examined (<http://aerapa.conference.ubbcluj.ro/2012/pdf/11%20beilicci.pdf>).





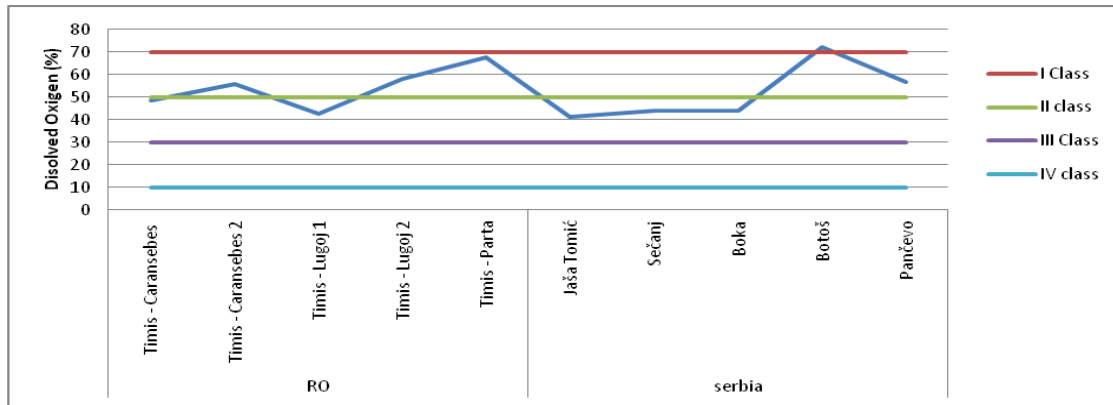
*Graph 10: Concentrations of dissolved oxygen (%) at the part of Bega that flows through Serbia*



*Graph 11: Concentrations of dissolved oxygen (mg/l) at the part of Bega that flows through Serbia*

Looking over complete part of Bega river where analysis were done, it can be noticed there is a slight increase of concentration of dissolved oxygen after entry in Serbian part of Banat, which states that water is less loaded with oxygen consumption pollutants.

Level of oxygen saturation were between 41,4 and 72,3%. Lowest concentrations were noticed at sampligg spot Lugoj 1 in Romania and at the cross border profile near villige Jasa Tomic.



Graph 12: Concentrations of dissolved oxygen in Tamiš river (mg/l)

## CONCLUSION

Analyzing the data resulted from the surface water monitoring campaign of main Banat Rivers (Bega and Tamiš) it becomes clearly that is difficult to draw a clear conclusion. It is difficult to analyze this data especially due to untypical wetter conditions during May 2014, with unusual cold temperatures and frequent rain episodes.

However, analysis of water has generally identified that there has been a few "hot spots" which are under the strong influence of highly populated and industrialized urban areas.

If we would compare these analysed parameters from both sides, Romanian and Serbian, we will notice that Bega watercourse is significantly more loaded with pollutants on Romanian side. Opposite of that, Tamiš river is uniformly loaded at the both sides, even there are noticeable fluctuations of pollutants concentrations at the Tamiš river watercourse, that can be called "hot spots".

In Romanian part of Tamiš River as most critical spot was identified locality downstream to Parta village and the Tamiš River near the village is close to the recently closed Timișoara's dump/waste field. Most probably the very high values recorded on Tamiš River (near Parta) are caused by infiltration from the dump field. The measurements in this location should be extended to other pollutants, especially heavy metals. At the Serbian as critical spot was identified highly industrialized city Pančevo, where parameters were significantly higher than other places.

Characteristic for analysed watercourses of Banat region is that water samples from selected localities are loaded with nutrients, especially nitrites and phosphorus, which causes relatively low concentrations of dissolved oxygen. Considering that analysed watercourses are mostly lowland rivers, that are flowing through intensive agricultural areas, this is quite expected.

With the aim of comprehensive understanding of surface water in Banat, it is necessary to implement analysis of water and sediment at more localities with the expand the scope of parameters that, beside chemical analysis, would include biological analysis of representative and sensitive species.

Also, one of the measures which is very important for improvement of water quality in rivers is treatment of industrial wastewater, stricter control of diffuse sources, such as landfills, agricultural areas, farms, but also raising of the public awareness about importance of water ecosystems



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## PHYTOREMEDIATION: BOOSTED CADMIUM UPTAKE BY ORGANIC, CHEMICAL CHELATES AND MICROBIAL INOCULANTS IN MAIZE

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Phytoremediation is green approach to clean up toxic heavy metals from polluted soils with a motive to extract excessive metals from soils through hyperaccumulative crop genotypes. Cadmium (Cd) is among the most mobilized and toxic metal to the living organisms. Health hazards associated with lethal intake of Cd included renal (kidney) damage, anemia, hypertension and liver damage. A green house experiment was carried out with maize (*Zea mays*) grown on artificially spiked soil (100 µg Cd g<sup>-1</sup>) with EDTA (2 mmol kg<sup>-1</sup> in 5 split doses), FYM, vermicompost (VC) and Microbial inoculants (*Azotobacter* and *Pseudomonas*). Growth of maize was better in farm yard manure (FYM) or vermicompost (VC) amended soil as compared to no-Cd- enriched soil. The growth was little suppressed in EDTA applied soil whereas it was better in bioinoculants treated soil. The application of FYM and Vermicompost (VC) increased the dry matter yield of maize either alone or in combination with bioinoculants. The application of EDTA caused a significant decrease in biomass of crop plants. Application of bioinoculants increased the dry matter yield of both root and shoot but not significantly because bioinoculants show greater sensitivity towards cadmium. Cadmium concentration was observed maximum under EDTA with bioinoculants treatments, however Cd uptake was maximum in Vermicompost with inoculates treatments. The Cd concentration in shoot over Cd<sub>100</sub> treatment increased in Cd<sub>EDTA</sub> followed by Cd<sub>VC</sub> and Cd<sub>FYM</sub> in the absence of microbial inoculates. The corresponding trend in the presence of microbial inoculates were as same, respectively. Similar trend was also observed in root as in order Cd<sub>EDTA+M</sub> > Cd<sub>VC+M</sub> > Cd<sub>FYM+M</sub> > Cd<sub>100+M</sub>. The remarkable root and shoot Cd content increase was observed with microbial inoculates in Cd<sub>EDTA+M</sub> treatment over Cd<sub>EDTA</sub> treatment. The FYM, Vermicompost and EDTA also increased Cd uptake significantly with and without microbial inoculates in root shoot biomass. The results indicated that Vermicompost in combination with bioinoculants is better and proven implication for the phytoremediation of Cd by maize crops from Cd-polluted soil being higher uptake value in shoot in Cd<sub>VC+M</sub> followed with Cd<sub>EDTA+M</sub>, Cd<sub>FYM+M</sub> and Cd<sub>100+M</sub> treatment combinations.

**Keywords:** Phytoremediation; Maize; FYM; Vermicompost; Bioinoculants; Cd uptake

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## **DEVELOPMENT OF BASIC PHYSICAL PARAMETERS OF SOILS IN COLD MOUNTAIN CLIMATE CONDITIONS**

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### **ABSTRACT**

Work is focused on the analysis and evaluation of the trend development of selected physical parameters of soil in soil ecological management in conditions of the cold mountain climate. The research project was carried out during the years 2010–2014 under production conditions in the investigated area Liptovská Teplička (48° 57' N; 20° 05' E), situated in the marginal region of north-eastern Slovakia. The ecological farming system has been applied here since 1996. The area of Liptovská Teplička is situated in the Low Tatras National Park at an altitude ranging from 846 to 1492 m a.s.l. In terms of geomorphological division, it is a part of the sub-assemblies of the Kral'ovohol'ske Mountains. The whole area is situated in the mild zone with sum of average daily temperatures above 10°C ranging from 1600 to 2000 mm and average precipitation of 700-1200 mm. Soil samples for physical parameters determination were taken in spring time in connected stand on 11 permanent research sites. Soil bulk density, soil porosity and maximum capillary capacity were studied and evaluated as the general physical properties in Kopecky physical cylinder with a capacity of 100 cm<sup>3</sup>. The results were evaluated by mathematical – statistical methods by using the statistical program STATISTICA 10. A statistical significant effect in the monitored years and agroecosystems on all observed soil physical parameters was confirmed by an analysis of variance. To ensure the sustainability of agricultural land and country is essential to increase attention in soil management in the new climatic conditions.

**Keywords:** *ecological management of soil, soil bulk density, soil porosity and maximum capillary capacity*

### **INTRODUCTION**

Climate change is emerging as a result of internal variability of the climate system, as well as external factors (natural factors such as solar radiation, cloudiness, precipitation and anthropogenic factors, eg. increasing concentrations of greenhouse gases) in the atmosphere. In Slovakia we trace the trend for the last 100 years of the growth of average annual air temperature (T) of 1.1 °C and a decrease in annual precipitation totals 5.6%. According to the results of research in the Slovak Republic after 2025 is likely to increase the average temperature of the soil during the growing season by 1 °C and decrease the average values of soil moisture at the time of the growing season by about 10% (Škvarenina et al, 2010; Sobocká et al, 2005). Soil is one of the basic elements of the environment, while it is irreplaceable and non-renewable natural resource. It is characterized by the full set of properties. Physical properties of soils are the specific features of the land, are significantly influenced



by how the weather changes and they can be changed by the modification of environmental conditions (Fazekašová et al., 2011; Kotorová and Šoltysová, 2011; Fazekašová et al., 2014). The aim of this work was to analyse and assess the trend development of selected physical parameters of soil in ecological management on soil in conditions of the cold mountain climate.

## MATERIALS AND METHODS

The research project was carried out during the years 2010–2014 under production conditions in the investigated area Liptovská Teplička (48° 57' N; 20° 05' E), situated in the marginal region of north-eastern Slovakia. The ecological farming system has been applied here since 1996. The area of Liptovská Teplička is situated in the Low Tatras National Park at an altitude ranging from 846 to 1492 m a.s.l. In terms of geomorphological division, it is a part of the sub-assemblies of the Kral'ovohol'ske Mountains. The whole area is situated in the mild zone with sum of average daily temperatures above 10°C ranging from 1600 to 2000 mm and average precipitation of 700-1200 mm. The soil conditions are relatively homogeneous, the largest area being represented by Cambisols, mostly moderate and strongly skeletal, mainly in the subsoil, medium-weight and heavy in granularity (loamy sand, loam, clayey loam). From the relief viewpoint, the majority of the land is situated on slopes (Fazekašová 2012). Soil samples for physical parameters determination were taken in spring time in connected stand on 11 permanent research sites which are used as arable land (AL) and permanent grassland PG) (Figure 1).

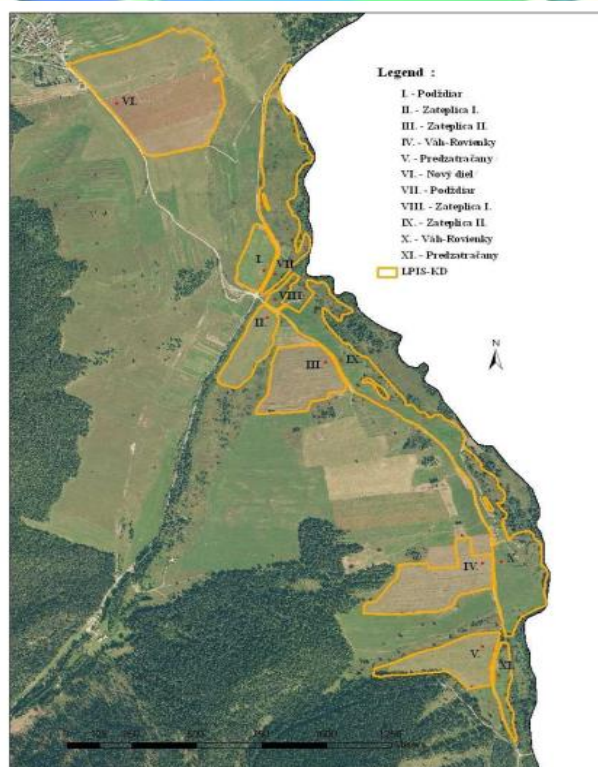


Figure 1: The map of localization of sampling sites in Liptovská Teplička (Slovakia)



Soil bulk density, soil porosity and maximum capillary capacity were studied and evaluated as the general physical properties in Kopecky physical cylinder with a capacity of 100 cm<sup>3</sup> (Fiala et al., 1999). The results were evaluated by mathematical - statistical methods by using the statistical program STATISTICA 10.

## RESULTS AND DISCUSSION

The measured values of bulk density ranged from 0.91 to 1.35 t m<sup>-3</sup> (Table 1, Figure 2) on arable land and ranged from 0.74 to 1.31 t m<sup>-3</sup> on the permanent grassland. The average values of bulk density were increased by 14% on arable land compared to permanent grassland. Reached values comparable with the average values for a given soil type and class (Líška et al., 2008; Fulajtár, 2006). General porosity is closely related to bulk density. From the total pore volume, this should not fall below 38% for sandy soil and below 48% for clayey-loamy soil (Líška et al., 2008).

As seen from Table 1 and Figure 3, the values show that, in the observed time frame, porosity levels ranged between 49.08 and 65.53% on arable land and ranged from 50.68 to 72.20% on the permanent grassland. The average value of the porosity was significantly higher on permanent grassland (50%). Considering this parameter, optimum conditions were created for the growth of most arable crops, which are given by general porosity between 55 and 65% and 20 and 25% soil air content (Rode 1969).

Maximum capillary capacity is hydro-physical parameter, which is closely linked with particular water supply in the soil profile and the content of clay particles and is located in a fairly wide range. In the time series of 2010-2014, the maximum capillary capacity ranged from 17.97 to 45.25% in arable and from 19.85 to 50.14% in permanent grassland (Table 1, Figure 4).

The average value of maximum capillary capacity of the arable land was 16% higher compared to permanent grassland. We also confirmed that the soils with high content of clay particles are characterized by a wide range of the maximum capillary capacity (Kotorová and Šoltysová, 2011). A statistical significant effect in the monitored years and agroecosystems on all observed soil physical parameters was confirmed by an analysis of variance (Table 2).

Table 1 Measured value of physical soil parameters on localities with ecological farming system in years 2010-2014

Parameter	agroecosystem	average	min	max	st. deviation
bulk density [t.m <sup>-3</sup> ]	AL	1.165000	0.910000	1.350000	0.136021
	PG	1.002400	0.740000	1.310000	0.156665
Porosity [%]	AL	55.89000	49.08000	65.53000	5.073018
	PG	62.21600	50.68000	72.20000	5.923303
maximum capillary capacity [%]	AL	31.39000	17.97000	45.25000	7.582850
	PG	37.62840	19.8500	50.14000	8.707337

AL - arable land; PG - permanent grassland

Table 2 Analyses variance of physical parameters in monitored area in years 2010 - 2014

Parameter	Source of variability	Degree of freedom	F-value calculated	P significance
bulk density	agroecosystem	1	23.919	++
	year	4	6.420	++
	residual	49		
	total	54		
porosity	agroecosystem	1	25.384	++
	year	4	6.221	++
	residual	49		
	total	54		
maximum capillary capacity	agroecosystem	1	6.847	++
	year	4	12.586	+
	residual	49		
	total	54		

Agroecosystem (arable land and permanent grassland), ++P < 0.01    +P < 0.05

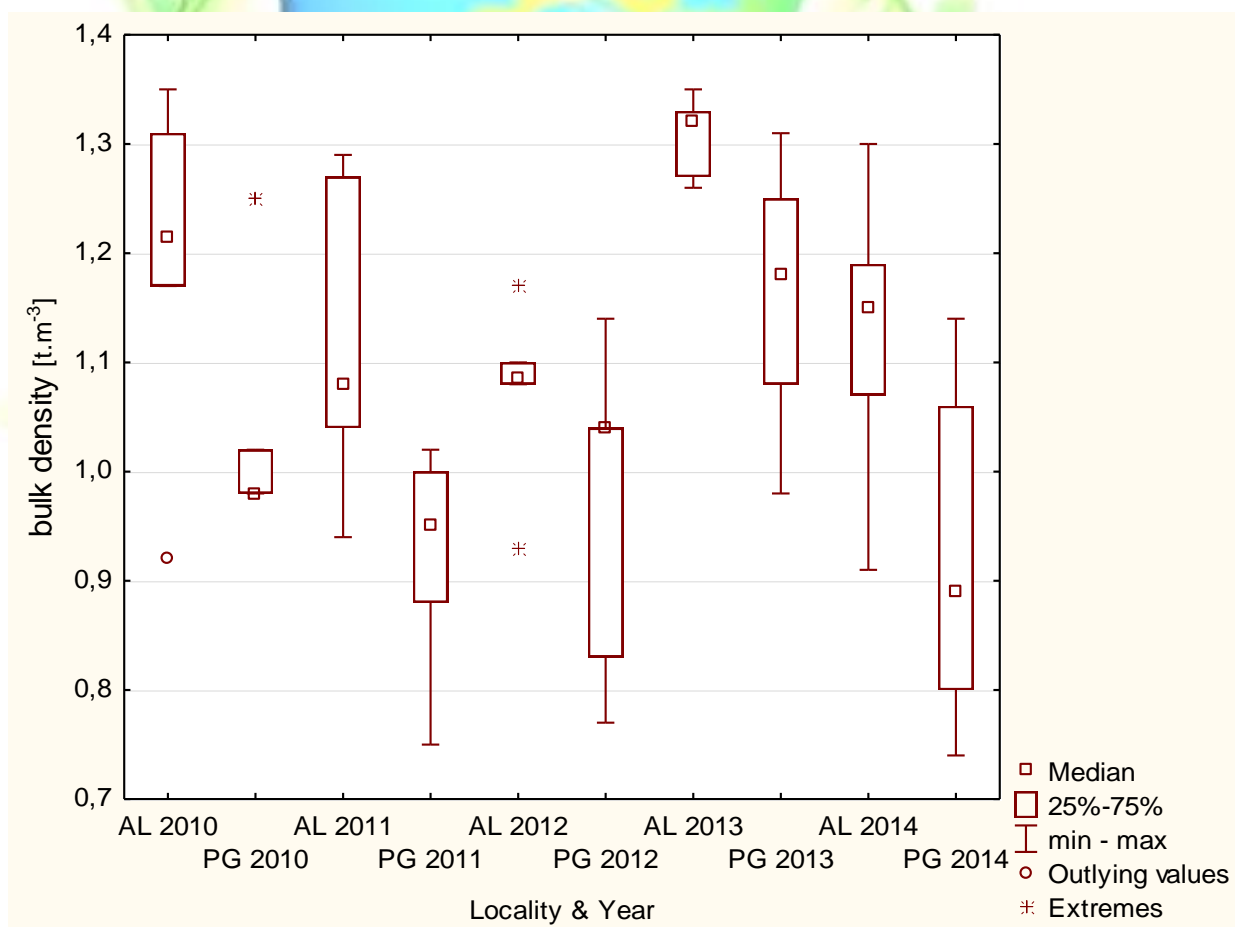


Figure 2 Bulk density of soil on localities with ecological farming system in years 2010-2014

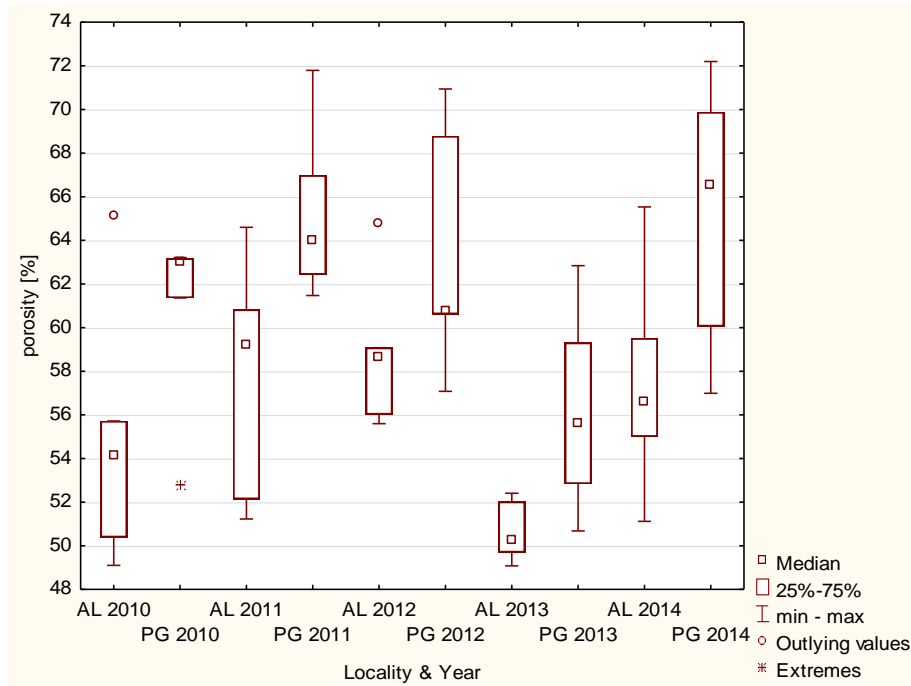


Figure 3 Porosity of soil on localities with ecological farming system in years 2010-2014

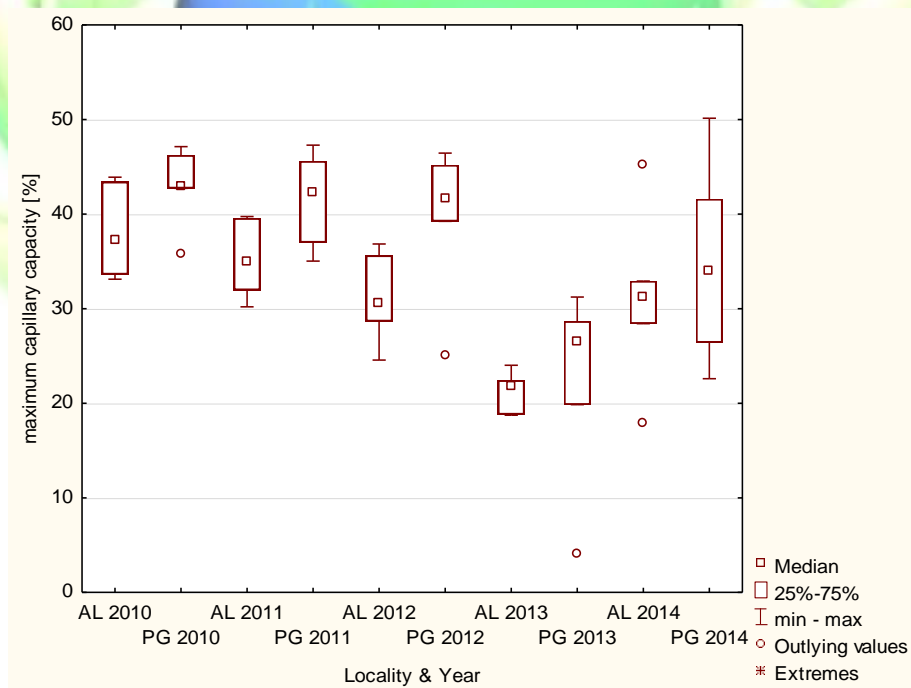




Figure 4 Maximum capillary capacity of soil on localities with ecological farming system in years 2010-2014

**CONCLUSION**



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Ecological farming systems are an important tool to maintain and preserve soil fertility and stability of agro-ecosystems. In terms of climate change the application of technological processes according to the principles of ecological farming on soil can contribute to enhancing the protection and preservation of soil quality.

Results of long term research showed that the observed physical properties of the soil reached similar values for a given soil type and kind. We also found that the values of bulk density, porosity and maximum capillary capacity level in the agro-ecosystems, which are used as permanent grassland significantly more favourable values.

A statistically significant effect in the monitored years and agro-ecosystems on all observed soil physical parameters was confirmed by an analysis of variance.

## ACKNOWLEDGMENTS

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## **EIGENVECTOR BASED SEGMENTATION METHODS OF HIGH RESOLUTION AERIAL IMAGES FOR PRECISION AGRICULTURE**

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### **ABSTRACT**

The analysis of farm land aerial images is a fast developing field in precision agriculture. Nowadays high resolution light weight multi-spectral cameras are commercially available for aerial applications. Images taken by Unmanned Aerial Vehicles (UAVs) provide useful information about the actual crop condition. With an average camera 3.5 cm per pixel resolution can be easily achieved. It is huge information for a 50-100 ha field to process.

The aim of this paper is to demonstrate how spectral clustering based algorithms can be used to evaluate multi-spectral high resolution aerial images to monitor the vegetation conditions. Spectral clustering techniques are based on the eigenvalues and eigenvectors of the similarity graph generated from the pre-processed image. Our algorithm consists of two phases: a pre-process and a clustering phase.

Multiple tests have been run on real aerial images coloured by different vegetation indices. Our approach showed that spectral clustering combined with reduction techniques could produce desirable results, well measurable and dense regions in acceptable computation time.

**Keywords:** Spectral clustering; Precision agriculture; Image segmentation

### **INTRODUCTION**

#### **Aerial images for Precision Agriculture**

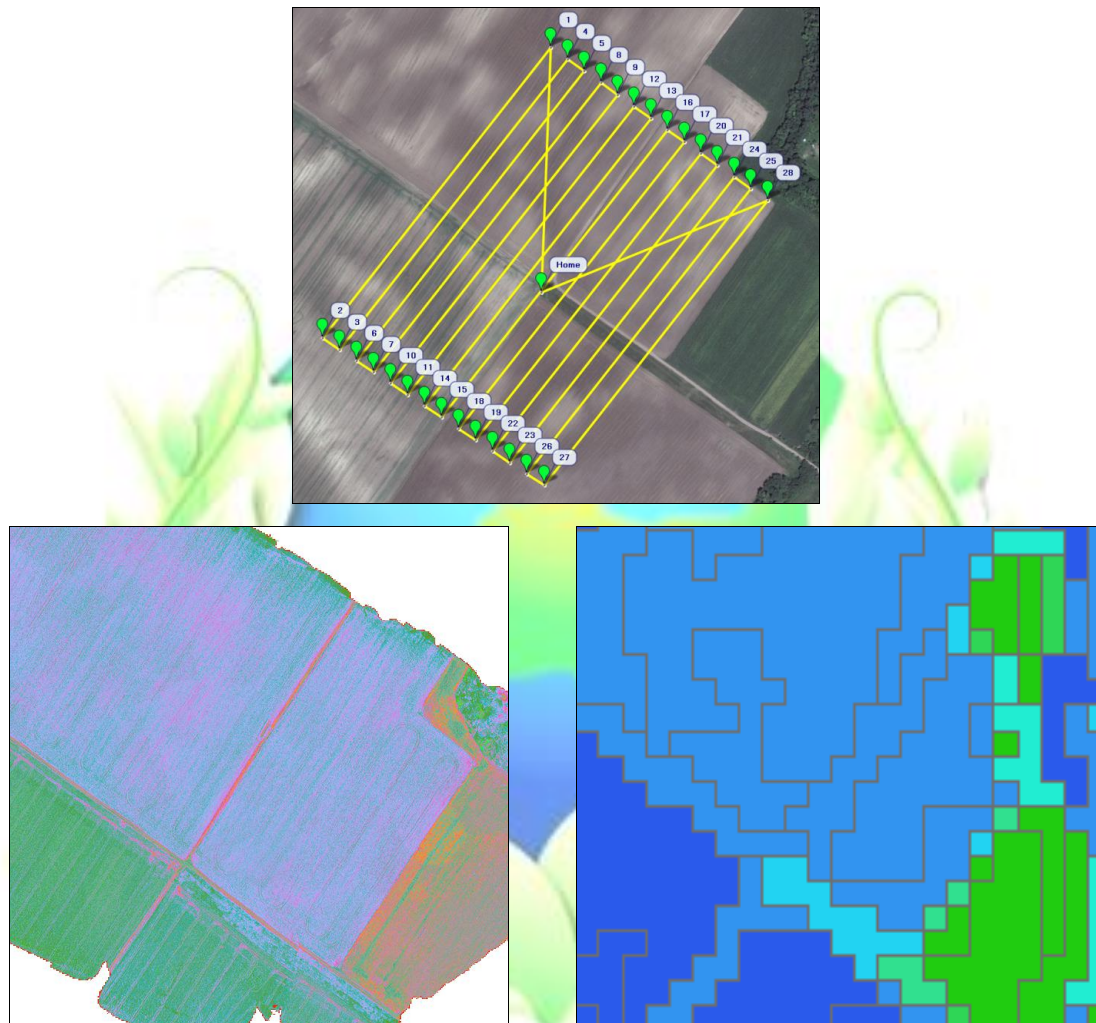
Precision agriculture software (e.g. ARCGIS or QGIS) need high resolution images over the surface to create different maps of soil parameters. These images can be taken from ground vehicles with sensors like DUALEM 1S and VERIS 3100 presented in [6], can be satellite images like in [3] or taken with aerial vehicles presented in [8]. The disadvantage of using a ground vehicle is the continuous contact with the vegetation. With grown corn it cannot be done until the harvest. The satellite images (multispectral or simple RGB) has a very weak resolution (Landsat8: 15-30 m/pixel) compared to an aerial (UAV) platform with 0.03 m/pixel. Therefore aerial images have much better performance for small fields (under 200 ha). These aerial images can be done with 1 or 2 flight within an hour with a small size UAV. It is fast and ideal for checking vegetation problems using NDVI pictures from RGB or multispectral images, calculating wildlife damage, flooded areas or inland waters. Precise segmentation of these images is mandatory.

#### **UAV mapping**

Small size UAVs like Skywalker (1.8 m wingspan) equipped with a commercial open source autopilot like Ardupilot (Arduplane) and a RGB (Canon A2300) or multispectral (ADC micro) 100-200 g weight camera can map a 30-60 ha area with one flight under 30 minutes of pattern flight (Fig. 1).



The captured images can be stitched together with software like Trimble UAS Master or similar under a few hours depending on computer power. From the generated high resolution (3.5 cm/pixel) orthophotos additional maps like NDVI or Green NDVI (Normalized Difference



**Figure 1.** Flight plan for the UAV over peas and colza field (top). NDVI map using UAV (left) and Landsat 8 satellite (right).

Vegetation Index) can be generated. From these maps the plant health can be defined.

On Fig 1. the NDVI map from UAV and Landsat 8 can be seen – satellite images has very low resolution, unsuitable for small fields. Dark blue areas indicate good plant health, while green means weak. Additional irrigation or treatment strategies can be defined based on these maps.

To keep the useful information coded in these images precise and good quality segmentation methods must be used. This paper presents a two-phased method based on superpixel reduction and spectral clustering techniques to recover different health state regions on high resolution landscape images.



## SEGMENTATION METHODS FOR LARGE SIZE UAV IMAGES

In this section we present a two-phased method to segment large size images using spectral clustering algorithm. Before detailing our implementation, we first summarize some necessary concepts.

### Superpixel based image reduction

To deal with often large size UAV images specific simplification techniques are needed. A possible approach to reduce the complexity of the original image is to group its pixels into larger regions called superpixels. With the proper choice of the amount of reduction the image gets much easier to process, and actually we lose no relevant information. There are several existing reduction techniques to choose from, such as coarsening methods introduced in [5], Quadtree structures [4] or split-and-merge techniques [9].

The SLIC (simple linear iterative clustering) algorithm is a very effective but relatively easy to implement reduction technique, invented by Achanta et al. [1]. It adapts a  $k$ -means clustering approach to generate superpixels. The only parameter of the algorithm is the desired number of superpixels which are approximately equally sized. During the process, each pixel of the original image is associated to precisely one cluster. After that, superpixels can be handled as relatively homogenous regions.

### Spectral graph partitioning

Image segmentation can be viewed as a graph partitioning problem in the following sense. Assume that a suitable similarity measure is defined between each pixels of the image to be segmented. The image now can be treated as an undirected weighted graph, where the vertices of  $G$  are the pixels of the image. The weights of the edges represent the likelihood that the pixels belong to the same segment. Depending on the actual problem, one can add all the possible edges between vertices or only some of them (e.g. the ones that belong to neighbouring pixels on the image). According to the defined similarity measure, the weights of edges are determined. Now, the whole image is represented by graph  $G$  of which vertices should be separated into disjoint subsets such way, that the similarity within a subset is high, and between two subsets is low. This gives a partition of the vertices, which is called a cut. Let the cost of a cut defined by

$$cut(A, B) = \sum_{u \in A, v \in B} w_{u,v}$$

where  $w_{u,v}$  is the weight of the edge between vertices  $u$  and  $v$ , and  $A, B$  are subsets in  $V$ .

The optimal bipartition of  $V$  minimizes the cost of the cut [7]. Efficient solvers exist to determine minimal cut values however they don't always give feasible results. A well known way to determine a cut which does not have undesired properties on images was introduced by Shi and Malik [7]. Their measure (known as  $Ncut$ ) depends on the total dissimilarity between subsets as well as the total similarity within subsets, so it has the desired properties we want.  $Ncut$  values are computed by

$$Ncut(A, B) = \frac{cut(A, B)}{assoc(A, V)} + \frac{cut(A, B)}{assoc(B, V)}$$



where  $cut(A, B)$  is defined as above, and  $assoc(X, V)$  is the total weight of edges from vertices in  $X$  to all other vertices in  $V$ .

Using matrix notations a minimize problem can be written in the following form:

$$\min_{(A,B)} Ncut(A, B) = \min_y \frac{y^T (D - W)y}{y^T D y}$$

where  $D$  is a diagonal matrix with  $d(i) = \sum_i w_{ij}$  on its diagonal, and  $W$  is a symmetric matrix with  $W_{ij} = w_{ij}$  (the similarity matrix), subject to

$$\begin{aligned} y_i &\in \{1, -b\} \\ y^T D \mathbf{1} &= 0 \end{aligned}$$

for some constant  $b$ . As shown in [7] the relaxed form of the above expression (which is the Rayleigh quotient by the way) can be minimized by solving the eigenvalue problem

$$D^{-\frac{1}{2}}(D - W)D^{-\frac{1}{2}}x = \lambda x$$

for eigenvectors with the smallest eigenvalues. Using the second smallest eigenvector one can divide the vertices of  $G$  into two separate subsets. Further partition steps can be taken recursively to refine the partition. Once, when  $G$  has been split into the appropriate number of subgraphs, a segmentation of the original image can also be obtained by labelling each pixel with the identifier of the subgraph it belongs to.

### The segmentation algorithm scheme and our implementation

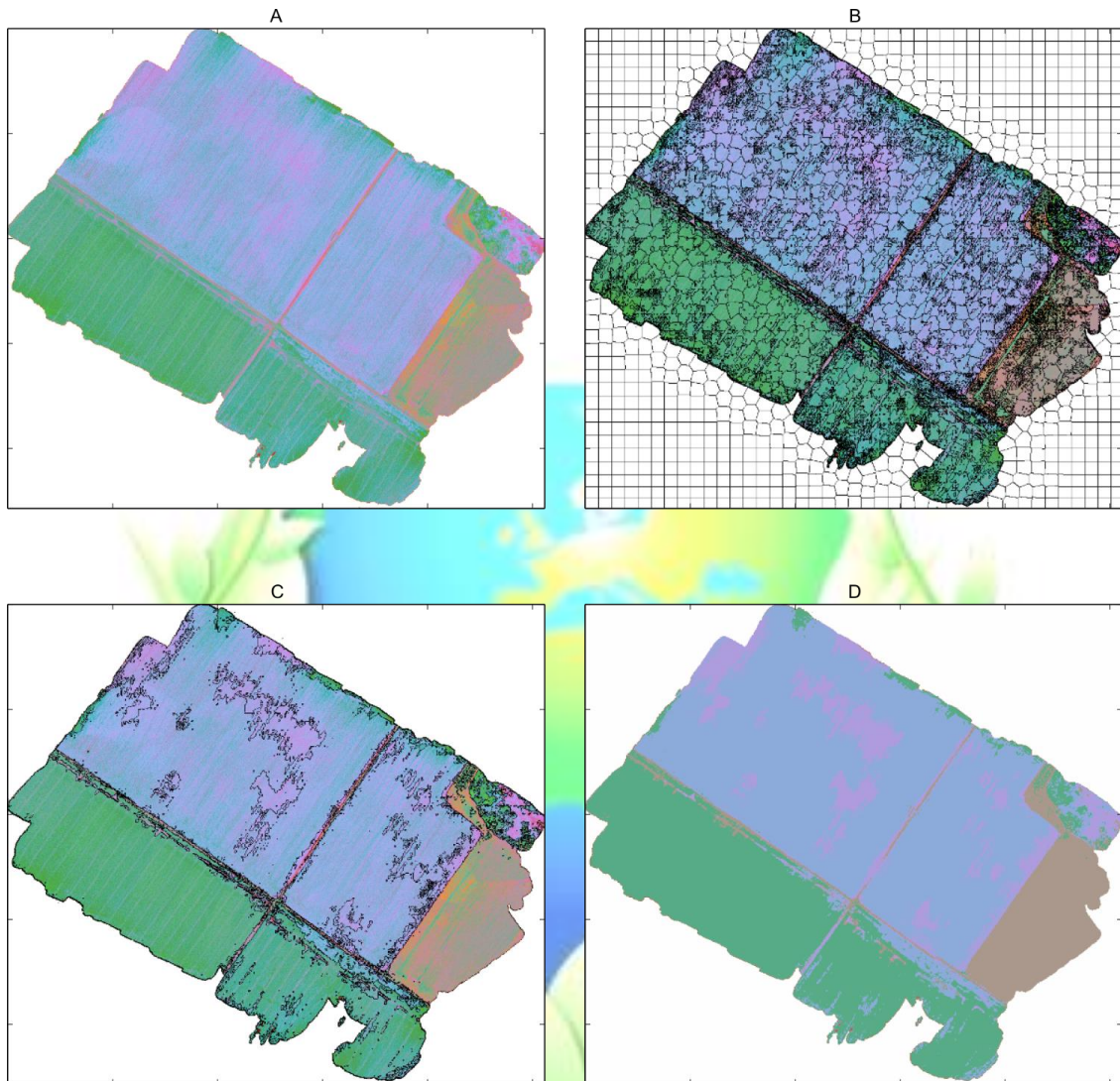
Our algorithm scheme consists of two stages: a pre-processing stage and a segmentation stage. Since UAV taken agricultural landscape images are often have large size (usually far more than  $10^6$  pixels), it is nearly impossible to use similarity matrices of all pixels of the actual image.

Based on this observation the pre-processing phase realizes a reduction of regions, to achieve a manageable version of the original image. The previously presented SLIC clustering is used to reduce the number of possible regions to a maximum of a few thousands.

As a second phase, the similarity graph  $G$  of the specified image regions is built. The exact similarity measure functions are detailed in the next section. Using the previously presented  $Ncut$  algorithm, the graph gets split until the desired number of subsets reached. Finally, a label is assigned to each pixel representing the correspondent segment.

The algorithm was implemented in *Python* language using *Numpy*, *Scipy* and *Scikit-image* modules.





**Figure 2** (A) The original image coloured by NDVI index. (B) Pre-processed image using the SLIC algorithm (see text for details) (C) Reduced regions after spectral clustering. (D) Different type of vegetation regions coloured by their average colour. Shades are related to plant health

## RESULTS AND DISCUSSION

### Technical results

Our implementation was tested on different aerial images. One of our aims was to determine places with different vegetation state of plants through its NDVI values. Since the colours of the original image correlate directly with the vegetation health state of the area, it seemed logical to use the Euclidean distance of the colour vectors as a similarity measure of regions. Precisely, the similarity weight of two regions  $a$  and  $b$  is defined by



$$w(a, b) = e^{-\frac{1}{\mu} \|F(a) - F(b)\|^2}$$

where  $F(v)$  is the feature vector of region  $v$  (currently its colour coordinates in RGB colour space),  $\|\cdot\|$  denotes Euclidean norm, and  $\mu$  is some scaling factor determined experimentally. Note that  $w(a, b)$  always represents a probability. For image pre-processing, the SLIC algorithm presented above was used.

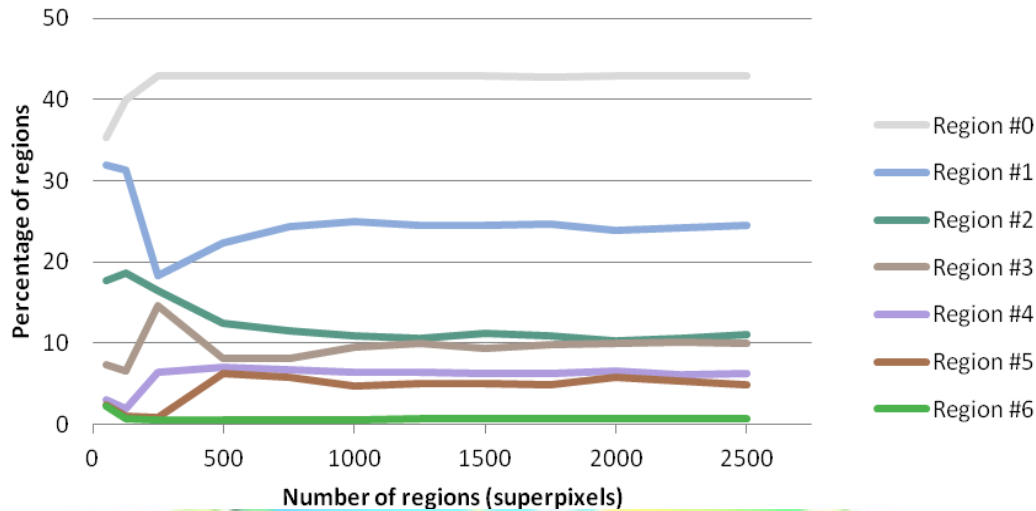
To solve the eigenvalue problem, an ARPACK-based routine was applied, which computes a few eigenpairs of a large scale real symmetric matrix. The method is a variant of the Implicitly Restarted Arnoldi Method (or in a special case a Lanczos method) [2], and scales linearly with the matrix size.

### Experimental results

Figure 2. shows a typical result of a segmentation and its process. The value of desired partitions was set to seven, so six different vegetation levels (and the background) can be separated on the image. The area of each region was calculated based on the segmentation results.

The number of superpixels generated in the pre-processing phase takes fundamentally effect to the final results. As Fig. 3. shows, there are an approximately optimal number of superpixels. Generating more than this, the final results will not show significant improvement, but it takes more time to do the job. As it can be seen, a relatively low number of superpixels cause large fluctuations in the percentage of segmented regions. This fluctuation comes from the random choice of the SLIC cluster centres. After a critical value of superpixels (depending on the size and the homogeneity of the original image) the percentages seems to stabilize around a specific value, and involving more superpixels does not give us more information on region sizes.

Fig. 4.B shows the mean squared error as a function of the number of superpixels that confirms our assumption that the rule “the more the superpixels, the fine results we get” does not always stand.



**Figure 3.** The percentage of region area versus the number of regions. Colouring corresponds to shades on Figure 2.D. (Region #0 represents the background of the image). As it can be seen, with approximately 1000 superpixels fine segmentation can be produced in relatively short time (see Fig.4.A for performance details).

### Variants of the basic implementation

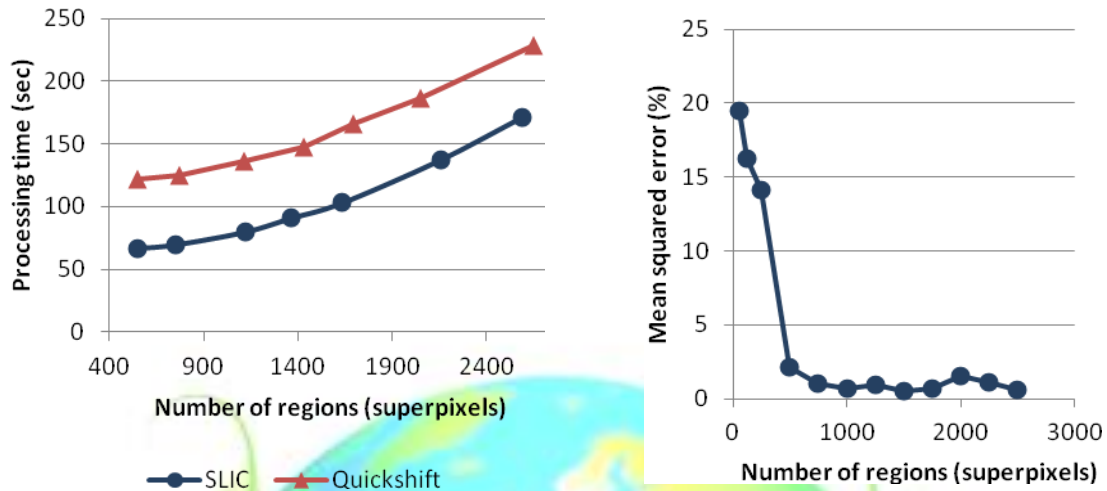
**(V.1)** For image pre-processing SLIC clustering is not the only possibility, however it seemed to be the best option in some respects. A mean-shift-like clustering algorithm called Quickshift [10] was also tested. While SLIC needs the number of desired clusters –which usually depends on the actual size of the image, and can only be determined from test runs– Quickshift needs only the following image-independent parameters (according to *Scikit-image* documentation):

- *kernel\_size*: width of Gaussian kernel used in smoothing the sample density
- *max\_dist*: cut-off point for data distances
- *sigma*: width for Gaussian smoothing as pre-processing

Our test runs showed that SLIC performs slightly better than Quickshift, as it can be clearly seen on Fig. 4.A. We note that the computation time of the similarity matrix increases quadratic with the number of superpixels.

**(V.2)** Using only the RGB colour information of superpixels, one can choose different feature vector for generating similarities, which is more suitable to the characteristics of the actual task. As an example, feature vectors consist of colour values of regions in HSV colour space was tested. Our experiments showed that HSV-type feature vectors have only slight influences on segmentation.





**Figure 4.** (A) Total processing time of an image using SLIC or Quickshift as pre-processor. (B) A typical look of mean squared error function as the number of superpixels increases.

## CONCLUSION

In this paper we have presented a two-phased method for large scale landscape image segmentation. Our implementation first groups the pixel of the original image into superpixels, than merges them using the spectral properties of a similarity graph. The implementation was tested on NDVI coloured UAV aerial landscape images. With the proper choice of the reduction rate, manageable pre-processed images were obtained, which provided feasible result that can be useful for monitoring the health state of plants in agricultural farmlands.

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## **HOW GRANULAR ACTIVATED CARBON ADSORPTION HELPS REMOVAL OF ORGANIC SUBSTANCES, FLAVOUR AND ODOUR AGENTS IN DRINKING WATER**

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### **ABSTRACT**

In the Köszörűvölgyi reservoir higher and higher number of algae species have evolved over the last years, which is characteristic of surface waters. Furthermore, the concentration of trihalomethane (THM) compounds resulting from chlorination increased, and taste and smell worsening substances appeared in the water. The aim of our work was to study the operation and trial run of Köszörűvölgyi water works, presenting a new technology used for removal of organic substances, flavour and odour agents in water. The new filtering system was built in not only to remove taste and odour substances from the water, but also to reduce the amount of total organic carbon (TOC), including volatile organic carbon (VOC) compounds, and highly mutagenic compounds, like hydroxyfuranones (MX) derivatives. The efficiency of the filter is based on three processes: adsorbing particles, diffusion of gases and chemisorptions. This is the most common purifying method in our country when the sand filters are supplemented by granular activated carbon for high efficiency adsorption.

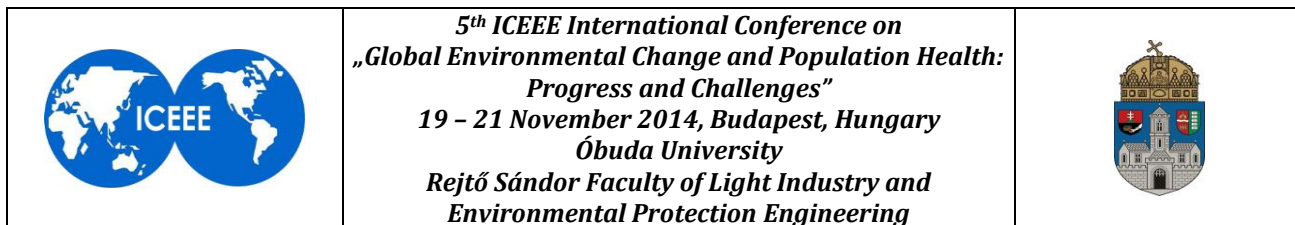
The test run started in July 2013 with preconditioning for the proper operation of the existing facilities. Equipments were tested and ensured their proper operation before the test run. During the test period there was not such a failure, which would have led to a halt in the operation of the equipment or would have aborted the test run. Only minor errors happened but were fixed, as these are not expected to reoccur in the future. It can be stated that the reliability of the system is appropriate. The newly built process equipment met the requirements imposed on them, and resulted in an improvement of the quality of the water. Testing the pH, UV<sub>254</sub> and COD<sub>ps</sub> values in the water before and after the GAC filter unit supported the hypothesis, that with the installation of activated carbon filter the organic materials, the concentration of flavours and odours can be decreased significantly. The presented water purification technology contributes to a healthy, high-quality drinking water supply which is a legitimate expectation of our society. Everyone has the fundamental right to clear drinking water, which can be achieved using known and new water purification technologies.

**Keywords:** *drinking water, filtering system, flavour and odour, granular activated carbon, removal of organic substances, water purification technology*

### **INTRODUCTION**

Every individual has the right to drink healthy, high quality water, but it could not lead to wasteful water-usage and excessive pollution. Due to growing anthropogenic impact, contamination of water has been increasing more and more intensely. Waterworks are facing a





lot of problems these days. The answer in most cases is the technological expansion of water treatment plants.

The technological development, ignorance, impoverishment, improper disinfection and increasing pollution causing a major problem nowadays, and the decrease in quality and quantity caused by climate changing is making the situation even worse. Society's demand for high quality water is rising continuously which is satisfied by new analytical and water cleaning technologies (Jolánkai et. al., 2009). Drinking water can be supplied by surface water, bank filtration systems and spring water. However only few large urban areas such as Christchurch in New Zealand have access to sufficiently pure water of sufficient volume that no treatment of the raw water is required (Cotter, 2012). In most cases, water undergoes different cleaning procedures before it flows into the network. Water quality protection is becoming more and more important due to the ever increasing anthropogenic effects (Jolánkai et. al., 2009).

The challenges of supplying an increasingly higher quality of water to an increasing human population on a planet with a limited freshwater supply is shaping the water utilities and advanced treatment processes in the 21st century (Hall and Dietrich, 2000). To satisfy both human and nature's needs on the highest possible level is almost impossible. We can not apply a standard methodology which is appropriate to measure the quality of different types of waters. There is no „good water” or „bad water”, just water applicable for different usage, that's why water is often categorized around the purpose of usage. In general we differentiate water types for: drinking, industrial utilization, irrigation, underwater ecosystem sustenance and other purposes (Bodáné-Kendrovics, 2013).

According to the Ministry of Rural Development and ISO 24510 Activities relating to drinking water and wastewater services, the drinking water is the water: which can be used for drinking, cooking, food preparation or other domestic purposes intended, regardless of its origin, and that comes from water pipe or tank. Which are used in food production, including all materials and products for the manufacturing, processing, preservation and marketing, which are used for human consumption. Unless the County Government Office of Public Health's services finds that the quality of the water can not affect the quality of finished product (food).

When selecting tight water cleaning technology, it is necessary to consider the characteristics of raw water. The clarified water has to meet the requirements specified for usage type. The aim of our work was to study the operation and trial run of Köszörűvölgyi water works, presenting new technology used for removal of organic substances, flavour and odour agents in water. The built in filter with granular activated carbon (GAC) is a proven option to remove certain chemicals, particularly organic chemicals from water. GAC filters also can be used to remove chemicals that give objectionable odours or tastes to water such as hydrogen sulfide (rotten eggs odour) or chlorine.

In recent years in the Köszörűvölgy water reservoir the quantity of algae has risen significantly, which means the trihalomethane (THM) compounds have shown up too. Source of THM precursors (compounds participating in other compounds production) can be the increased volume of certain algae species, other animal populations. Further reason can be the high concentration of organic materials or the presence of organic material-rich deposit (Öllös, 1998). As a result, the taste and odour effects are strengthened in the water. Even low concentration of highly volatile organic or non-organic (organoleptic) compounds can cause strong taste and/or odour regardless of their natural or industrial origin.

When raw water is filtrated through an activated carbon filter, the most important process is the adsorption on the filter's surface. During this gas and liquid molecules bond on a solid surface. An other major process on the activated carbon filter is diffusion when carbon

slowly detoxicates gas molecules. And finally the chemisorption, when molecules bond chemically to carbon.

## MATERIALS AND METHODS

### Description of activated carbon filters and their application

#### Powdered Activated Carbon

The activated carbon powder is added directly to the water and the organic materials bond to the surface of powder particles. The powder particles with the bound chemicals are separated through solid-liquid phase separation.

#### Granular Activated Carbon

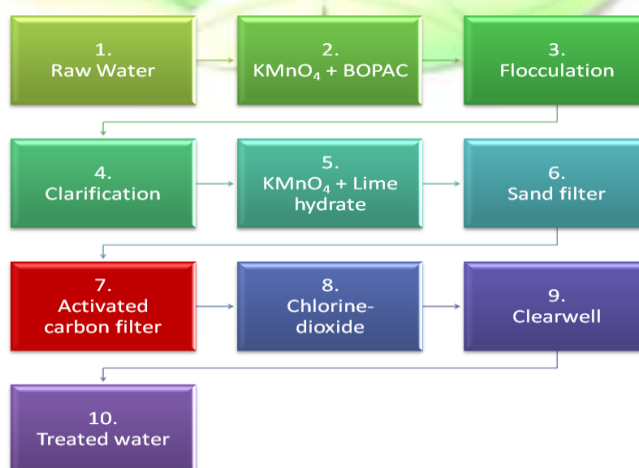
Granular activated carbon is made from raw organic materials (such as coconut shells or coal) that are high in carbon. Heat, in the absence of oxygen, is used to increase (activate) the surface area of the carbon. This is why these filters are sometimes referred to as “charcoal” filters. The activated carbon removes certain chemicals that are dissolved in water passing through a filter containing GAC by trapping (adsorbing) the chemical in the GAC.

It is very important that the type and concentration of contaminants, and average water use, be known in order to determine the correct size and components of the system. All treatment systems require proper installation and periodic maintenance. Eventually, the ability of the GAC to bind and remove chemicals is used up and the GAC needs to be changed. How often the GAC should be changed needs to be based on contaminant levels and water use. While some filters may last for several years if contaminant levels and/or water use are low, higher levels or use may require more frequent change-outs.

The granular activated carbon was piled in a column and it’s operating principle is similar to a filter: the water flows through the carbon piles and organic materials bond to the absorbent surface. The necessary time is 15-20 minutes.

#### Installation of the new system at Kőszörűvölgy waterwork

The reservoir and water treatment facilities near Kőszörűvölgy was built to provide high quality drinking water for people in towns, resorts, sanatoriums and other public institutions around it. The system’s starting point is the reservoir with the associated water treatment facilities. Water from the reservoir goes through the following process to reach consumers (Figure 1).





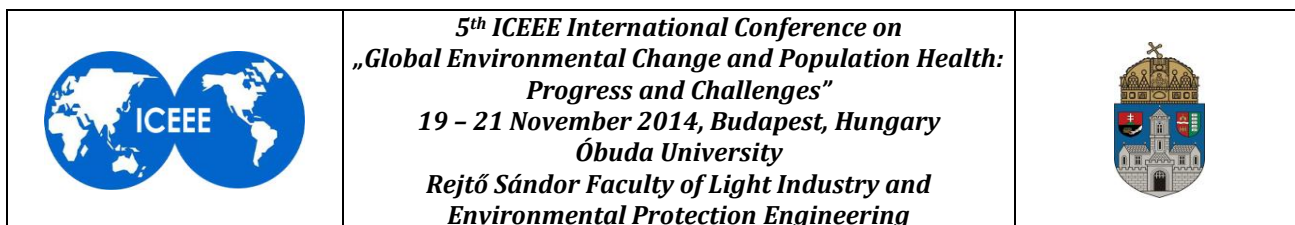


Figure 1. Flow diagram of the water purification process at the Köszörűvölgy Waterwork. BOPAC – Poly(aluminium-chloride) coagulant (Remiás, 2012)

During the year 2013 significant changes have been done in the underlying water treatment technology. An activated carbon filter has been built in the process after the sand filter, and the chlorine gas disinfection method has been replaced by a chlorine dioxide disinfection method (Figure 1).

The PROMINENT CDVc20-120 chlorine dioxide producing equipment was built-in along with a steel container. Before selection of the NORIT GAC 1240 W activated carbon filling, lot of different aspects were considered. Finally this bitumen based agglomerated type activated carbon was chosen. To be able to start the test run on 23<sup>rd</sup> July 2013, we had to ensure that the existing equipment worked properly. The container was loaded with activated carbon, then filled up with water to soak for 24 hours. The purpose of the soaking was to eliminate air bubbles from the activated carbon filter's particles to reduce the risk of material waste. This was followed by loosening the filler, to minimize the carbon particles loss with water. The next step was the washing, pumping water from the clean water pool through the filler with increasing flow rate, started at 5 km/h, until all the air bubbles were eliminated. After that the water flow rate was increased until we reached the maximal bed expansion. A pressure test at 3.6 bar was also performed that proved successful: no changes in the pressure of the system were noticed. To ensure that there is no contamination in the pipeline, high pressure air blowing was applied for disinfection purposes. We could not channel back the water used throughout the test into the clear water reservoir, until we earned permission by presenting the necessary measurements on the 3<sup>rd</sup> September.

#### **Measuring pH value**

We used the method and equipment for measuring the pH according to Jolánkai et. al. (2009).

#### **Measuring UV<sub>254</sub> absorbance**

This UV absorbance value characterizes the amount of organic materials in water. It is able to detect aromatic organic compounds, different types of pesticides which can derive from agricultural, pharmaceutical or chemical production activities. UV<sub>254</sub> is a measure of ultraviolet absorption at a wavelength of 254 nm. UV<sub>254</sub> is a surrogate measure of natural organic matter (NOM) in water (Yavich, 2012).

#### **Measuring Chemical Oxygen Demand - COD<sub>ps</sub>**

This is the amount of oxygen needed to oxidise the organic materials in water. It can be measured by using KMnO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> oxidants (COD<sub>ps</sub> and COD<sub>cr</sub>, respectively). We performed the COD<sub>ps</sub> according to the method of Jolánkai et. al. (2009).

#### **Clearing efficiency, COD<sub>ps</sub>**

Clearing efficiency (%) was calculated from the appropriate COD<sub>ps</sub> data to show the ineffectiveness of the water filter units: [%]=(INPUT-OUTPUT)/INPUT\*100

### **RESULTS AND DISCUSSION**

#### **The pH value**

We measured the hydrogen ion concentration in the water which shows how much compound the water contains that affect it's acidity or alkalinity (Figure 2). The hydrogen ion



concentration in natural waters is influenced by the amount of free carbon dioxide. Furthermore, humic materials, carbonate and hydroxid ions also affect pH value.

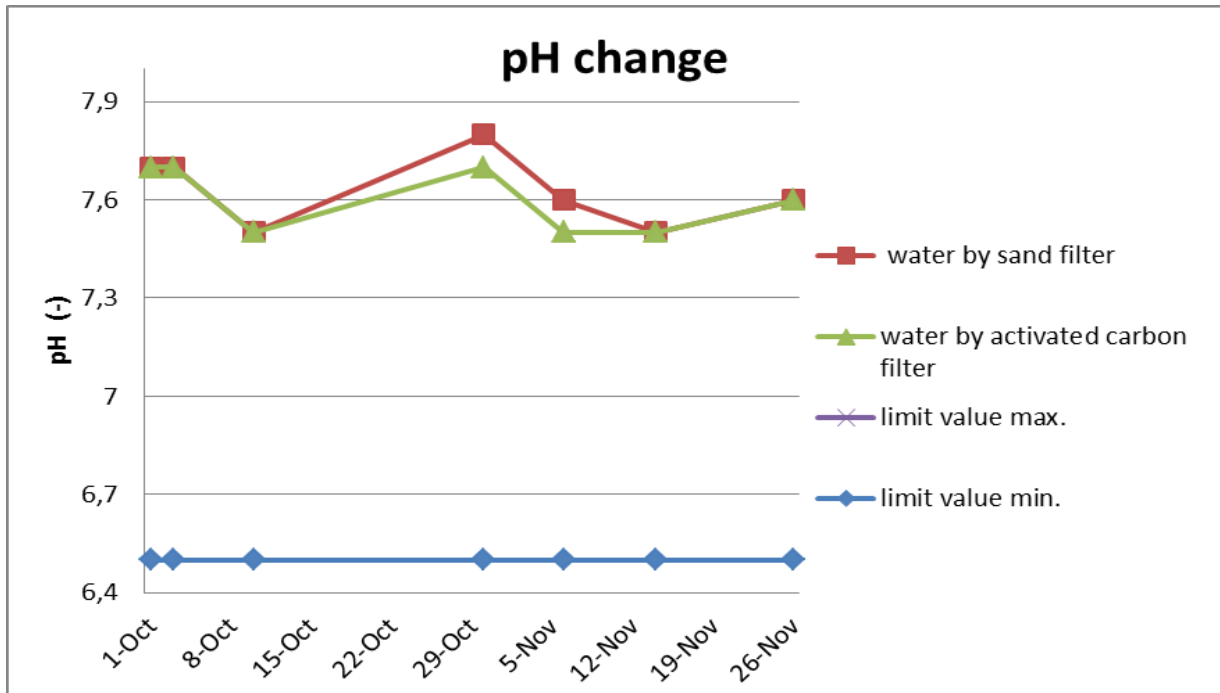


Figure 2. Measured pH value in the treated water after sand filter (red line) and after GAC filter unit (green line) during the test run

We found no significant differences between the pH values in the water filtered by sand and GAC filter units (pH7.5-7.8). So the newly built in activated carbon filter unit do not effect the pH value.

### UV<sub>254</sub> changes

Figure 3. shows the UV<sub>254</sub> measures in sand-filtered and activated carbon-filtered water. The higher the value the more organic material goes through each type of filter. These organic materials can be aromatic organic compounds, different types of pesticides which can derive from agricultural, pharmaceutical or chemical production activities.

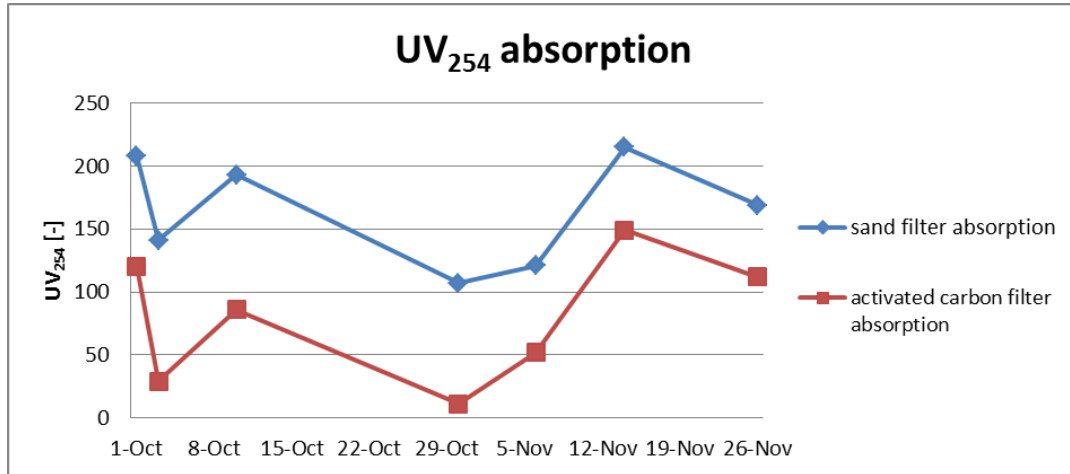


Figure 3. UV<sub>254</sub> absorption of purified water before (blue line) and after (red line) the Granular Activated Carbon filter unit

The organic material concentration was found much lower (significantly lower) in the activated carbon-filtered water (Fig 3, red line) on all the measured samples for each day of the test run. The lowest value (15) and thus organic material concentration was measured on 30th October. These results confirm the effectiveness of the new filter.

#### Chemical Oxygen Demand - COD<sub>ps</sub>

Figure 4. shows the chemical oxygen demand of organic materials measured in sand-filtered and activated carbon-filtered water. In each sample the measures were found higher for the sand-filtered water than for the activated carbon-filtered water. These results also show that the new filter unit met the expectation to reduce the organic material concentration. There were no KOI<sub>ps</sub> measures that exceeded the 3.5 mg/l limit for drinking water (Table 1).

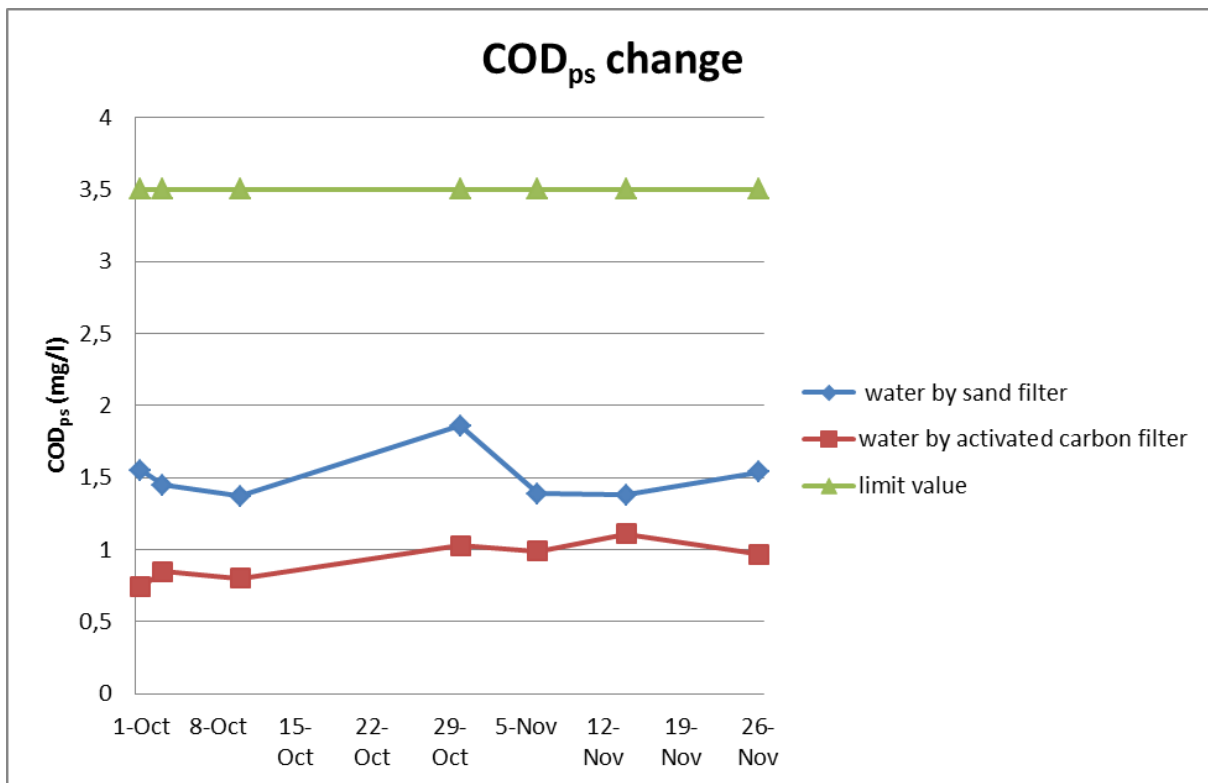


Figure 4. COD<sub>ps</sub> changes during the testrun in sand- and activated carbon-filtered water

### Clearing efficiency, COD<sub>ps</sub>

The measured COD<sub>ps</sub> data and the calculated efficiency of the cleaning are showed in Table 1 and Figure 5.

Table 1. COD<sub>ps</sub> data and Clearing efficiencies of sand filter and GAC filter units

Date	COD <sub>ps</sub> , mg/l			Clearing Efficiency	
	In water after clarification (input1)	In water after sand filter (output1=input2)	In water after activated carbon filter (output2)	Sand filter	Activated carbon filter
1-Oct	1,5	1,41	0,74	6,0%	47,5%
3-Oct	1,6	1,45	0,85	9,4%	41,4%
10-Oct	1,9	1,37	0,8	27,9%	41,6%
30-Oct	1,9	1,86	1,03	2,1%	44,6%
6-Nov	1,9	1,39	0,99	26,8%	28,8%
14-Nov	1,8	1,38	1,11	23,3%	19,6%
26-Nov	1,8	1,54	0,97	14,4%	37,0%



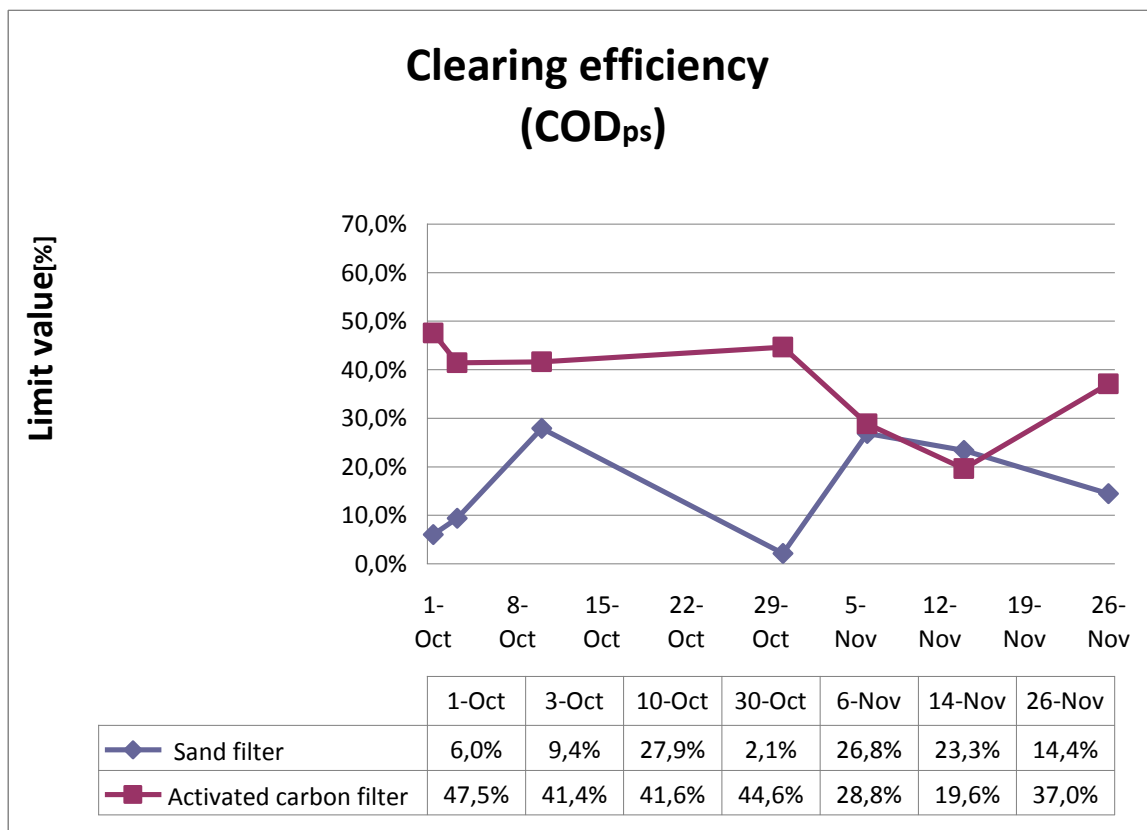


Figure 5. Clearing efficiency of sand filter (blue line) and GAC filter (red line)

Based on Figure 5. above, we can state that the activated carbon filter unit removes organic material more effectively than the sand filter with one exception (14-Nov). So the assumption that activated carbon filter is more effective in reducing organic materials than sand filter is confirmed.

## CONCLUSION

During the test period there was not such failure, that would have led to a halt in the operation of the equipment or would have aborted the test run. Minor errors, which are not expected to reoccur in the future were managed to fix. It can be stated that the reliability of the system is appropriate. The newly built in process equipment met the requirements imposed on them, and resulted in an improvement of the quality of the water. Measurement results supported the hypothesis, that after the installation of activated carbon filter the organic materials, the concentration of flavours and odours decreased significantly compared to baseline. The presented water purification technology contributes to a healthy, high-quality drinking water which is a legitimate expectation of our society: everyone has the fundamental right to clear drinking water, which can be achieved using known and new water purification technologies.

The results of the test proved the effective functioning of the activated carbon filter, the requirements in terms of water quality.

## ACKNOWLEDGMENTS

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### Figures and Table:

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*Figure 2.* Measured pH value in the treated water after sand filter (red line) and after GAC filter unit (green line) during the test run

*Figure 3.* UV<sub>254</sub> absorption of purified water before (blue line) and after (red line) the Granular Activated Carbon filter unit

*Figure 4.* COD<sub>ps</sub> changes during the testrun in sand- and activated carbon-filtered water

*Figure 5.* Clearing efficiency of sand filter (blue line) and GAC filter (red line)

*Table 1.* COD<sub>ps</sub> data and Clearing efficiencies of sand filter and GAC filter units

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## **THE NATURE OF THE SELECTED ENVIRONMENTAL BURDENS IN THE SLOVAK REPUBLIC**

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Regions in the Slovakia show different level of the load of the individual components of the environment. The load indicates a decreased quality of life of the population. The factors of the load of environment are mainly of the anthropogenic origin. Within the eco-regionalization on the territory of the Slovakia were identified five levels of environmental quality and 7 of load areas where is disrupted and strongly disrupted environment. A negative is that all load areas have been developed in the Slovakia in the lowlands and low-lying basins, which are according of the main factors and conditions (relief, climate, soil) our highest quality areas for agriculture. Environmental burdens are the accompanying element of loaded areas. The aim of this paper is to highlight the current status of selected sites of environmental burdens in Slovakia. Analytical data about them, we obtained especially on the basis of field research, soils samples analysis, orthophotomaps analysis, of literary and other sources and using the interview. Environmental burdens constitute on our territory highly negative barriers and risk elements that harm the environment. They are the remnants after of the industrial and agricultural production and after mining activities and damaged areas inherited after a stay Soviet army, deserted areas after liquidation of manufacturing enterprises. The loads was polluted the surface and ground water, air, soil, geological bedrock, and in many cases significantly influenced the physiognomy of some landscapes types. The inclusion of these elements in the current landscape is not possible without prior surveys and subsequent elimination of the impact of hazardous substances on the environment. Localities of environmental burdens come from time horizon of ill-conceived socialist industrialization of Slovakia and the environment was not in attention in this period. The burdens take up according of the estimate around 10% territory of the state. They are scattered throughout Slovak Republic. The estimated number of environmental burdens in the Slovak is 30,000 and of which about 5% (1500 localities) are among the high risk. Ministry of Environment of the Slovakia acceded to the systematic identification of environmental burdens in year 2006. The task was coordinated Slovak Environmental Agency and the result is a register of environmental burdens in which of registered 1818 burdens of three categories: A probable burdens, B burdens, C remediation and reclamation eliminate burdens. On the conclusion is should be noted that register of burdens is incomplete both in terms of number of locations, but primarily in terms of the absence of analytical data on those areas that are private property. Registration the environmental burdens does not solve this issue and many of burdens continue to harm the environment. In this paper we will deal with some of them. The only option which should be applied in practice is the law on environmental burdens No. 405/2011 Coll. adopted by the National Council of the Slovakia 1 January 2011 determining the rights and obligations of the originator environmental burden.

**Keywords:** Environmental burdens; Load of environment; Field research; Hazardous substances

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## **SCREENING OF AUTOCHTHONOUS *STREPTOMYCES* SPP. ISOLATED FROM WESTERN ALGERIA AND DETERMINATION OF THEIR ANTIMICROBIAL ACTIVITY**

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Isolation and characterization of new strains of *Streptomyces* is a topic of great interest in the search for new antibiotics or new bioactive molecules of interest. This study is devoted to the development of collection of the genus *Streptomyces* strains from samples of different habitats that have undergone different treatments (CaCO<sub>3</sub>, heat). The isolation and purification of the strains were prepared on ISP2 medium gave better results compared to other media used; their conservation has been done on liquid ISP2 medium 15% glycerol. The best treatment samples with satisfactory results by *Streptomyces* diversified presence and absence of fungal contamination compared to other treatments was that of CaCO<sub>3</sub>. In total 85 strains suspected be related to the genus *Streptomyces* have been isolated, selected and stored. Antibacterial activity of different isolates was tested against the following pathogenic bacterial strains: *Escherichia coli*, *Staphylococcus aureus*, *Candida albicans*, *Klebsiella pneumoniae* ATCC 4352, *Pseudomonas aeruginosa* ATCC 27853 and *Listeria monocytogenes* NCTC. Three strains (TB1, SM2.2 and SM1B1) presented an interesting antibacterial activity on almost all pathogenic strains used; their inhibitory potential was demonstrated by the double-layer technique incubation of 28°C for 12 days. Furthermore, the extraction of these three strains synthesized molecules by fermentation was performed for 7 days. The extraction of secondary metabolites from the float is provided by chloroform and concentration from the organic phase required the use of rotary evaporator. In another step, a thin layer chromatography (TLC) was performed on a silica gel plate to separate the different metabolites synthesized. The samples were placed 1 cm above the boundary of the eluting system chloroform, after migration, visualization was done by a plate Ultra Violet, and the revelation showed the presence of UV-absorbing molecules and the presence alkaloids. Over the word, the research of novel *Streptomyces* strains is important in order to satisfy the increasing request of the market and to obtain new functional products.

**Keywords:** *Streptomyces*; ISP2 medium; *Staphylococcus aureus*; TLC; antibacterial activity

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## IDENTIFICATION BY DNA METHODS OF *STREPTOCOCCUS THERMOPHILUS* ISOLATED FROM ARTISANAL FERMENTED PRODUCT

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Algeria remains dependent on the importation of bacteria involved in industrial fermentations. *Streptococcus thermophilus* is an essential agent in dairy technology, including the production of yogurt. *Streptococcus thermophilus* isolates from 'Smen', a traditional fermented milk product provided from steppe region were subjected to taxonomical investigations and tested for antagonistic activity, acidifying power and proteolyses properties for possible inclusion in a starter culture preparation. The identification procedure included phenotypic investigations, molecular characterization by using species-specific primers from *glcK*, *dnaE*, *thrS*, *proA* and *serA* housekeeping genes in order to distinguish among reference, and wild strains of *Streptococcus thermophilus* and for their differentiation from *Enterococcus* spp. The acidifying capacity was deduced from pH measurement, proteolytic activity was realised in SMY medium and the inhibitory activity against two pathogenic strains, namely *Staphylococcus aureus* and *Escherichia coli* was conducted. A collection of 20 isolates Gram-positive, catalase-negative and cell morphology with a long chain were presumptively identified as *Streptococcus thermophilus* on the basis of phenotypic characterization. A total of 14 strains were tested by PCR DNA identification analysis and these indigenous isolates were unambiguously characterised by their housekeeping gene sequences. Their performance and physical properties were not significantly different from commercial starters strains used in this study. To our knowledge, this is the first report on the isolation and molecular characterization of *Streptococcus thermophilus* strains from traditional fermented milk product in steppe area of west Algeria. Other techniques have been used for the isolation and detection of strains producing exogenous polysaccharides (EPS) from *Leuconostoc* spp. It was therefore suggested that wild bacterial populations should be preserved in order to protect the traditional lactic fermentation and for product innovation.

**Key words:** *Smen*; *Streptococcus thermophilus*; DNA; steppe area; product innovation

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## **SOME ASPECTS OF WASTEWATER TREATMENT AND SLUDGE UTILIZATION IN HUNGARY**

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### **Abstract**

*Hungary's accession to the European Union in 2004 marked the start of a new era. The completion of legal harmonization brought in new emission standards and thresholds, and this was followed by EU-assisted projects to build and reconstruct wastewater treatment plants. The utilization of sludge after it leaves the wastewater treatment plant is now a solely private-sector operation. There are new political priorities: increasing state involvement, buying out of major – formerly privatized – service providers, reintegration of isolated service providers, and legally-imposed reduction of public utility charges. As a result, a demand has arisen for a greater central, i.e. government role in sludge utilization.*

**Keywords:** *European Union, legal harmonization, utilization, sludge, political priorities, public utility charges*

### **INTRODUCTION**

In Hungary, the political transition from the Soviet sphere of interest to the Western European community was closely linked with moves to join the European Union. The initial transition took place between 1989 and 1990. Formal accession to the EU took place only in 2004, but preparations and legal harmonisation started in the late 1990s. This paper analyses the effects of these processes and of events since then on wastewater treatment and sludge utilization.

Construction of the wastewater drainage network and treatment facilities did not keep pace with the development of the drinking water supply. Prior to the transition, 76% of homes were connected to the public water supply and only 41.3% to a public sewer. This gap has been greatly narrowed made up thanks to EU funding.

Nowadays, water supply connection is close to 100%. In 2013, the rate of wastewater drainage and treatment reached the figure of 82% nationwide, 8% of which did not involve connection to a public sewer. This improvement has been concentrated in Budapest and the towns. By 2015, all towns and villages larger than 2000 PE must have a sewer connection and biological treatment. Since the Danube Basin – which includes the whole of Hungary – qualifies as a sensitive area, 80% of treatment works have nutrient removal capability.

The situation in villages smaller than 2000 PE, however, is less advanced. The means by which EU and national funding may be provided for these villages is currently being drawn up for the next 7-year planning period.

Hungary has a relatively large number of small villages. Villages with population of less than 2000 make up 75.3 % of all towns and villages and hold 17% of the population. Young people, however, tend to move away from them owing to lack of local job opportunities. Effort is

required in the coming period to provide wastewater drainage and treatment which is in proportion to these villages' abilities to sustain themselves.

The developments so far have resulted in water supply and wastewater charges which are beyond the financial means of much of the population. Research in this area has found that this is also true for the other utilities – gas, electricity and district heating.

Charges in Budapest in the last nine years:

Water:           in 2005: 131.6 +15 % VAT = HUF 151.34/m<sup>3</sup>  
                      in 2014: 172.4 + 27 % VAT = HUF 218.95/m<sup>3</sup>  
                      Increase: 44.67%

Sewage:         in 2005: 186.1 +15 % VAT = HUF 214.02/m<sup>3</sup>  
                      in 2014: 300.23 + 27 % VAT = HUF 381.29/m<sup>3</sup>  
                      Increase: 78.16%

In 2005, the total price for these services was HUF 365.36/m<sup>3</sup>; in 2014 it was HUF 600.24/m<sup>3</sup>, an increase of 64.28%. In other towns and cities, particularly small towns and villages, this can be 50–80% greater. The state currently subsidises households where charges are higher than 1000 HUF/m<sup>3</sup>. In 2013, the government required utility companies to reduce their charges by 10%, and the 2014 prices reflect this.

Incomes have not grown at the same rate. The rises in electricity, gas and district heating charges have made them among the highest in Europe, relative to income.

“Figure 1 shows the average burden of charges among households connected to both the water supply and drainage in the service areas of different companies (water utilities). Each column corresponds to one company. The burden of charges for the two services together varies between 1.5% and 3.5% of income. For most companies, the figure lies between 2% and 3%, which is under the frequently-published threshold of 3–4.5%, but is considerably above the 2004 Central European average of 1.6–1.7%.” [1].

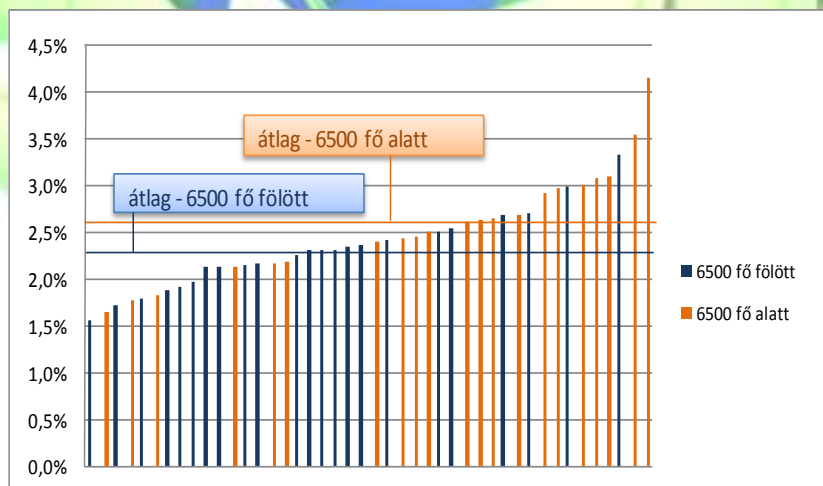


Figure 1: Water charges as a proportion of income in towns with both services, by average population, 2009 [1]

Átlag - 6500 fő alatt: average - under 6500 inhabitants;

Átlag - 6500 fő fölött: average - over 6500 inhabitants



## HOW DEVELOPMENTS HAVE AFFECTED THE MANAGEMENT OF SEWAGE SLUDGE

Disposal of wastewater sludge has not been included in waste management development projects. Thus even after the construction of Budapest's Central Wastewater Treatment Plant and a nationwide increase in sludge of nearly 30%, no solution has been found for its disposal. Transport over long distances greatly increases the costs of disposal and, indirectly, the sewage charge. The new wastewater treatment plants built in cities other than Budapest have added biogas production to their sludge treatment, from which they generate electricity. In most of these plants, the sludge is further treated by composting. Ways of using the resulting compost, however, did not emerge alongside the developments. Compost should be sold on the open market, but sales problems have caused large quantities to accumulate at many sites. The licensing authority does not have information on the amount of compost sold. A serious question is whether the high costs of composting are justified purely for stabilising the sludge if there is no market for it. The use of sludge for energy purposes in Hungary at present goes no further than producing biogas. Wastewater plants produce some 100,000 m<sup>3</sup>/d of biogas, generating 9.2 MW of electricity. This procedure is attractive as a means of reducing operating costs. It has a negative effect, however, on further energetic use, i.e. on incineration. Not surprisingly, such utilisation does not exist for communal sludge in Hungary. The figures are little better for communal waste as a whole: only 5% of the present 18 million tonnes of waste is utilised in this way, falling far short of the other EU member states [2]. The direct agricultural use of sludge is described below. This form of utilisation involves sludge which has been treated in some way and is deposited on designated land. It does not include compost sold on the open market. Figures 2 and 3 shows a decrease in the amount of sludge deposited in the last 13 years, at the same time as wastewater treatment developments have resulted in increasing total quantities of sludge. Other figures show that the amount of sludge deposited per unit area has also decreased by 30% in the same period, so that the efficiency of disposal has also deteriorated.

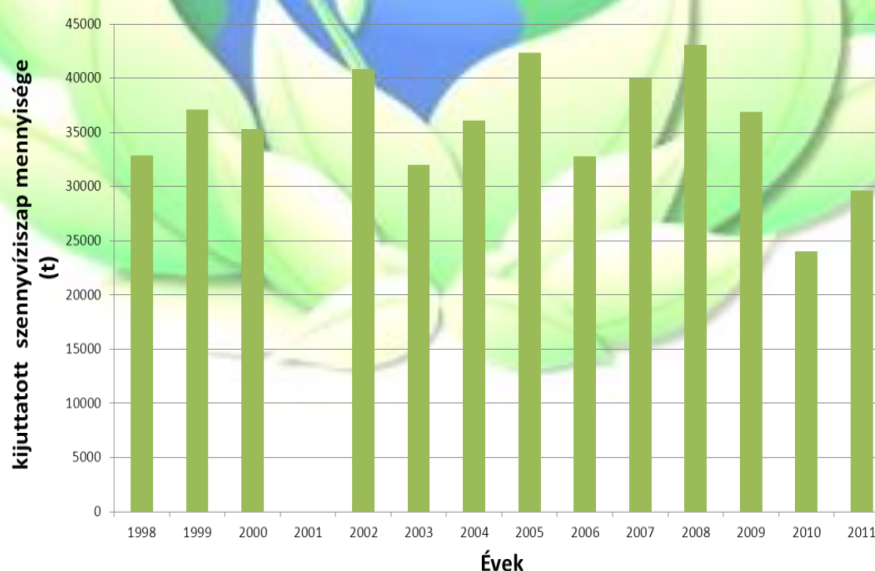


Figure 2: Trend of agricultural use of sewage sludge in Hungary [3]  
Évek: Years, Kijuttatott szennyvíziszap mennyisége (t): Quantities of sludge (T)

There are several reasons why agricultural utilisation has declined. The conditions of depositing it have become much stricter. The table below shows the change of permitted heavy



metal content of sludge used for agricultural purposes in the last 25 years. EU regulations are expected to become even tighter. Thresholds will also be set for organic constituents, and this will impose further restrictions.

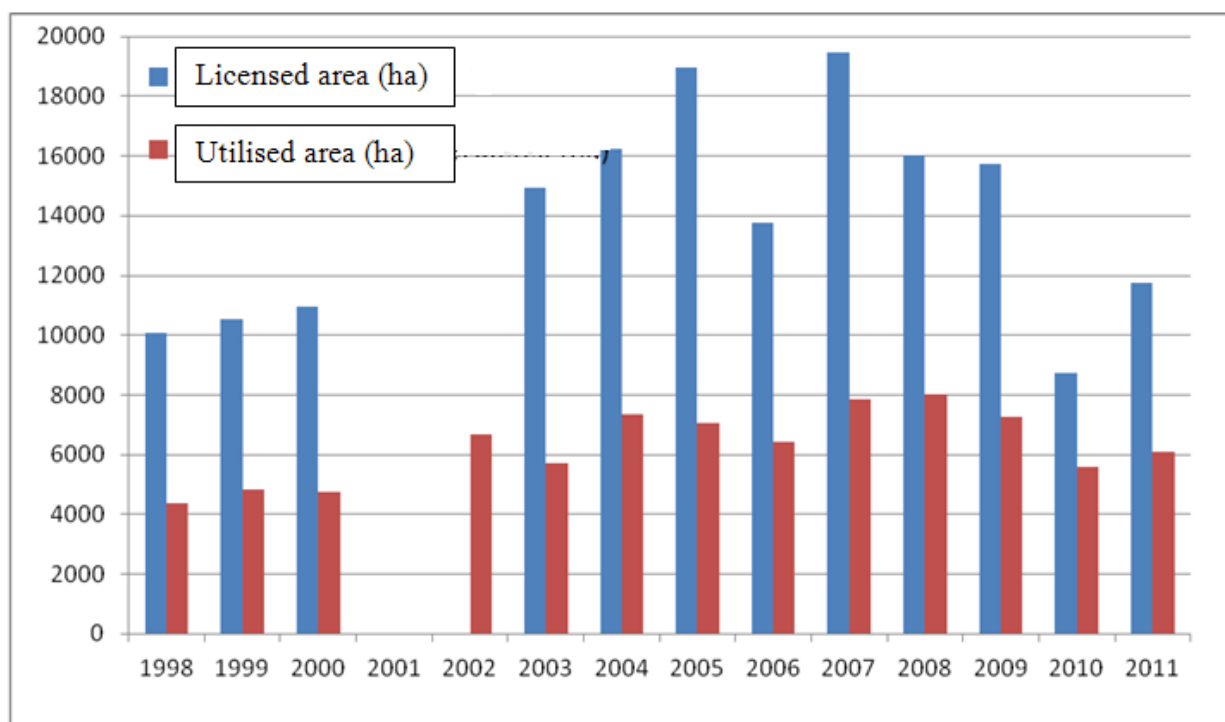


Figure 3: Areas of agricultural use of sewage sludge in Hungary [3]

In the 1990s, following the political transition, Hungary met the thresholds for sewage sludge set by EEC Directive 86/278. EU legal harmonisation set off a process of tightening the rules, as shown in Table 1.

Table 1: Concentration limits for toxic elements in sewage sludge [4]

Heavy metal	Former Hungarian limits (1990)	86/278 EEC	Current Hungarian limits (50/2001. Korm. rend.)	Planned Hungarian and EU limits (2016)
	mg/kg dry matter			
Cd	15	20-40	10	0.8
ΣCr/Cr VI	-	-	1000	100
Cu	1000	1000-1750	1000	1000
Ni	200	300-400	200	30
Pb	-	750-1200	750	120
Zn	3000	2500-4000	2500	2500
Hg	10	16-25	10	0.8
ΣPAH	-	-	10	3
ΣPCB	-	-	1	1
TPH	-	-	4000	4000

Mo	20		20	20
As	-		75	75
Co	-		50	50
Se	-		100	100

The EU member states apply the restrictions on toxic elements in different ways, and the overall picture is highly varied. Figure 4-5 show the toxic element threshold values in EU states. Figures 4 and 5 show that Hungary occupies a middle position as regards the strictness of thresholds. A new decree, however, will require further tightening to be introduced in 2016.

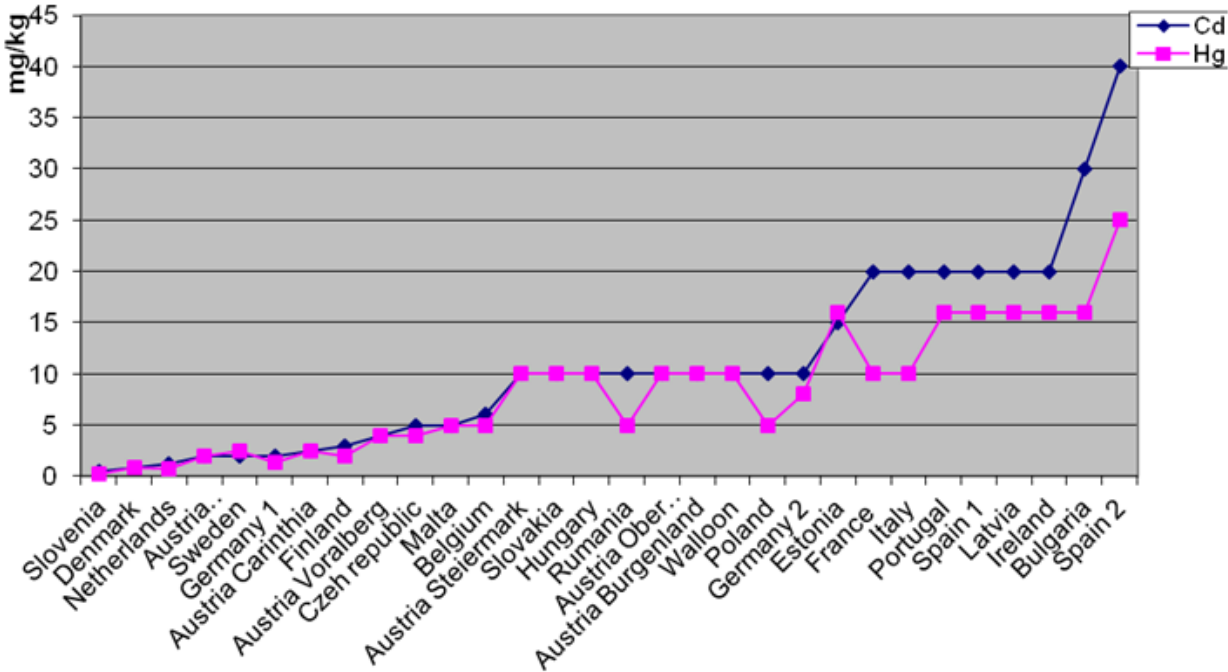


Figure 4: Limits for Cd and Hg content of sewage sludge for agricultural use in the EU (mg/kg) 2010 [3]

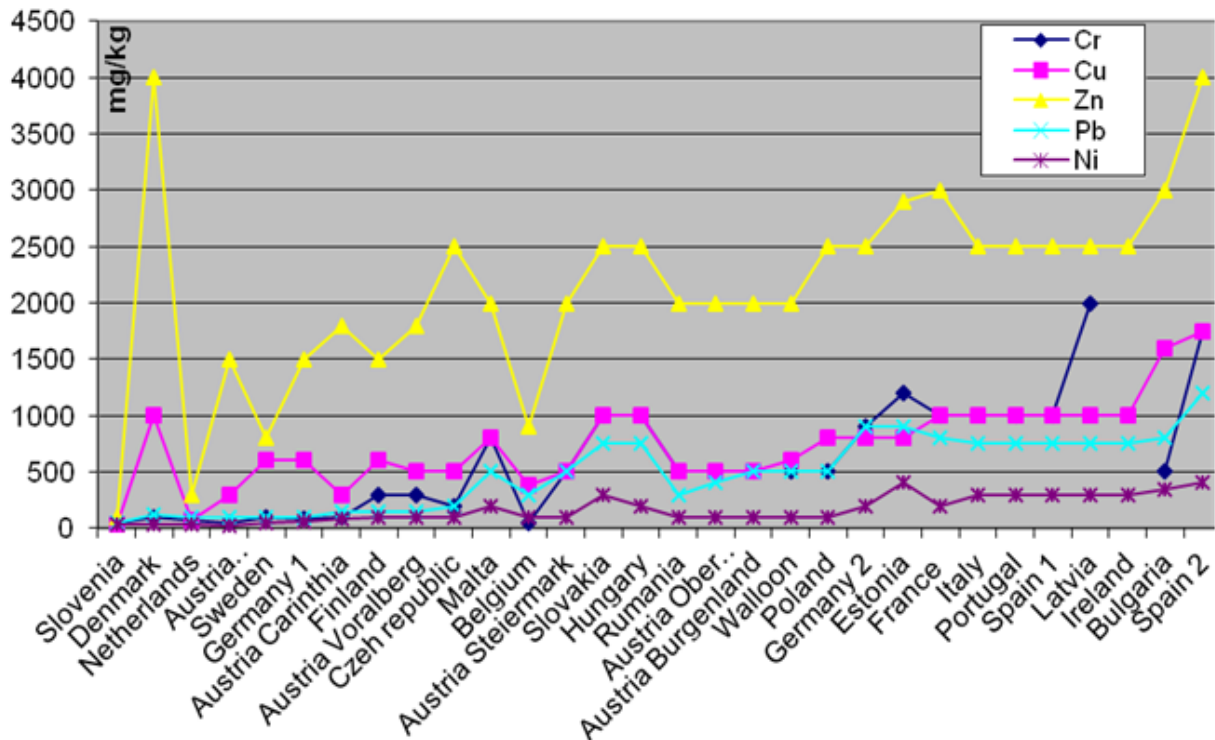


Figure 5: Limits for Cr, Cu, Zn, Pb, and Ni content of sewage sludge for agricultural use in the EU (mg/kg) 2010 [3]

Austria is an interesting case. In the fertile Burgenland in the eastern part of the country, the thresholds for some elements are 4–5 times higher than in Lower Austria. Reduction of thresholds for toxic elements is also an aim for EU regulation. Research in Hungary, however, has found that agricultural utilisation of wastewater sludge has no toxic effect on soil if used in the prescribed doses. [5,6]

Other examinations showed the reduction of heavy metals in sludge, result are presented on Figure 6. Other studies have shown that wastewater sludge has a beneficial effect on the microbiological activity of soils. [7]



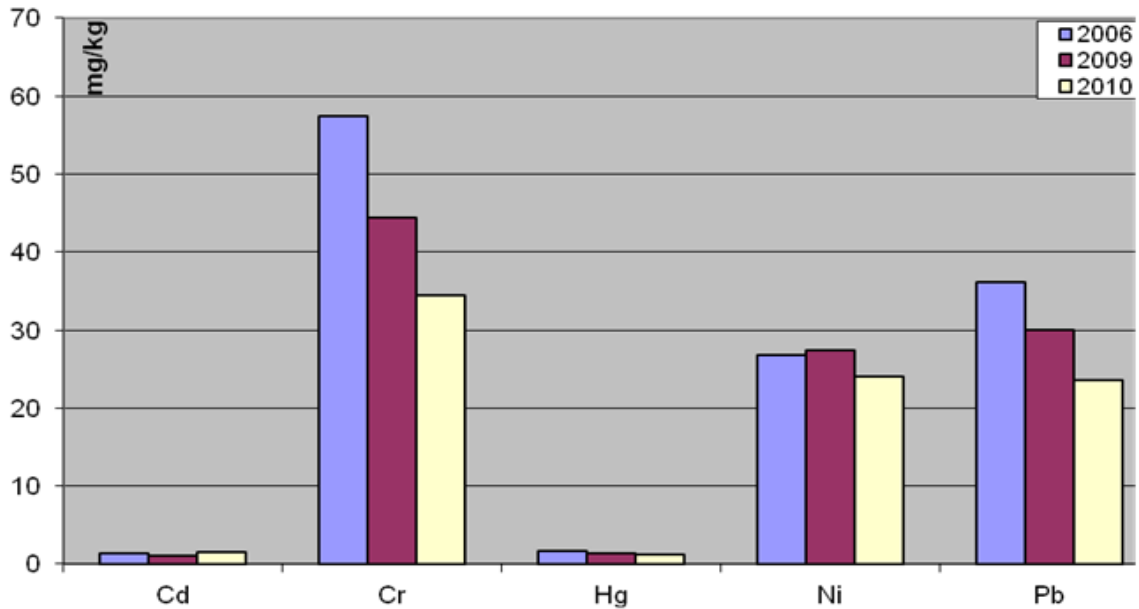


Figure 6: Changes of heavy metal content in sewage sludge in Hungary (mg/kg) [3]

Another factor which has contributed to the declining trend of agricultural sludge utilisation is the change of land ownership: land formerly run by large socialist enterprises was sold off and broken up into parcels.

The consequences of this process on sludge utilisation in Hungary may be characterised by analysis of utilisation costs. Surprisingly, these – without energetic utilisation of the sludge – match or surpass sludge utilisation costs in Germany, figure 7. The highest mono incineration costs in Germany are less than € 400 per tonne-dry matter, while recultivation costs in Hungary are more than € 550 per tonne-dry matter. As a basis for comparison of disposal costs, we used the data of the German federal environment protection office. [8]

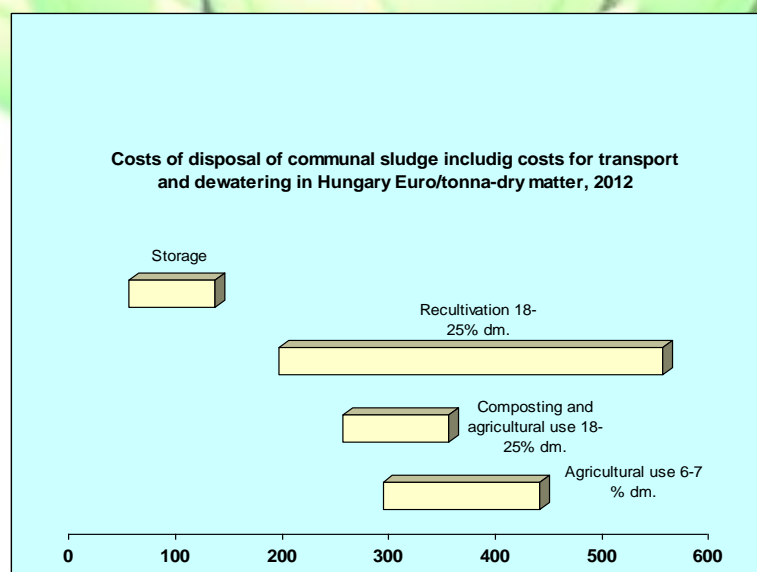


Figure 7: Cost of disposal in Hungary [9]



## **NEW POTENTIAL MEANS OF SLUDGE UTILISATION**

New, patented techniques for improved sludge utilisation have resulted from research and development in Hungary over the last decade. One example is the Lignimix process:

The main innovation in the process is wet grinding (shearing) of municipal sewage sludge (or liquid manure) to which carbonaceous minerals (lignite or brown coal) have been added. The resulting radical mechano-chemical impingement converts the sludge into a stable suspension.

Powdered lignite is added to sewage sludge of 5-6 % dry matter, and the mixture is continuously subjected to shear stress in a wet grinder (Kavitron).

Positive changes in sludge treatment:

- Lignite disintegrates and forms a homogeneous suspension with the sludge
- The suspension immediately loses most of its bad smell
- When the suspension fully dries, its pathogen count falls by 2 to 5 orders of magnitude
- Desiccation occurs fast and uniformly
- The dry matter obtained (70% or less water) becomes stable (e.g. no rotting, no changes in properties)

Utilisation of LIGNIMIX:

- Fuel: burns exactly as brown coal
- Soil conditioner: a more promising application due to valuable ingredients recycling into the soil
- Lignite suspensions gradually undergo complete humification
- The wet suspension can yield up to 20% more biogas than sludge treatment by putrefaction [10]

## **CONCLUSION**

- Sludge utilisation makes up a substantial proportion of wastewater treatment costs: as much as 40–50%. The choice of treatment technique is thus very important, and must harmonise the possibilities with the demands.
- Sludge treatment should be managed at the level of national strategy. Free-market elements that inhibit rational and economic utilisation should be eliminated.
- A balance should be struck between agricultural and thermal utilisation. Thermal utilisation should be increased at the expense of expensive and less efficient recultivation utilisation.
- Each member state should find the sludge utilisation method that best suits its needs and capabilities. Sludge treatment at the wastewater works and utilisation elsewhere must be viewed and planned as an integrated process.
- Future regulation of toxic elements should be made consistent with the capacity of differently-endowed agricultural areas to ensure efficient agricultural utilisation.

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## GROUNDWATER CIRCULATION MODEL FOR DISCOVERING ENVIRONMENTAL CONTAMINATION OF SPRINGS

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### ABSTRACT

A *case history* is discussed in the present paper. Summarized, in particular, are the original methods and the most interesting results of an environmental and hydrological research-work, carried out on waste deposits abandoned in quarries, in ITALY, near the city of Rieti, northeast of Rome, in Lazio Region. An interdisciplinary team – ad hoc organized – had the following strategic goal: to study all the aspects of environmental problems of the whole area and organize a **knowledge integrated system**, useful for land-use planners and for land rehabilitation engineering and design activities. It is important to emphasize that *Remote Sensing Integrated Analyses* represent a crucial and basic tool for the entire Research-work. Particular emphasis was given to the original reconstruction of the “**groundwater circulation model**”. Thanks to this interesting result, it was possible to make a very important and unsuspected discovery: the direct environmental interaction between the different systems “quarries-waste deposits” located on a *fan* [5 km northeast of Rieti] and the springs located nearly 2 km east of Rieti. The negative contamination of the mentioned springs was stopped by Public Authorities.

**Keywords:** *Vision, Interdisciplinary, Remote Sensing, History, Environmental.*

### INTRODUCTION

The city of Rieti – northeast of Rome (nearly 80 km), in Lazio Region – is located on a foothill [405 m. above s.l.] of the Reatini Apennines rising to 2,216 m. at Mount Terminillo. The Velino River flows through the center of the city and the whole area is rich in water. Important springs – used for a number of different activities – are located nearly 2 km east of Rieti. Unfortunately, in the period between 1980 and 1990, the area sustained a very large environmental degradation. In fact, the number of waste deposits abandoned in disused quarries increased, year after year [Fig.1]

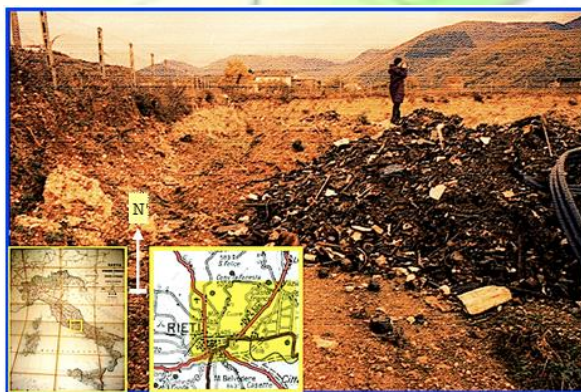




Fig. 1. Location of the area studied

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To plan the reclamation of the whole area, an interdisciplinary *Research team* was organized by a private consortium together with local public Institutions. A central feature of this Research-work has been the interdisciplinary approach. Different skills and capabilities have been aggregated to develop the Research activities, not just as an "assembly line" which adds on various specific contributions without any mutual integration. Many eminent scholars and investigators of the Research-team operate, today, within the «*intraVidére*» Research-Institute. For this reason, it may be appropriate to speak a few words about the said Research-Institute.

The company «*intraVidére*» is the natural evolution of creative, entrepreneurial experiences, pursued in a variety of geographical and cultural backgrounds. It provides continuity for interdisciplinary scientific and professional experiences that have evolved in different forms from as far back as **1949**. To do research for producing innovative goods and services, "revealing" what exists in reality, but that the eye is unable to see [this is the meaning of the Latin word «*intraVidére*»], is the mission of «*intraVidére*». Its important added values are the strong synergy between **Creativity** and **Science** and the capability to **create innovation**, designing and implementing "**Technological Integrated Processes**", in which different advanced technologies and avant-garde methodologies interact (thanks to sophisticated *Algorithms* tailor made) for achieving visionary goals and opening *new ways*.

The *Research team* had the following strategic goal: to study all the aspects of environmental problems of the whole area, together with their mutual interactions, for organizing a **knowledge integrated system**, useful for land-use planners and for land rehabilitation engineering and design activities.

For this purposes, the following three main lines were fixed: **a)** Detect and Identify all the quarries and, for each quarry, Analyze the characteristics of the whole system "quarry-waste deposit"; **b)** Classifying the different systems "quarries-waste deposits" and, for each system, Study the surrounding lands, by geomorphological, hydrogeological and geotechnical point of view; **c)** Discover and Check the environmental interaction between the different systems "quarries-waste deposits" and the corresponding surrounding lands.

## **MATERIALS AND METHODS**

- **Overview of the Research Activities**

To plan the work programme, the *Research team* has proposed an innovative *interdisciplinary system*, in which the following five main Thematic Areas have been selected:

- Historical Research
- Remote Sensing Integrated Analyses
- Geomorphology and Geolithology
- Investigation Program
- Hydrogeology and Environmental Geotechnics

- **Historical Research: Methods Adopted and Historical Documents**

Main Activities. A detailed study about historical natural disasters – specially flooding events – has been carried out, within the first stage. It should be noted that the proposed procedure has allowed to taken into account not only the natural events centered on the Region in which Rieti is located, but also the effects [so frequently overlooked] due to "seemingly far disasters", occurring in other geographic areas, but causing localized damages also within Rieti urban areas.





Fig. 2. Velino River in Rieti and the famous “Cascata delle Marmore”

A complex effort has been the search of historical documents to be selected and processed: it seems interesting to mention a large number of historical maps and a precious collection of aerial photographs made by the RAF (*English Royal Air Force*) flying between 1943 and 1947.

- **Remote Sensing Integrated Analyses: Methods followed and Image Processing**

Main Activities. *Remote Sensing Integrated Analyses* represent a crucial and basic tool for the entire Research-work.

1. Integrated Processing of *Multispectral and Multitemporal Images* have been planned and implemented. Sophisticated analyses have been carried out collecting and processing data generated by different platforms: Satellite, Aerial, Land platforms.

The Satellite data have been acquired by three distinct platforms, each with different sensors, instruments, resolution, and other specific parameters (orbits, altitude, etc.) : LANDSAT, SPOT and ERS-1 Satellite.

2. 4 *multitemporal* groups, of Aerial Photographs – taken between 1955 and 1990 – have been selected and processed. In addition there are also the mentioned RAF Aerial Photographs (1943 – 1947), very useful tools: The scale varies for each flight from 1 : 5,000 to 1 : 73,500, common is 1: 7,600 to 18,000..

A difficult effort has been performed to achieve a propaedeutic basic goal: the exact superposition among the different Multitemporal Aerial Photographs. For this purpose, each Aerial Photo selected has been digitized and geo-referenced in a *tailor-made* “Basic Geographical Information System”, after application of geometric/radiometric corrections. The correction process has removed image distortions and has re-sampled the imagery to a uniform



ground sample distance and a specified map projection: this is very useful for correlation with the mentioned Historical Maps.



Fig. 3. Rieti: Historical Water Map

3. Data generated by Land Platforms have been acquired by a *mobile laboratory* and consist of two distinct techniques: “*Multitemporal Photography in Infrared False Colour*” (spectral band between 0.5 and 0.9  $\mu\text{m}$ ) and “*Multitemporal Thermographic Monitoring*”: the thermal infrared band is comprised in this case between 2.0 and 5.6  $\mu\text{m}$ . Both types of analysis are based on the use of what are known as “passive” sensors, i.e. sensors which record what is spontaneously emitted by the object.

All the information obtained and calculations performed have been reprocessed in a unitary context, on the basis of specific methodologies, mostly of an innovative type and in some cases specially developed by the Research-team. Where necessary, following an iterative procedure, the basic calculations have been reprocessed, using parameters compatible with different types of analyses and procedures. All the images resulting from the analyses briefly described above have been subjected to appropriate analog and/or digital processing. The calculations performed have been of various types, ranging from the most common to the most complex [filtering, derivation and integration, slicing, etc.] and sophisticated [calculations using “cluster analysis” *algorithms* or involving the conversion of an image into its Fourier representation], right up to the construction of numerical models. The results of these calculations have allowed the greatest possible amount of knowledge to be “extracted” from the images in relation to specific objectives [Ciuffi *et al.*,1997].

- **Hydrogeology and Environmental Geotechnics: Methodologies and Data Processing Main Activities.** The synergies between Environmental Geotechnics, Hydrogeologic Studies, Historical Research and Remote Sensing Data Processing have been decisive.

The Environmental Geotechnics Studies and the Hydrogeologic Research have been developed following three different lines, distinct but strongly interactive:

1. “study of the system “quarries-waste deposits” located on a *fan*;



A detailed analysis of the complex system “quarries-waste deposits” has been carried out. Each quarry has been processed, on the basis of the characteristics of its waste deposits. Finally, an **Environmental Zoning Map** has been designed and implemented.

2. “study of the surface drainage pattern”;

The study of the “*surface drainage pattern*” around an urban area requires the knowledge of several “invisible” elements buried or quite lost. For this reason, the objective has been to detect the said elements and to study them, together with the very limited visible flowing, for reconstructing the said “surface drainage pattern”.

3. “study of the *groundwater circulation model*”.

It has been emphasized that the reconstruction of the “*shallow groundwater circulation model*” has been one of the basic results of the entire Research-work. The study has been developed following different stages, selecting and processing the results generated by distinct Thematic Areas.

The said different stages can be summarized, as follows.

1. The first step has been the analysis of *fracture density*, based on the “*Linear Features*” processing.
2. In the second stage, a detailed study of permeability has been conducted. Each lithological class has been associated to one of the two main groups of permeability: “**primary permeability by porosity**”, “**secondary permeability by fracturing**”.
3. A *permeability matrix* has been created ad hoc. Different classes of permeability have been determined.
4. The *Remote Sensing Integrated Analyses* together with the *Historical Research* have allowed the determination of the zones of **water storage** and the areas of **water recharge**, together with the *preferential groundwater flow directions* and the *sheet water flow directions* [Marcolongo, 1987].
5. The results of the analyses above described have been further processed all together (using *Algorithms* ad hoc devised), on the basis of a devoted iteration process implemented for constructing the “**3-D groundwater circulation modelling**” [Fig.5].

## RESULTS AND DISCUSSION

The most interesting results are clearly showed in the following **Fig.4** and **Fig.5**. In addition, it is opportune to summarize the following points.

1. The detection and construction of the “invisible” “**3-D groundwater circulation modelling**” of the area studied is a “crucial result” achieved, within the Research-work.
2. Thanks to the said “crucial result”, it has been possible to make a very important and unsuspected discovery: the direct environmental interaction between the different systems “quarries-waste deposits” located on a fan [within Vazia area, nearly 5 km northeast of Rieti] and the mentioned springs located nearly 2 km east of Rieti.





WASTE DEPOSITS ABANDONED in QUARRIES located on a **FAN**

“ ENVIRONMENTAL ZONING MAP ”

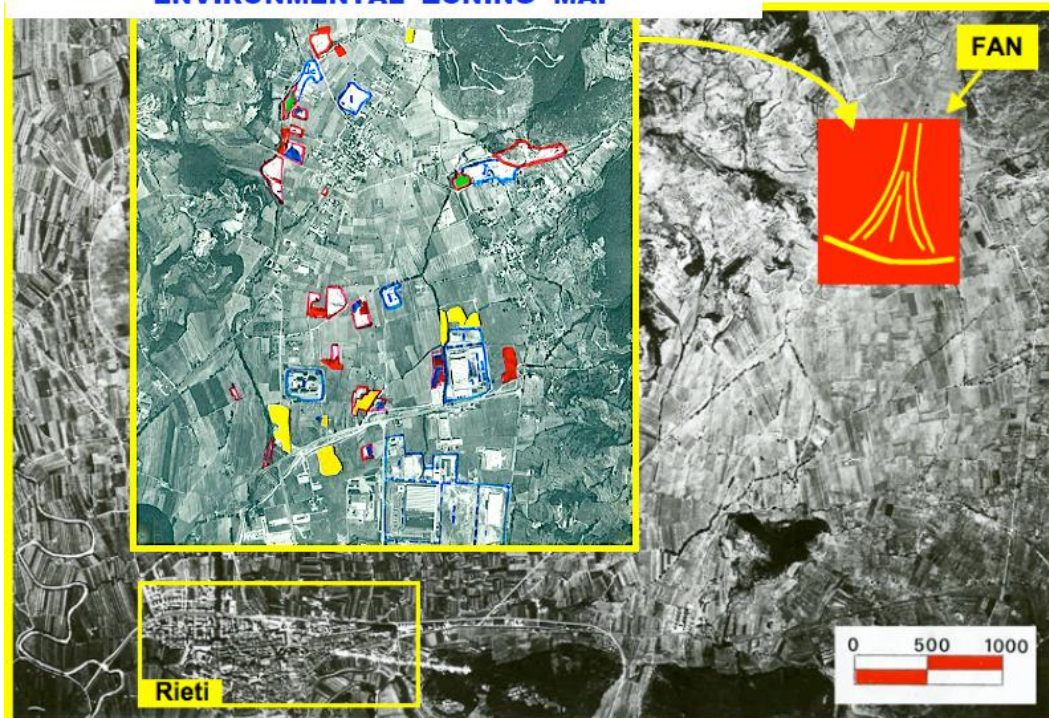


Fig. 4. Environmental Zoning Map

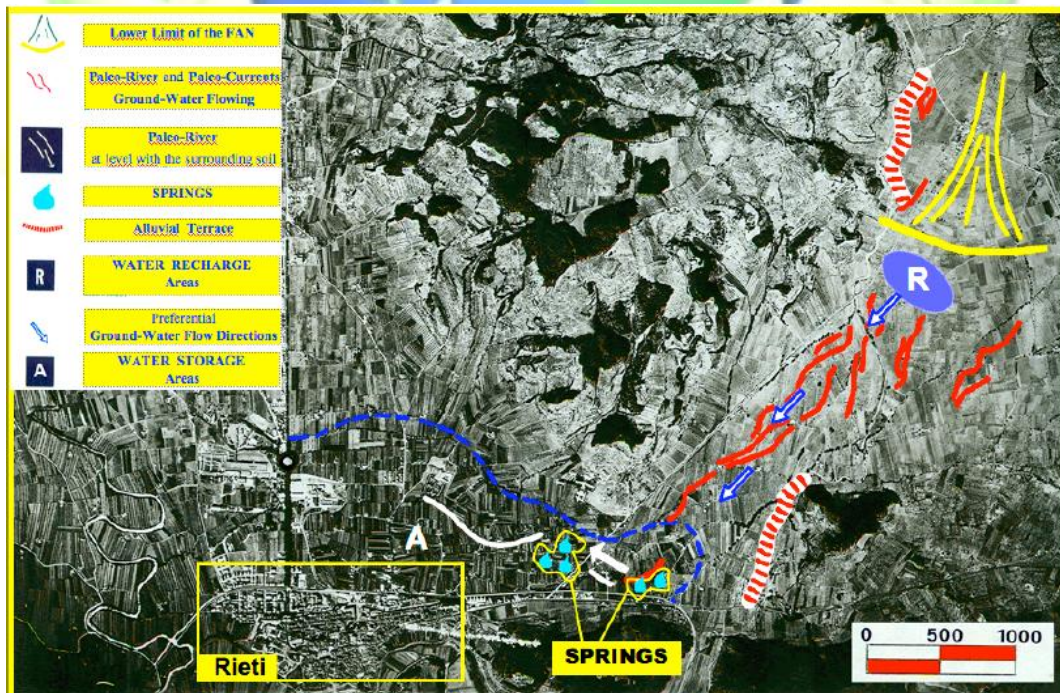




Fig. 5. GroundWater Circulation Model



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## CONCLUSION

The final two points are for the main conclusions.

1. The “negative” discovery has generated a “positive” solution. The Public Authorities have intervened to stop the contamination of the springs and immediately start a chemical and bacteriological monitoring program.
2. In addition, it has also obtained an important result by socio-economic point of view. In fact, it has been possible to plan the reclamation work, pursuing a very accurate focus, without wasting time and money.
3. It has been confirmed that it is necessary – more and more in this third millennium – to *OVERTURN the VISION* and develop *NEW FRONTIERS*. The most interesting lesson that emerges can be summarized as follows: in any research activity a real interdisciplinary approach is an incredible and powerful tool. This tool allows to organize “intelligent synapses” within and among all the different multi-thematic aspects of reality, for successfully facing the **charming challenges of complexity**.

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## DEGRADATION OF ENDOCRINE DISRUPTING PESTICIDES USING ADVANCED OXIDATION PROCESSES AND THEIR COMBINATIONS

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### ABSTRACT

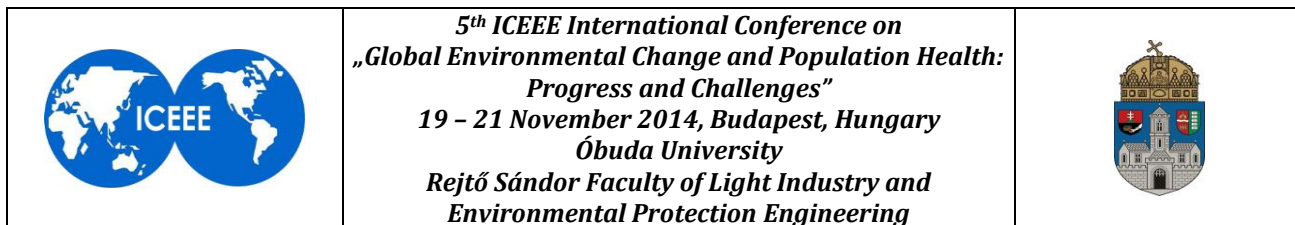
In this study the oxidative transformation of six pesticides (diuron, linuron, monuron, fenuron, atrazine and acetochlor) having endocrine disrupting effects has been investigated. The efficiency of various advanced oxidation processes, such as ultraviolet photolysis, ozonation, the combination of photolysis and ozonation and heterogeneous photocatalysis were compared using the identical experimental apparatus to ensure the comparability of the results. The efficiency of the methods was compared on the basis of the initial rate of transformation determined. The direct ultraviolet photolysis was found to be much more effective than ozonation for chlorinated compounds except in the case of fenuron. When the combination of ozonation was applied simultaneously with photolysis, the initial rate of transformation generally exceeded, that determined in the case of ultraviolet photolysis, and were found to be one magnitude higher than in the case of ozonation. This is due to the fact that, in this case the organic substances can react either with the radicals formed from the ozone, or by direct photolysis. Heterogeneous photocatalysis is a less effective but also less selective compared to photolysis, but still more effective than ozonation. In general it can be concluded, that during this study the effectiveness of the methods generally follows the order of UV/ozonation > photolysis ≥ heterogeneous photocatalysis > ozonation. The comparison of the chromatograms, which belongs to the treatment time when the initial concentration decreased to 50 %, proved that the quality and quantity of intermediates formed is determined by the oxidation process most likely because of the different reaction ways of their formation.

**Keywords:** pesticides, AOPs, photolysis, ozonation, heterogeneous photocatalysis

### INTRODUCTION

Nowadays the utilization of pesticides is necessary for agricultural uses. Phenylurea herbicides are one prominent group of such chemicals, which are mainly used for the pre- and post-emergence control of broadleaf weeds and grasses in non-agricultural areas (railways, roadsides), but also in cases of certain plants. Two well-known examples of these compounds are diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and linuron (3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea), the former being used as a total herbicide and antifoulant in paints, while the latter is used in cotton fields in addition to its weed control uses (USEPA 1995, Yebra *et al.* 2004, Holmes 2014). These compounds usually have low water solubility (42 and 63,8 mg/L for diuron and linuron respectively) and are persistent in soils, having half-lives of 20-231 days for diuron and 38-67 days for linuron (Katsumata *et al.* 2005). They also usually have a low acute toxicity (above 2 g kg<sup>-1</sup> for rats for diuron), and poisoning is only likely following ingestion, however they and their metabolites are proven or possible endocrine disruptors. Linuron reduces testosterone production and also inhibits the activity of the 5α-reductase (enzyme of





the human androgen metabolism) while diuron is listed as a priority hazardous substance by the Water Framework Directive of the European Commission (Lambright *et al.* 2000, Lo *et al.* 2007, Wilson *et al.* 2009). In addition, the main metabolites of phenylurea herbicides are aniline derivatives, which are oxidants of the haemoglobin, while also being possible endocrine disruptors themselves (Rao *et al.* 2010).

Atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) is a triazine pesticide, which is mainly used for weed control in corn and sugarcane crops as well as on turfs such as residential turfs and golf courses (Roberts 1998). It is the most widely used herbicide in the US, China and Australia, but it has been banned in the European Union for its persistent water contamination. In the United States it is the most frequent water contaminant in drinking water. It also has a low water solubility (70 mg/L) and a long half-life 60-100 days in soil, for which it is considered a persistent organic pollutant (Silva *et al.* 2004). There are studies that show that atrazine can be highly toxic to non-target organisms, and is also a possible endocrine disruptor leading to birth defect, and also being a human carcinogen (Hayes *et al.* 2011).

Acetochlor (2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide) is a representative of the chloroacetanilide herbicide class. It is being utilized throughout the world, mainly in China and the United States (Ye 2003). In the US it is used as a direct substitute to herbicides of known concern, one of them being atrazine in case of important plants, as well as maize crops. The half-life of acetochlor is ranging between 3.4 and 12.9 days (Mills *et al.* 2001). It is also a known carcinogen and endocrine disruptor (Hill *et al.* 1997, Green *et al.* 2000).

A promising way to deal with these water contaminants is the use of advanced oxidation processes (AOPs) that are based on the generation of radicals of high reactivity that are capable to initiate the degradation of organic matter. Typical AOPs are ozonation, which is used as a supplementary water treatment method, photolysis, heterogeneous photocatalysis, Fenton-reactions and the combination of these methods or even the use of additives such as hydrogen-peroxide (Hoigne 1998). While many of these processes can be effective by themselves, their combinations are proven to be more effective (Meunier *et al.* 2006). One of the most basic combinations is to combine either of the advanced oxidation processes with ozonation, resulting in UV/ozone method or photocatalytic ozonation.

This article compares the effectiveness of ultraviolet photolysis at 254 nm, ozonation, their combination and heterogeneous photocatalysis in the transformation of the aforementioned pesticides in a laboratory scale system.

## **MATERIALS AND METHODS**

### **Materials**

The pesticides used were the following: diuron (Sigma-Aldrich, 98% purity), monuron (Sigma-Aldrich, 99% purity), fenuron (Santa Cruz Biotechnology, 99% purity), linuron (Sigma-Aldrich, Pestanal) and also atrazine (Sigma-Aldrich, Pestanal) and acetochlor (Sigma-Aldrich, Pestanal). All measurements were taken in ultrapure Milli-Q® water. For the photocatalytic experiments Aeroxide® P25 TiO<sub>2</sub> (Evonik Industries) was used. Oxygen gas of 99.5% purity was used in the case of ozonation, while air of 99.5% purity was used in the case of direct photolysis and heterogeneous photocatalysis.

### **Experimental setup**

In the case of ozonation and its combination the light source was a low-pressure mercury vapor lamp, which emits 254 nm ultraviolet (UV) and 185 nm vacuum ultraviolet (VUV) light (UV/VUV lamp). This lamp (GCL307T5VH/CELL, LightTech, Hungary) was covered with a high





purity quartz sleeve which transmits both 185 nm VUV and 254 nm UV light. Ozone was generated by the VUV photolysis of pure molecular oxygen in gas phase.

In the case of the direct UV photolysis the sleeve of the same low-pressure mercury vapor lamp was made of commercial quartz (GCL307T5/CELL, LightTech, Hungary), which transmits the 254 nm UV light and absorbs the 185 nm VUV light (UV lamp).

Another light source, a specific fluorescent lamp (LightTech, Hungary), which emits 300–400 nm (maximum of intensity at 365 nm) UV light, was applied during heterogeneous photocatalysis.

The electric (15 W electric input) and geometric parameters (227 mm arc length, 307 mm length and 20.5 mm external diameter of the sleeves) of the different light sources corresponded to each other. The emitted photon fluxes were determined by ferrioxalate actinometry (Hatchard *et al.* 1956) and were found to be  $8.10(\pm 0.65) \times 10^{-6} \text{ mol}_{\text{photon}(254\text{nm})} \text{S}^{-1}$  for low-pressure mercury vapour lamps (UV/VUV and UV) and  $1.20(\pm 0.06) \times 10^{-5} \text{ mol}_{\text{photon}(300-400\text{nm})} \text{S}^{-1}$  for the specific fluorescent lamp.

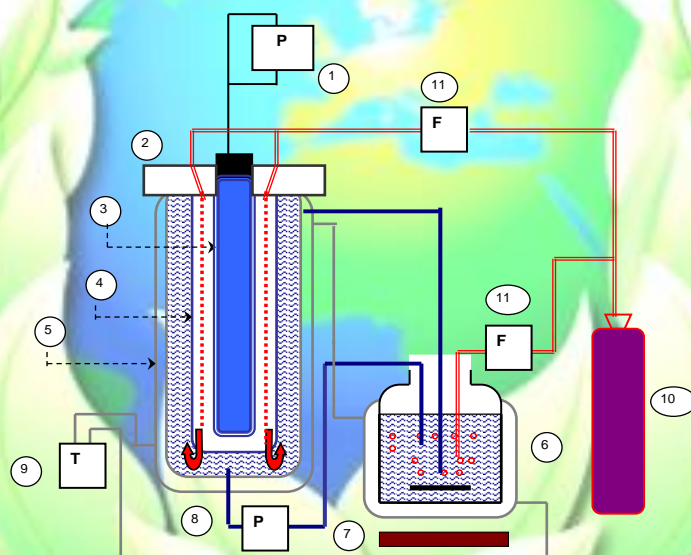


Figure 1: The experimental apparatus

1: power supply; 2: teflon packing ring; 3: light source with sleeve; 4: envelope; 5: reactor; 6: reservoir; 7: magnetic stirrer; 8: pump; 9: thermostat; 10: air bottle; 11: flow meter

All experiments were performed in the same photoreactor (Fig. 1). The light source, surrounded by an envelope was centered in a water-cooled, tubular glass reactor (340 mm length, 46 mm inner diameter). In the course of the measurements, envelopes (320 mm length and 28 mm internal diameter) made of various materials were used. The thermostated ( $25 \pm 0.5$  °C) solution of pesticide ( $500 \text{ cm}^3$ ,  $c_0 = 3.7 \times 10^{-5} \text{ mol dm}^{-3}$ ) was circulated ( $375 \text{ cm}^3 \text{ min}^{-1}$ ) continuously and stirred with a magnetic stirrer bar in the reservoir. Before each experiment, air was bubbled through the solution at least for 10 minutes. The injection of the air was continued throughout the whole experiment. The kinetic measurements were initiated by switching on the light source.

Ozonation, UV photolysis or the combination of these methods could be applied by the careful selection of the light source and the apparatus envelope. Ozonation was performed using UV/VUV lamp and perforated glass envelope. Oxygen was flowed through the Teflon packing

ring between the wall of the lamp and the envelope, which separates the gas phase and the aqueous solution, as shown on Fig. 1. The ozone was generated by the direct VUV photolysis of molecular oxygen and bubbled through the perforated envelope into the solution.

Using UV lamp and a non perforated quartz envelope, UV photolysis at 254 nm could be investigated. In case of the combination of UV photolysis with ozonation, perforated quartz envelope was used. When heterogeneous photocatalysis was applied, the specific fluorescent lamp and the non-perforated glass envelope was used. For the photocatalytic experiments 0.5 g dm<sup>-3</sup> TiO<sub>2</sub> was used. Thus, the efficiency of these processes could be compared at the same energy consumption.

### Analytical methods

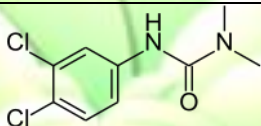
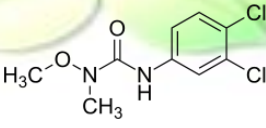
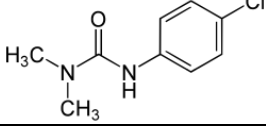
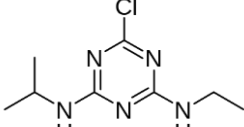
The values of the molar absorbance of the pesticides at 254 nm were determined according to the Lambert-Beer law, using Agilent 8453 spectrophotometer.

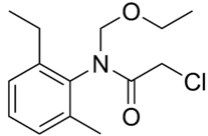
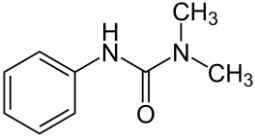
The concentration of ozone in the gas phase was determined using the same spectrophotometer in a flow cell (l = 1.00 cm) according to the Lambert-Beer law at 254 nm ( $\epsilon_{254\text{ nm}}=2952\text{ mol}^{-1}\text{dm}^3\text{s}^{-1}$ ) (Atkinson *et al.* 2001), and was found to be  $1.37 \times 10^{-5}\text{ mol dm}^{-3}$ , using oxygen.

Samples taken were analysed using an Agilent 1100 modular high performance liquid chromatograph (HPLC), equipped with UV-Vis detector. The separation of aromatic compounds was achieved on a LiChroCART® C-18 column. The eluent consisted of acetonitrile and water in case of diuron, linuron and atrazine (50:50, 50:50 and 60:40 % V/V respectively) and methanol and water in case of fenuron, monuron and acetochlor (60:40, 60:40 and 80:20 % V/V respectively) with a flow rate of 0.8 cm<sup>3</sup> min<sup>-1</sup>. The quantification wavelength for UV detection was 210 nm.

### RESULTS AND DISCUSSION

Table 1: The name, formula, molar absorption coefficient at 254 nm and the quantum yield of the photoinitiated transformation of investigated compounds

Generic name	IUPAC name	Formula	Molar absorbance (mol <sup>-1</sup> dm <sup>3</sup> cm <sup>-1</sup> )	Quantum yield
<b>Diuron</b>	3-(3,4-dichlorophenyl)-1,1-dimethylurea		16135	0.0115-0.019*
<b>Linuron</b>	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea		15612	0.036**
<b>Monuron</b>	3-(4-chlorophenyl)-1,1-dimethylurea		14256	0.05***
<b>Atrazine</b>	1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine		3791	0.04-0.06*

<b>Acetochlor</b>	2-Chloro- <i>N</i> -(ethoxymethyl)- <i>N</i> -(2-ethyl-6-thylphenyl)acetamide		676	not found
<b>Fenuron</b>	3-phenyl-1,1-dimethylurea		4909	0.005***

\*(Sanchez *et al.*)

\*\* (Benítez *et al.* 2006)

\*\*\* (Schöler 2006)

As Figure 2, Table 1. and Table 2. show, the direct ultraviolet photolysis is an effective method for the transformation of the target substances, except fenuron. The rate of transformation changed approximately in the order of the value of molar absorbance, and followed this order: atrazine  $\cong$  linuron  $\cong$  monuron > diuron  $\cong$  acetochlore >> fenuron. There was no significant difference among the rates of transformation of the chlorinated phenylurea pesticides, such as linuron and monuron having relatively high value of both molar absorbance and apparent quantum yield for their photoinitiated transformation. Although diuron has similar molar absorbance, but the value of the quantum yield is much lower than that of monuron and linuron. Opposing this, acetochlor has a relatively low molar absorbance, its rate of transformation was found to be similar to that of atrazine, which can be explained by the difference of values of their quantum yield. Among the selected target substances fenuron was the only one pesticide, which does not contain chlorine atom and it has the lowest value of both the quantum yield, and the initial rate of transformation, which was found to be one order of magnitude lower than that of chlorinated compounds.

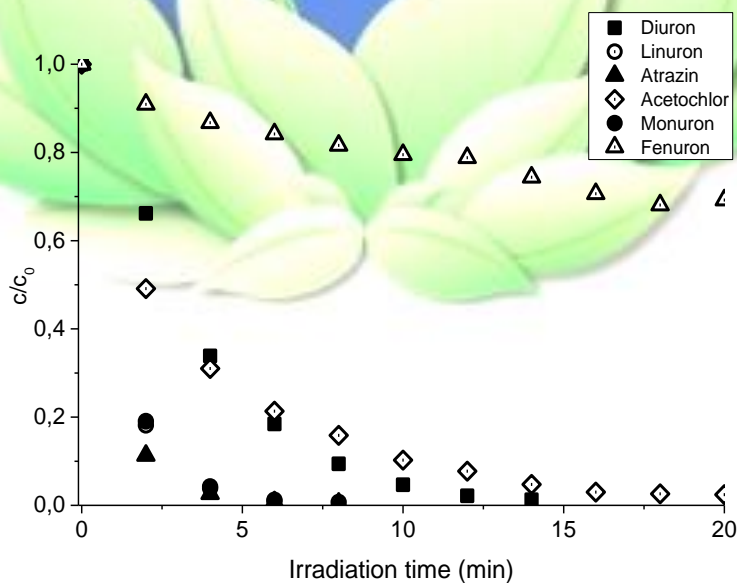


Figure 2: The concentration divided by the initial concentration of target substances versus time of treatment in the case of the ultraviolet photolysis



Table 2: The initial rate of transformation ( $r_0$  ( $\times 10^{-8}$  mol dm<sup>-3</sup> s<sup>-1</sup>)) and the half-time ( $t_{1/2}$  (min), the duration of treatment, when the half of the initial concentration is transformed)

Compound	UV		Ozone		UV and ozone		Heterogeneous photocatalysis	
	$r_0$	$t_{1/2}$	$r_0$	$t_{1/2}$	$r_0$	$t_{1/2}$	$r_0$	$t_{1/2}$
<b>Diuron</b>	10.3	3.0	0.7	50	17.5	1.5	3.2	8.3
<b>Linuron</b>	25.7	1.2	1.9	21	26.0	0.5	4.3	3.7
<b>Monuron</b>	25.1	1.2	2.0	30	29.6	0.5	4.3	5.8
<b>Atrazine</b>	27.4	1.1	0.5	148	14.6	2.0	2.6	12.5
<b>Acetochlor</b>	10.7	2.0	2.0	67	13.2	1.5	0.3	3.9
<b>Fenuron</b>	1.3	31.1	2.0	20	12.4	1.5	4.5	5.1

In the case of ozonation the ozone was photogenerated by the 185 nm vacuum ultraviolet light having relatively low intensity, thus the concentration of ozone in gas phase was quite low ( $1.37 \times 10^{-5}$  M). The rate of transformation approximately followed this order: fenuron  $\cong$  monuron  $\cong$  linuron  $\cong$  acetochlor > diuron  $\cong$  atrazine. Comparing the rates of transformation, they were found to be generally one order of magnitude lower than in the case of direct photolysis, except that of fenuron, which was found to be nearly two times higher. The decomposition of ozone in aqueous solutions is initiated by the hydroxide ion. At neutral pH and/or under acidic conditions, molecular ozone should be the dominant oxidant species. During the ozonation of chlorinated compounds the pH was neutral or acidic and strongly decreased, consequently, ozone reacts mainly as molecular ozone in these cases. Referring to the reaction mechanisms, molecular ozone can react with organic substrates either through cyclo-addition to unsaturated bonds or in electrophilic and nucleophilic reactions. The value of the reaction rate constants of aromatic compounds containing chlorine with molecular ozone is generally much lower than that of the non-chlorinated ones.

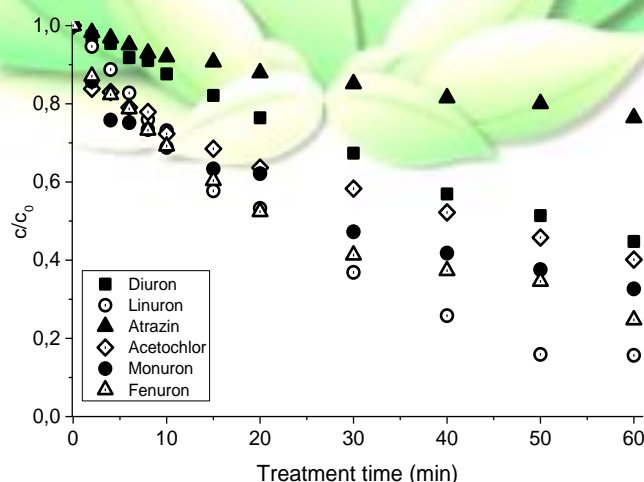


Figure 3: The concentration divided by the initial concentration of target substances versus time of treatment in the case of the ozonation

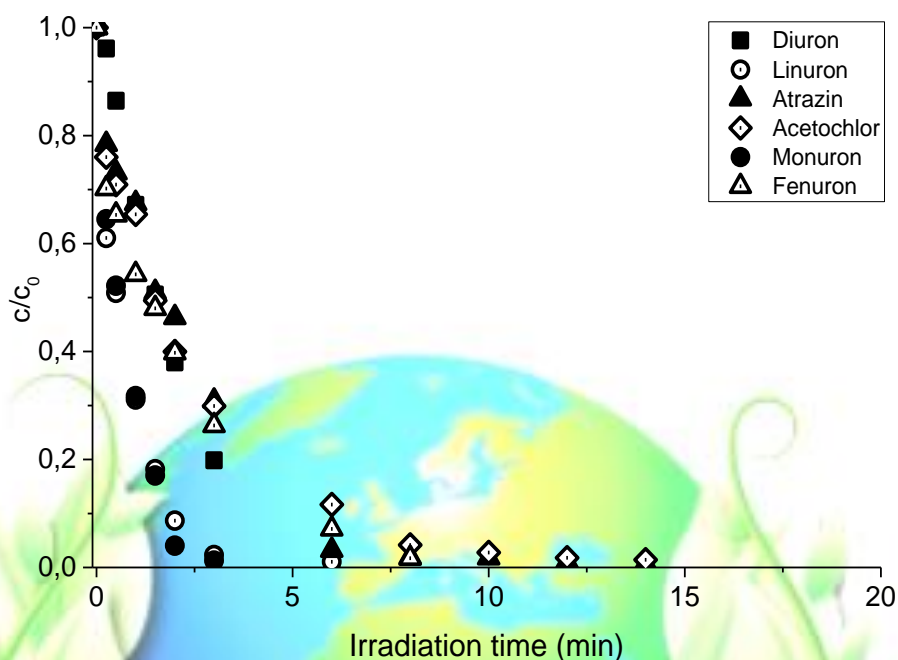


Figure 4: The concentration divided by the initial concentration of target substances versus time of treatment in the case of the combination of ultraviolet photolysis and ozonation

Using the combination of UV photolysis and ozonation the rate of transformation approximately followed this order: monuron  $\cong$  linuron  $>$  diuron  $>$  atrazine  $\cong$  acetochlor  $\cong$  fenuron. Linuron, monuron and atrazine had the highest rate of transformation determined in the case of UV photolysis and the addition of ozone to the UV irradiated solution did not cause significant change. This can be explained by that the relative contribution of the direct photolysis to the transformation remained dominant because of the high molar absorbance and quantum yield. At the same time, in the case of diuron and acetochlor the values of the rate of degradation exceeded those determined in the cases of UV photolysis.

Based on the values of the initial rate of decomposition it can be concluded that applying the combination of UV photolysis and ozonation a synergistic effect occurred in the case of fenuron. The addition of ozone, although in a relatively low concentration, caused one order of magnitude higher rate of transformation.

Both UV photolysis and ozonation are quite selective methods in the oxidative transformation of organic substances. Their combination via UV photolysis of ozone itself can produce reactive species, mainly hydroxyl radicals. Consequently, the combination of UV photolysis with ozonation generally results in a less selective and more effective method for the oxidative transformation of organic substances.

It has to be mentioned that the relative contribution of direct photolysis to the transformation probably remains high in the case of each substance having high molar absorbance and because of the relatively low concentration of ozone. Under the experimental conditions applied, the light absorption of ozone was negligible compared to that of pesticides.

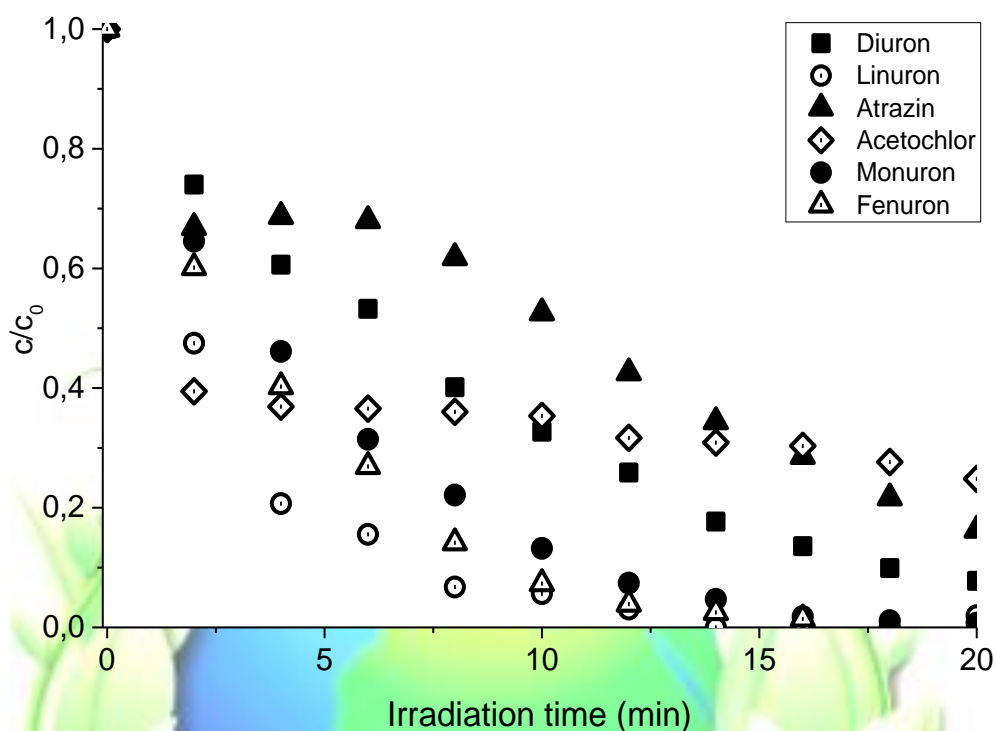


Figure 5: The concentration divided by the initial concentration of target substances versus time of treatment in the case of heterogeneous photocatalysis

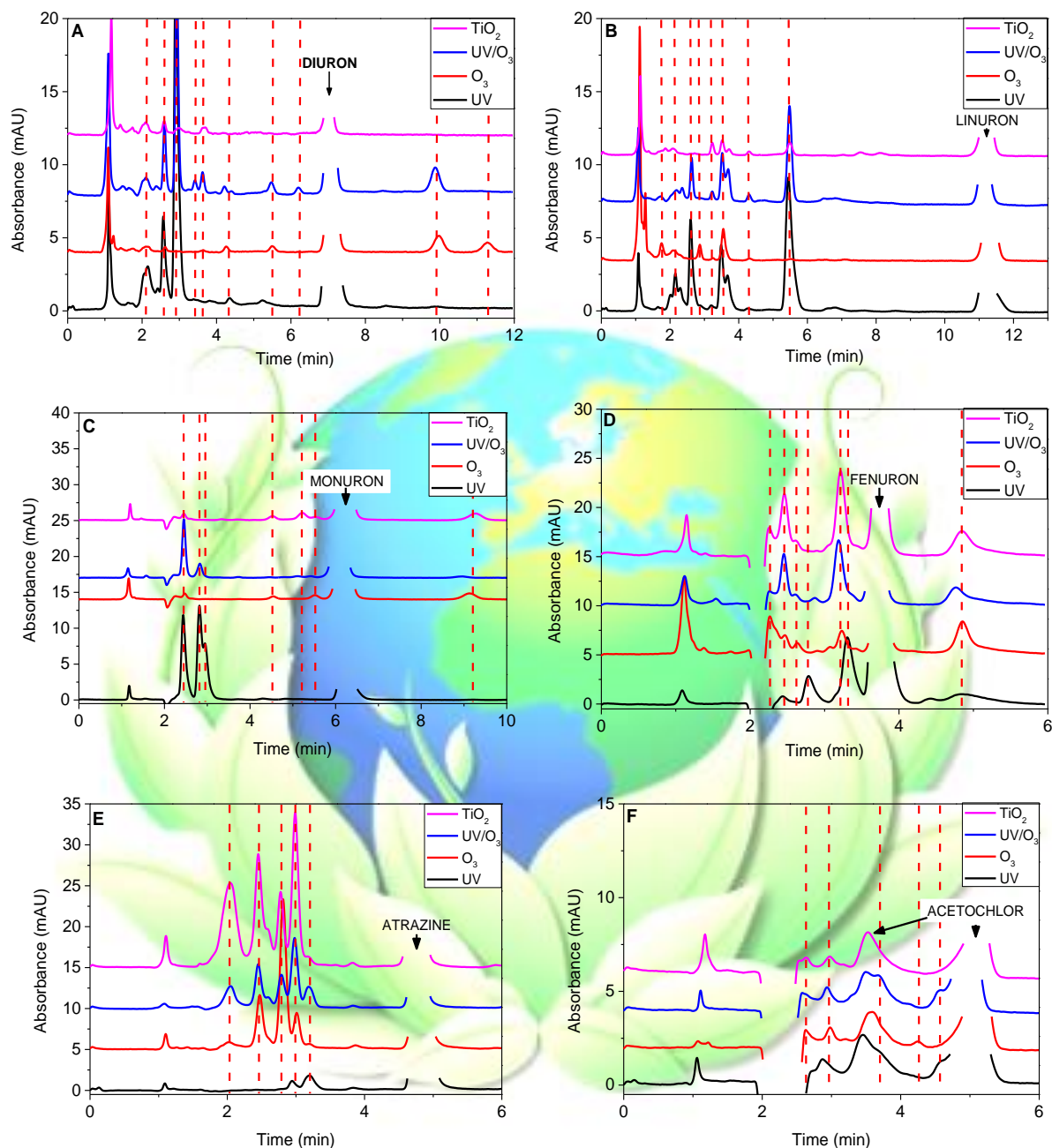
In the cases of application of heterogeneous photocatalysis the rate of transformation approximately followed this order: fenuron  $\cong$  linuron  $\cong$  monuron > diuron  $\cong$  atrazine >> acetochlor (Table 2 and Figure 5.). In the case of the heterogeneous photocatalysis the adsorption/desorption feature of the organic matter onto the titania has to be taken into account. On the other hand, the optimal rate of transformation strongly depends on the concentration of substance and the photocatalyst (Ahmed *et al.* 2011).

In the present work the values of the rates of transformation changed between  $0.3$  and  $4.5 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$  and were found to be lower than that determined in the case of UV photolysis and its combination with ozonation, but highly exceeded that determined in the case of ozonation.

### The effect of the advanced oxidation processes on the evolution of by-products

In the next part of the study we compared the methods by the forming by-products as different methods may yield different metabolites. The comparison of the chromatograms, which belongs to the treatment time when the initial concentration decreased to about 50 %, proved that the quality and quantity of intermediates formed is determined by the oxidation process most likely because of the different reaction ways of their formation.







**Figure 6:** Chromatograms, at about 50 % of initial compound transformed: A: diuron, B: linuron, C: monuron, D: fenuron, E: atrazine, F: acetochlor

## CONCLUSIONS

In this study six different pesticides were treated using advanced oxidation processes. The efficiency of methods was compared according to the initial rates of transformation determined. The initial rate of transformation of chlorinated compounds changed between 10.3 and 27.4 in

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the case of UV photolysis, 0.5 and 2.0 in the case of ozonation, 13.2 and 29.6 in the case of combination of UV photolysis with ozonation and  $0.3$  and  $4.3 \times 10^{-8}$  mol dm<sup>-3</sup> s<sup>-1</sup> in the case of heterogeneous photocatalysis. Of all processes, generally ozonation proved to be the least effective, while the combination of ozonation and photolysis can be considered the most effective process. Photolysis and heterogeneous photocatalysis are both effective for the transformation of the target molecules, although photolysis was more selective toward the chlorinated compounds. From the comparison of the chromatograms that can be concluded, the treatment process determines the forming products, because of the different mechanisms of the methods.

### ACKNOWLEDGEMENTS

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## **ROLE OF WOMEN AND MEN IN RURAL COMMUNITY DEVELOPMENT IN NORTH AFRICA IN RELATION WITH GLOBAL CHANGES**

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### **ABSTRACT**

Rural women and men have a unique ability to reduce poverty and malnutrition in the developing world. But gender inequality, particularly in the North Africa, is undermining their potential to become agents of change. The fight against rural poverty depends on increased efforts to redress gender imbalances and empower rural women. As a part of ongoing work to makes women and men equal partners in rural development is illustrated. The policy dialogue and strategic planning on gender equality in rural development, as well as promote operational knowledge and practical implementation tools.

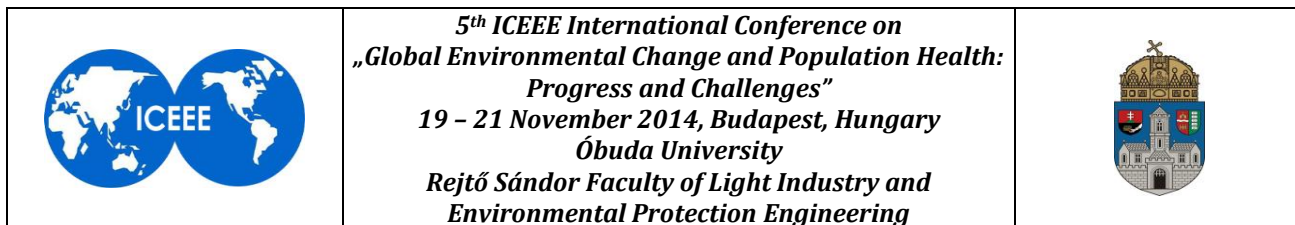
Women in the North Africa face daily challenges due to gender norms in society. These norms are rooted in culture and family structure and affect the way women are able to participate in their economy and public sphere. In an age an increasingly open economy, governments in the North Africa would benefit financially from incorporating more women into their workforce.

Currently, many educated women in developed countries in the North Africa, do not enter the workforce, even after obtaining tertiary degrees. While the individual country's infrastructures in the region differ, women face significantly higher discrimination in North Africa countries compared to any other global region. While women have recently increased efforts to improve gender equality through protests, domestic efforts in oppressive countries need the support of international organizations, such as the United Nations, to uproot the traditional gender norms of the region. Gender equality itself is not only a humanitarian issue; countries would increase economic output a position in the global economy. Through education reform, change in gender laws, and improved access to loans, women would be able to change the gender limitations that exist in the North Africa.

*Keywords: Population, Agricultural Labor, Education, National Income, Employment, Rural Community Development*

### **INTRODUCTION**

Climates, landscapes, and civilizations brings together a collection of studies on the history of complex interrelationships between humans and their environment. At a time when climate change, overpopulation, and scarcity of resources are increasingly affecting our ways of life, the lessons of the past provide multiple reference frames that are valuable for informing our future decisions and action plans. This topic highlights on a link between climate and humans, synoptic approaches to explore large-scale cultural patterns, regional studies for contextualizing cultural complexity, and environmental determinism and social theory.



### **Major challenges for agriculture and rural development**

The Near East and North Africa region is one of the world's driest and most water-scarce regions. In many areas in the region, demand for water already outstrips supply. Although the region contributes relatively little to greenhouse gas emissions, it will be among those hardest hit by climate change. Climate experts predict that, in future, the climate will become hotter, drier and more variable. Over the next 15 to 20 years, average temperatures are estimated to rise by at least 2°C, and possibly up to 4°C. Higher temperatures and reduced precipitation will increase the occurrence of drought, as is already evident in the western part of North Africa. Densely populated low-lying coastal areas in Egypt, Kuwait, Libya, Qatar, Tunisia and the United Arab Emirates are particularly at risk from rising sea levels and saltwater intrusion into agricultural land (IFAD, 2011).

Climate change threatens to increase food insecurity, diminish already scarce water resources and hinder economic growth. These pressures will increase the likelihood of conflict, migration, and poverty and inequality. By 2080, agricultural output could decrease by 40%. To some degree, the region has an advantage in that its inhabitants have been adapting to high temperatures and water scarcity for thousands of years, and have developed strategies for coping with these environmental constraints. The region is a repository of traditional and institutional knowledge that could be widely applied in efforts to address climate change across the globe (IFAD, 2011).

As elsewhere on the continent, poverty in Northern Africa is concentrated in rural areas. The percentage of rural poor people living below the national poverty line varies dramatically, from 6% in Tunisia to 90% in Somalia and 87% in the Sudan. Rural poor people constitute about one third of Tunisia's poor population and about three fourths of Somalia's poor. Beginning in the late 1980s, countries such as Egypt and Tunisia undertook structural adjustments with the aim of reducing poverty. Rural poverty in the region has its roots in limited availability of good arable land and water, and the impact of droughts and floods.

Political conflict has disrupted agriculture and aggravated poverty in countries such as Somalia and the Sudan. Among the obstacles to reducing rural poverty in Northern Africa are poor transport and social infrastructure, high rates of illiteracy (especially among women), weak local institutions, poor integration with the national economy, and the migration of rural youth to urban areas. In Northern African countries in general, rural poor people have very little political influence. This is especially true of women.

The rural population is poorly organized and often lives in isolated zones, beyond the reach of social safety nets and poverty programs. Government policies and investments in the region tend to favour urban over rural areas. Population ages 0-14 (% of total) in Middle East and North Africa was last measured at 30.82 in 2011, according to the World Bank. Population is based on the de facto definition of population. This page has the latest values, historical data, forecasts, charts, statistics, an economic calendar and news for Population ages 0-14 (% of total) in Middle East and North Africa.

### **Age dependency ratio - young (% of working-age population) in MENA**

Age dependency ratio; young (% of working-age population) in MENA was last measured at 47.81 in 2011, according to the World Bank (Table 1 and Figure 1). Age dependency ratio, young, is the ratio of younger dependents--people younger than 15- to the working-age population- those ages 15-64. Data are shown as the proportion of dependents / 100 working-age populations. This page has the latest values, historical data, forecasts, charts, statistics, an economic calendar and news for Age dependency ratio - young (% of working-age population) in MENA.

Table 1: World Bank Indicators - Middle East and North Africa - Population

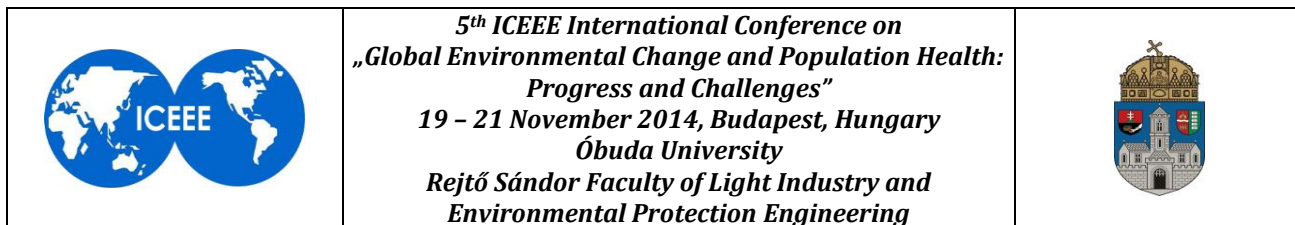
	Years			
	1990	2000	2010	
Birth rate; crude (per 1;000 people) in Middle East and North Africa	43.8	36.9	31.1	[+]
Death rate; crude (per 1;000 people) in Middle East and North Africa	7.6	5.7	5.3	[+]
Population ages 0-14 (% of total) in Middle East and North Africa	43.8	36.9	31.1	[+]
Population ages 15-64 (% of total) in Middle East and North Africa	52.8	58.9	64.3	[+]
Population ages 65 and above (% of total) in Middle East and North Africa	3.4	4.2	4.7	[+]
Age dependency ratio (% of working-age population) in Middle East and North Africa	89.8	70.7	57.2	[+]
Age dependency ratio; old (% of working-age population) in Middle East and North Africa	6.5	7.2	7.3	[+]
Age dependency ratio; young (% of working-age population) in Middle East and North Africa	82.8	62.6	48.3	[+]
Population growth (annual %) in Middle East and North Africa	3.4	1.9	1.7	[+]
Population; total in Middle East and North Africa	227411305.9	277413760.0	331017162.0	[+]



Figure 1: World Bank Indicators - Middle East and North Africa – Population

The Economies North Africa and Middle East (MENA) situated at important crossroads between Africa, Asia, Europe, the countries of the Middle East and North Africa (MENA) form one of the largest groups of developing countries in the world economy. Also includes a number of oil-rich

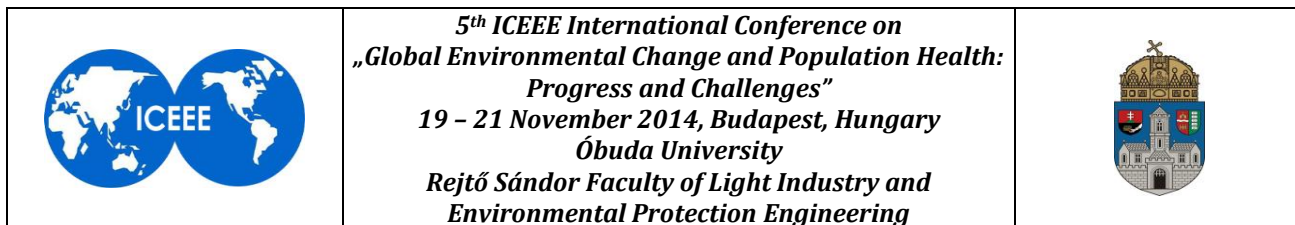




countries such as Saudi Arabia, Kuwait, Algeria, Libya it comprises mainly Middle-income developing countries whose / capita income levels and economic performance, including in regard to indicators of social welfare, fall appreciably below the mean levels of countries in other regions at similar rungs of the development ladder globally (Dean, 1997). Dean (1997) mentioned that moreover the circumstances and lacklustre economic performance of the populous low-to-lower-middle-income countries in Middle East and North Africa. Iraq, Syria, and Yemen in the Middle East, and Egypt, Morocco, and Sudan in North Africa are the subject of considerable international concern, including as measured by large shipments of international food aid to some prominent Middle East and North Africa (MENA) countries. In recent years, the NENA region has witnessed a series of socio-political events and economic reforms that have affected economic performance in various ways. On the positive side, the structural transformations initiated in the 1990s, albeit slowly, have resulted in a significant reduction in state involvement in previously owned enterprises, which in the longer term is expected to lead to rationalization. Furthermore, as a result of the World Trade Organization (WTO) membership, countries such as Egypt, Jordan, Morocco and Tunisia have seen considerable economic benefits from trade liberalization and more openness to the private sector. The surge in oil prices in the past few years has generated large surpluses for the oil-producing developing economies of Algeria and Libya. The direction of the development equation in those countries will depend on how the surpluses are invested. However, despite sizeable improvements, The Near East and North Africa (NENA) region Algeria, Djibouti, Egypt, Gaza and the West Bank, Jordan, Lebanon, Morocco, Somalia, Sudan, Syria, Tunisia, Turkey and Yemen.<sup>2</sup> The total population in the NENA region is estimated at 318 million (2005). The rural population in the sub-region is estimated at 151 million, representing close to 48% of the total population (2004). The LDCs in the region, such as Somalia, Sudan and Yemen, have the highest proportion of rural population, ranging between 60 and 74%. Lebanon's rural population represents only about 12% of its total population. During the period 1990–2004, the rural population of NENA grew on average at 1.55% annually. Variations among countries in the region depend, inter alia, on the endowment and distribution of natural resources, the presence and efficiency of social services, employment opportunities in the cities and the security situation (Beuchelt, 2006). The surge in oil prices in the past few years has generated large surpluses for the oil-producing developing economies of Algeria and Libya. The direction of the development equation in those countries will depend on how the surpluses are invested. However, despite sizeable improvements, trade protection structures, particularly for agricultural products, remain comparatively high in almost all NENA countries. On the negative side, the region suffers from a number of persisting structural problems that slow down the pace of economic growth and the capacity to reduce rural poverty Beuchelt (2006). Demographic growth, with its high rates by world standards—remains a constraint, as the labour market is unable to absorb the number of newcomers seeking employment every year. The imbalance between employment opportunities and new employment seekers, especially in the rural sector, represents a growing challenge to rural poverty reduction. Migration and remittances especially relating to intra-regional migration (e.g. Yemeni and Egyptian workers in the Gulf States)—fluctuate significantly with oil prices and with the incidence of regional conflict (Handoussa, 2006).

### **Trends in Agricultural Labor by Sex in the Middle East and North Africa**

Abdelali-Martini (2011) despited the importance of agricultural activities that are not represented in national statistics due to their unpaid and informal characteristics, the female share of the agricultural labor force in the Middle East and North Africa has greatly increased, from 34 % during the period 1990- 1995 to almost 45% in 2011, while men's contribution has

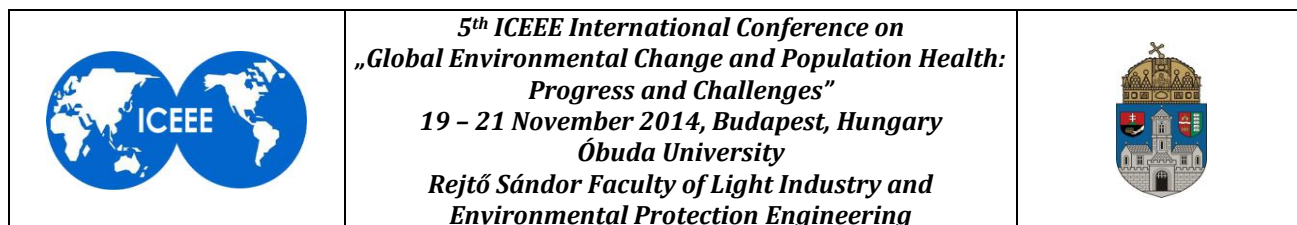


considerably decreased from 66 to 55% during the same period. The trend remains almost the same whether we include or remove the figures of agricultural labor of the Gulf States together with other Middle East and North Africa countries. There are disparities between the countries, and the trend is more important in countries relying greatly on agriculture such as Algeria, Jordan, Syria, Libya, Palestine, and Egypt. Women employed in agriculture (accounting for two thirds of all employed women in developing countries) work heavily as unpaid family labor in crop and livestock production, including post-harvest activities such as tomato paste, milk and other animal products' processing such as wool. They are responsible for storing and processing many products agrobiodiversity products (Abdelali-Martini et al., 2008) which are mainly marketed by men. It was found that old women handle marketing themselves for tomato paste in Syria and for some dairy products in Jordan (Abdelali-Martini and El-Jawhary, 2009; Abdelali-Martini and Hamed, 2009).

A research by Khelifi-Touhami et al. (2004b) indicated clear gendered roles of activities in production, and recommended the development of enterprises through the establishment of village cooperatives that will reduce the costs of processing and facilitate the marketing, but has not explored the differential empowerment impacts on women, men and children. Whether performing paid or unpaid work, classified as informal due to their casual and seasonal characteristic, women constitute a vulnerable group whose employment lack safety and decent work conditions. There is also segregation in the type of activities women are "allowed" to perform as a result of the social norms. Their activities also include collecting fuel and water in difficult conditions especially in mountainous areas of Algeria (Abdelali-Martini and Ait-Hamlet, 2005; Chouaki et al., 2010), Yemen, and Morocco. Household's chores are not considered as economic activities, but remain essential for households' livelihoods and wellbeing. Agricultural laborers include women working as wage labor in crop and livestock production as well as in production. Most crop production operations and tasks are performed by women manually, whereas men keep mechanized work that is less constraining, less time consuming and better paid. Many girls are contributing to crop agricultural activities including herding close to household's boundaries. Women perform home-based work for milk, wool and other postharvest processing activities for their own consumption and for the market, and to a limited extent some trading and marketing. However, gender differences in agricultural labor force participation rates, segregation in operations and tasks, safety and work conditions, children's employment, and wage gaps remain the main issues of agricultural labor markets. Furthermore, despite that in many of the MENA countries males are migrating away from agriculture, leaving the most difficult agricultural activities in women's hands, women's management of households and natural resources remain limited mainly due to the impacts of prevailing patriarchal system. Gender stereotypes indicate specific types of work for women under specific conditions, preventing them from entering other types of work traditionally reserved for men. Temporary casual workers are mostly women performing the majority of operations and tasks, and permanent workers are men employed for irrigation, mechanized work, as farm guards or managers. Women are responsible for the main crops produced in the region. As family labor, men and women share many activities, but women are entirely responsible for home gardens, and for household's livestock rearing (Abdelali-Martini, 2011). Main features of agricultural labor in the MENA region and gender gaps. A feminization of agricultural labor.

The number of wage workers in the region, and more particularly women's agricultural labor is rapidly growing. The region is characterized by migrant workers of both sexes, with a predominance of male migrants to neighboring countries seeking better paid jobs in non-agricultural sectors. Both smallholder farmers and landless rural households are increasingly relying on wage labor from their households to respond to additional households' needs. Since





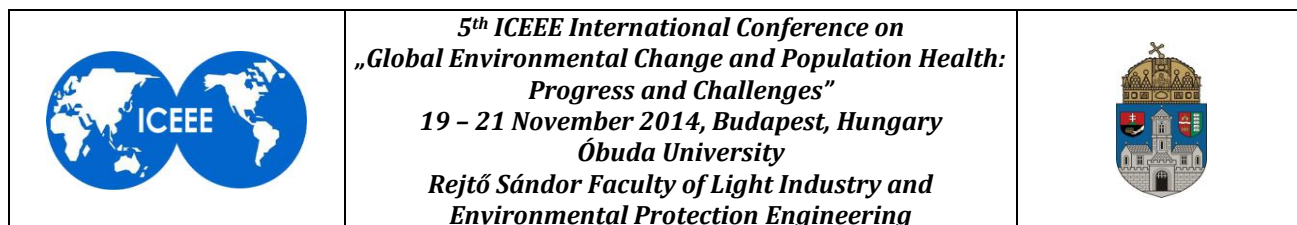
the 1980s women’s labor contribution to the total production was reported as much higher than that of men (Rassam, 1984; Rassam et al., 1988).

In contrast to 5 studies referring to the “feminization of agriculture” (Momsen, 1987; Boserup 1970; 1993) where agriculture is left to the management of women after males’ migration, research conducted in Syria (Abdelali-Martini et al., 2003a) on the “Feminization of Agricultural Labor” indicated an important increase in women’s agricultural labor in recent years resulting in a new division of labor due to globalization, population increase, and agricultural intensification impacting the differential gender roles as a response to labor market supply and demand. The case study underlines that “the feminization of agricultural labor” depicts the phenomenon that indicated an important increase in women’s agricultural labor in recent years resulting in a new division of labor due to globalization, population increase, and agricultural intensification impacting the differential gender roles as a response to labor market supply and demand. The case study underlines that “the feminization of agricultural labor” depicts the phenomenon that women are providing the bulk of agricultural labor but are not involved in farm management because male heads of households remain on farm, and other males work off farm in urban areas or migrate to neighbouring countries for work. In Yemen, previous studies indicated that women are increasingly important in the agricultural labor force, thus working more as wage labor in the Tihamah than in the highlands (Tutwiler, 1990).

Similar trends of the feminization of agricultural labor force were mentioned by Bouzidi et al. (2010) in some MENA countries. In Syria, Tunisia and Egypt, the majority of wage labor are single (95% and 82% respectively), whereas in Morocco, 57% of women laborers were married. However, this type of research remains limited for other MENA countries, mainly because statistics are need to back up micro-level studies. Research conducted in crop-livestock systems, areas with supplemental irrigation, and areas with full irrigation in Syria indicated that the household male and female labor force, aged between 12 and 65 years, contributes to household income through participation in crop management, livestock husbandry and paid work in agricultural and non-agricultural off-farm activities (Khelifi-Touhami, 2004a). Migration from agriculture. There is an increase in male migration out of the rural areas and agriculture in the MENA countries. Women are involved, to a less extent, in migration in Middle East countries such as Syria, Jordan, Lebanon and Egypt. They are always accompanied with their male relatives, and not submitted to any formal contracting or migration law (Abdelali-Martini et al., 2011a), but are making important contributions to household income and poverty reduction. In the few female-headed households found in the study area, women had more margins for decision-making. Migration of women agricultural laborers from Morocco to Spain is a recent phenomenon organized between the governments of Spain and Morocco under specific rules and laws for migration and work. The Syrian case study (Abdelali-Martini et al., 2011a) indicates that male migration negatively affects the education of male and female children, but particularly boys. Males’ absence from rural households resulted in a drop in the number of children attending schools. Women reported that with absence of fathers (child’s role model), it was difficult to manage children, and they were concerned with poor school attendance and performance. This could be a long-term negative impact of migration. Importance of women’s wage labor in agriculture and differential gender roles. As in many developing societies, Arab society does not acknowledge the true extent of women’s participation in social and economic activities and in the production of the components of human well-being, and it does not reward women adequately for such participation (UNDP, 2005).

Agro-industry and rural industrialization has increased the possibilities for women to access cash income through self-employment or to set up rural enterprises, and wage employment allows women to get out of the relative isolation of the home or their small rural communities





and gain self-esteem and confidence (UN, 2005). Agro-industry and rural industrialization has increased the possibilities for women to access cash income through self-employment or to set up rural enterprises, and wage employment allows women to get out of the relative isolation of the home or their small rural communities and gain self-esteem and confidence (UN, 2005). Wage labor in agriculture is rapidly growing in MENA as a result of rapid population growth, a limited natural base, and low wages in agriculture that are drawing men out of the sector and drawing more women into it, mainly because women have less flexibility than men for moving far from their households. Women are mainly concentrated in the production of high intensive labor crops such as legumes and vegetables where most activities are manual except plowing and sometimes planting, and men are performing mechanized activities (plowing, combine harvesting, planting, etc.) that require limited number of men during specific times, allowing flexibility to work outside the agricultural sector (Abdelali-Martini, 2008; 2011a).

Growth of agricultural labor in MENA was mainly driven by high population growth in areas where drought and poverty are the most acute, and the introduction of new crops for agroindustry such as sugar beet, potatoes and olives in Morocco and Tunisia. This has resulted in an emergence of the use of agricultural labor under specific arrangements where men and women labor contractors lead and supervise large numbers of women. Regarding market institutions, Elson (1999) indicates that the participation in labor markets does not automatically empower women mainly due to the absence of institutional change and labor market regulation.

In MENA, working towards achieving both efficiency goals and gender equality lies in the elaboration of efficient policies, but also in monitoring the implementation of these policies in combination with awareness and capacity building for women regarding their rights and obligations, and raising their bargaining power on wages and work conditions. Control over resources.

In the MENA region, like in other parts of the developing world, strengthening women's access to and control over productive resources/assets such as land, capital, knowledge, information and technologies remain important factors of an enabling environment for women's empowerment. Though the complexity of prevailing social system in MENA makes this more difficult, especially when women remain illiterate with no means to face the external world and women's behaviours are still bound by social ties.

Women who have assets are obliged to abandon them for the benefit of their brothers even if not in complete agreement because brothers constitute their fall-back positions (Agarwal, 1997). Precarious quality of education in rural areas. Literacy has been clearly recognized by The Fourth World Conference on Women, held in Beijing in 1995, as to have the capacity to empower women's participation in decision-making in society as well as to improve families' well-being (United Nations, 1995;1996). Also well established in the literature, education improves individuals' wellbeing and economic and social development. The improvement of education in urban areas of MENA is very encouraging and female's enrollment rates are sometimes bypassing those of males at all levels of the education system.

The Arab Human Development Report (UNDP, 2005) indicates that while literacy rates are not high in comparison with other developing countries, enrollments in high school and universities are very impressive. In 1997 female and male literacy rates of 46 and 71% in Arab countries were marginally better than 49 and 65% in Africa. While this remains true in urban areas, education is limited in rural areas where infrastructure is lacking, and schools availability is still limited especially beyond the primary levels in poor and small villages such as in the mountains of Ighil Ali in Algeria (Chouaki et al., 2010).

As indicated by Moghadam (2005), women have more options in an urban setting, whereas in rural areas, patriarchal family arrangements limit their options. Furthermore, the complexity of the subject and the diversity of options in the region suggest that a variety of socio-economic, cultural and political factors interact and generate these situations. The most challenging injustice is that many girls are excluded from education in rural areas, because of the lack of primary schools in their villages. This is particularly alarming in view of the labor market challenges of the new era of the 21st century. At the primary school level, one classroom is often home for students of different educational levels, an evidence that results in poor quality of education, which will be reflected on the economic and development growth of these populations and countries (Abdelali-Martini, 2011a).

### **EDUCATION: SOCIAL RIGHT AND A DEVELOPMENT IMPERATIVE CONTRIBUTES DIRECTLY TO THE GROWTH OF NATIONAL INCOME**

The productive capacities of the labor force. A recent study of 19 developing countries, including Egypt, Jordan, and Tunisia, concluded that a country's long-term economic growth increases by 3.7% for every year the adult population's average level of schooling rises. Thus, education is a key strategy for reducing poverty, especially in the NA region, where poverty is not as deep as in other developing regions.

According to the UN Population Fund, countries that have made social investments in health, family planning, and education have slower population growth and faster economic growth than countries that have not made such investments. In the increasingly open global economy, countries with high rates of illiteracy and gender gaps in educational attainment tend to be less competitive, because foreign investors seek labor that is skilled as well as inexpensive. Various global trends pose special challenges to women who are illiterate or have limited education. Economies' export orientation and the growing importance of small and medium-sized enterprises create opportunities for women, but women need the appropriate education and training to take full advantage of these opportunities.

access to Education is a key part of strategies to improve individuals' well-being and societies' economic and social development. In the MENA (countries and territories included in the MENA as defined here are listed in Table 2 and Figure 2), access to education has improved dramatically over the past few decades, and there have been a number of encouraging trends in girls' and women's education (Figure 3).

Primary school enrolment is high or universal in most MENA countries, and gender gaps in secondary school enrolments have already disappeared in several countries. Women in MENA countries are also more likely to enroll in universities than they were in the past.

Table 2 : Selected Socioeconomic Indicators in North Africa

Number of people ages 15 to 24 who are illiterate (thousands), 2000	Population in % of ages 15 to 24 who are illiterate (thousands), 2000		Number of people over age 15 who are illiterate (thousands), 2000		Population in % of % over age 15 who are illiterate (thousands), 2000			
	Male	Female	Male	Female	Male	Female	Male	Female
227	530	7	16	2,360	4,211	24	43	Algeria
1,678	2,500	24	37	7,374	12,253	33	56	Egypt
1	43	0.5	7	168	533	9	32	Libya

750	1,265	24	42	3,702	6,286	38	64	Morocco
27	106	3	11	621	1,307	19	39	Tunisia
296	655	4	9	3,819	6,696	17	31	Iran
1	9	0.5	4	155	246	20	38	Oman

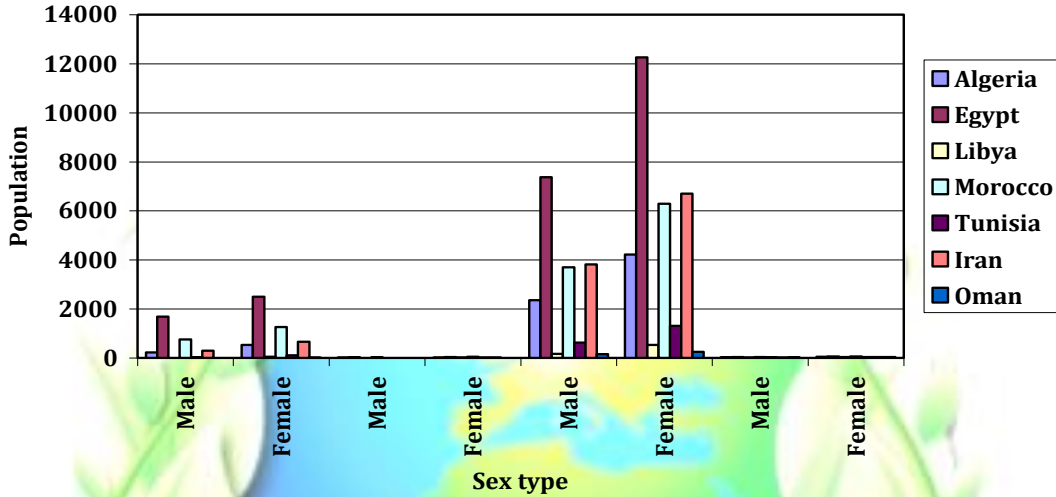


Figure 2: Selected Socioeconomic Indicators in North Africa  
Sources: UNESCO Institute for Statistics, "Literacy Statistics" ([www.uis.unesco.org](http://www.uis.unesco.org)), United Nations Development Programmed, Human Development 2002; UN Statistics Division.

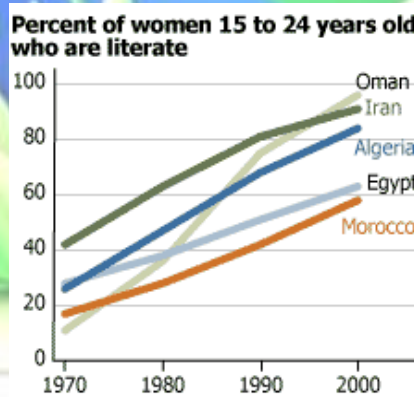




Figure 3: Literacy Rates among Young Women in Selected Countries, 1970-2000  
Source: United Nations Educational, Scientific and Cultural Organization (UNESCO) Institute for Statistics, "Literacy Statistics" ([www.uis.unesco.org](http://www.uis.unesco.org), accessed March 11, 2003).

**CULTURAL AND ECONOMIC FACTORS THAT REINFORCE THE GENDER GAP**

MENA countries generally have lower levels of women's education and labor force participation than other regions with similar income levels. The interaction between the region's economic structure and its conservative culture, in which traditional gender roles are strongly enforced, is largely responsible. Men in the MENA region are more likely to have direct access to wage



	<p style="text-align: center;"><i>5<sup>th</sup> ICEEE International Conference on „Global Environmental Change and Population Health: Progress and Challenges“ 19 – 21 November 2014, Budapest, Hungary Óbuda University Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering</i></p>	
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employment and control over wealth, while women are largely economically dependent upon male family members.

Gender discrimination in the MENA region is sometimes codified in law, frequently in family laws or civil codes. In many countries in the region, women must obtain permission from a male relative, usually a husband or father.

### **Education's Effects on Reproductive Choices and Employment**

Education helps women take advantage of opportunities that could benefit them and their families, preparing women for the labor force and helping them understand their legal and reproductive rights.

### **Employment**

As women's educational attainment in MENA countries has increased, more women have moved into the job market. But women's participation in the labor force is still low: Only 20% of women ages 15 and older in MENA countries are in the labor force the lowest level of any world region. The highest levels of native female labor force participation in MENA countries are found in Lebanon, Morocco, Turkey, and Yemen, where women constitute more than 25% of the labor force. But those rates are lower than rates found outside the region. Women who live in countries with a large agricultural sector, such as Egypt, tend to work mainly in that sector, although some MENA countries have been more successful in getting women into non-agricultural occupations. Morocco, Tunisia, for example, have been able to engage women in the countries' export manufacturing sectors. Most of the MENA women who work outside the agricultural sector are college-educated professionals employed mainly in government.

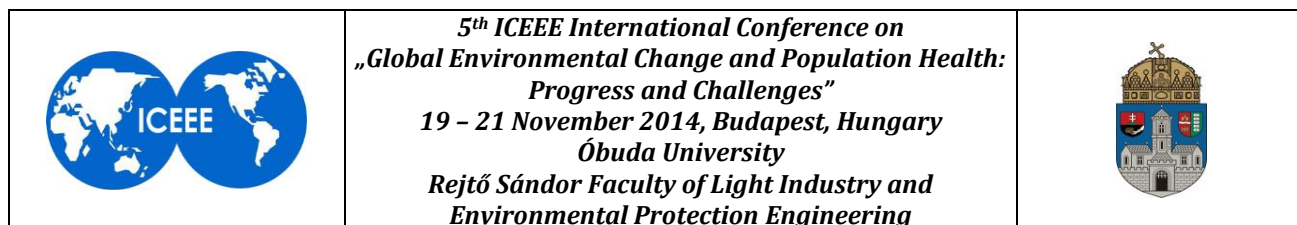
### **Ongoing Concerns**

MENA countries have made significant strides in making education available over the past few decades, but challenges remain. Access to education has improved, and the illiteracy rate among the region's young adults (people ages 15 to 24) is half that of the adult population (people ages 15 and up). More women are now pursuing higher education, reflecting their ability to graduate from secondary school. But illiteracy remains high in some countries, there are still wide gender gaps in parts of the region, and the quality of the education is a major concern throughout the region.

### **CONCLUSION**

Rural policy has seen significant developments in the past two decades. The key elements of these shifts have been:

As we work toward meeting the move toward developing new and better global targets, there are a number of areas that must be observed if we are to understand in greater depth the opportunities and constraints in rural women's lives, and to monitor progress towards rural women's empowerment and gender equality appropriately and effectively. These indicators could include, but are not limited to average annual dietary intake per capita access to employment, including the informal sector and agricultural self-employment; access to productive assets and financial services (e.g. land, credit, extension services, agricultural technology and education); access to social security and safety nets. Decentralization of policy administration and, within limits, policy design to those levels; Increase use of partnerships



between public, private and voluntary sectors in the development and implementation of local and regional policies.

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## **EFFECT OF PLANTED FORESTS ON CARBON CYCLE AND GROUNDWATER LEVEL IN JÁSZSÁG, HUNGARY**

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### **ABSTRACT**

During the last decade, - with the support of European Union - there was a significant increase in the planted forest area in Hungary. Afforestation was carried out mainly in the lowland, on arable land and grazing areas possessing less agricultural potential. Further large areas are expected to be forested in the future (~ 700,000 ha).

Inside the Jászság region (Great Hungarian Plain) the processes related to the groundwater depression under forested stands (poplar, black locust and common oak) in comparison to adjacent control plots (vegetation: cropland, pasture) were investigated. At three sampling sites (Jászfelsőszentgyörgy, Jászfákóhalma Jászberény) the differences in water level between the forest and the control areas were examined by the analysis of time-series data from seven groundwater monitoring well stations. In addition, based on the results of field and laboratory tests, a database were produced including soil and water chemical properties, physical properties, and biological parameters of the forests.

In the top 1 m soil organic carbon content was greater under the forest stands than under control arable land/grassland. CaCO<sub>3</sub> content of the soil + subsoil showed opposite tendency. The assumptions were clearly supported by the observed groundwater levels at Jászfákóhalma. The groundwater level curves intersect each other twice a year systematically. Water table is higher under the cropland at the growing season, and it is higher under the forest in the rest period

**Keywords:** *afforestation / water fluctuation / calcium carbonate / organic carbon*

### **INTRODUCTION**

Significant afforestation is planned in Hungary (700 000 ha), and this plan is also supported by the EU (Andrasevits et al., 2005). The areas available for afforestation are generally less profitable for field crop production. Based on the analysis of the soil types of the formerly forested areas, Führer and Járó (2005) stated that the Great Hungarian Plain can be the most important region for afforestation. However the hydrological and climatic role of the forest is most critical in the Great Hungarian Plain. From a hydrological viewpoint, two basic situations are encountered:

- When the water table is deeper than the root zone (these are very critical sites for afforestation), and



- when groundwater can be a source for transpiration. In the latter situation, groundwater uptake of a forest is the most frequent theme of this research.

In the shallow water table areas, forest vegetation can change the water balance of the soil (Nosetto et al., 2007). Forest evapotranspiration (sum of transpiration and interception) is generally higher than the evapotranspiration of neighboring grasslands, because of the increased LAI (leaf area index) and root depth of the woody vegetation (Calder, 1998; Nosetto et al., 2005). These properties of a forest are especially true in the Great Plain with a subhumid climate, where the precipitation is less than the water demand of woody vegetation, so trees can survive dry periods only if they use groundwater resources as well (Ijjász, 1939; Magyar, 1961).

Móricz et al. (2012) compared the water balance of different land uses in Nyírség (Northeast part of the Great Hungarian Plain), and found that a common oak forest has approximately 30% more evapotranspiration (758 mm a<sup>-1</sup>) than a neighboring fallow land (623 mm a<sup>-1</sup>). The difference is more significant (3 fold) in groundwater use of different vegetation types (oak: 243 mm a<sup>-1</sup>, fallow: 85 mm a<sup>-1</sup>). The groundwater consumption was close to 60% of the total transpiration in the oak forest and approximately 30% on the fallow plot. Groundwater consumption was approximately 40% less in the wetter vegetation period of 2008 than in the drier growing season of 2007, despite the fact that the groundwater level was deeper during the drier summer. Thus, during the drier period both vegetation covers relied considerably on the available groundwater resources.

Szilágyi et al. (2012) analyzed the evapotranspiration (determined by linear transformation of the MODIS daytime land surface temperature) in the Danube-Tisza Sand Plateau of the Great Hungarian Plain. On some locations annual ET is estimated to be larger (620 mm a<sup>-1</sup>) than the mean annual precipitation (550 mm a<sup>-1</sup>). These groundwater discharge areas in many locations overlap with forest cover. This negative water balance can be maintained if forests create a local depression in the water table so as to induce groundwater flow directed toward them.

Beyond hydrological impact of trees, inorganic forms of carbon in the soil and groundwater (CaCO<sub>3</sub>, Ca<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>), and Total Organic Carbon content of the soil (TOC) have also been studied. Amount of CaCO<sub>3</sub> in the topsoil decreased due to the acidifying effect of root acids released by the tree roots, or rather the result of infiltration water dissolving CO<sub>2</sub> from soil air (forming H<sub>2</sub>CO<sub>3</sub>). CaCO<sub>3</sub> has low water solubility, but the slightly acidic percolating rainwater solution is able to dissolve some of CaCO<sub>3</sub> and upon drying to precipitate it, and as a result, it migrates toward the deeper soil layers. As a result of higher amount of rainfall and/or snowmelt, CaCO<sub>3</sub> has been leached down, and – directed by the soil stratification, the morphology of the root zone and the groundwater fluctuation zone - an accumulation layer has been evolved. CaCO<sub>3</sub>, precipitated from groundwater, also contributes to CaCO<sub>3</sub> accumulation in the (sub)soil. Correlation analysis has been used for defining the relationships between CaCO<sub>3</sub> content of the soil and Ca<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> content of groundwater. Quantitative differences have been investigated as regards the Total Organic Carbon content of woody and herbaceous vegetation (control). Furthermore, depth profile of Total Organic Carbon and the effect of soil texture have also been studied.

This paper is a preliminary study of a detailed investigation on the effect of afforestation on the water and carbon cycle in the Great Hungarian Plain. The aim of the research is to describe the complex processes based on the systematic study of all affecting factors: climatic water balance, water table depth and groundwater ion distribution, (sub)-soil layering and forms of organic and inorganic carbon (in the frame of the OTKA NN 79835 project).

## MATERIALS AND METHODS

We took care to avoid any edge effect interference in our sampling design, thus the minimum distance of boreholes/monitoring wells were 50 meters from the border of the forested area in both directions.

The maximum depth of the boreholes was 11 m, limited by the augering equipment. Soil sampling was done to the depth of groundwater table + 1 meter. The samples were taken at every 20 cm increment from the topsoil (0-1 m), and at every 0.5 m increment below 1 m, in order to describe accurately the processes relevant for our hypothesis.

Water samples were taken with hand vacuum pump and samples were stored at cool conditions until laboratory analysis. (Tab. 1)

*Table 1. List of parameters and measurement methods used in this study  
Altogether 7 plots, 3 combinations of forested and nearby non-forested land were sampled in the  
above mentioned project in Jászszág region.*

	Parameter	Measurement method	
		Field measurement	Laboratory measurement
<b>1</b>	<b>Climatic factors</b>		
A	Precipitation	Measurement with meteorological stations (only at selected monitoring wells)	
B	Wind speed		
C	Relative humidity		
D	Solar radiation		
E	Air temperature		
<b>2</b>	<b>Hydrogeological factors</b>		
A	Geomorphology		
	Shallow or deep water table level	Water table level found during boring and stabilized after boring	
	Temporal water table level fluctuation (short-term, long-term)	Continuous water table level monitoring at 7 sample sites – time-series of water table level data	
B	Lithology		Determination of soil particle size distribution with pipette (only at monitoring wells), hy1 (hygroscopicity)
C	Groundwater chemical composition	EC, pH (from all groundwater samples)	concentrations of main anions and cations (only at monitoring wells)
<b>3</b>	<b>Biological factors</b>		
A	Evapotranspiration capacity: high e.g. forest, low e.g. grassland	Forest assessment (tree height measurement, trunk circumference measurement (at the height of 130 cm) – biomass calculation (based on wood capacity-curve,	



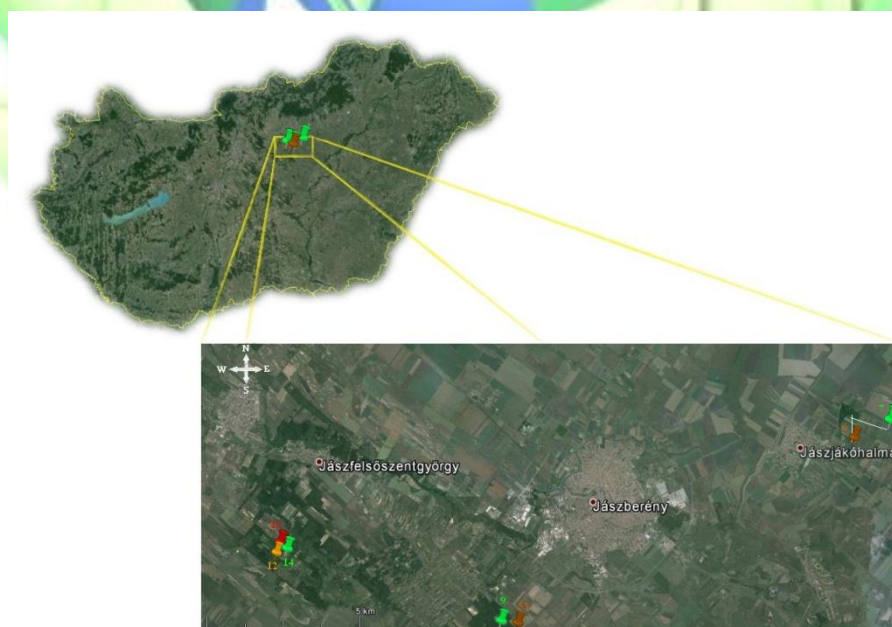
		where tree species, tree height and trunk circumference are known)	
<b>4</b>	<b>Soil factors</b>		
B	pH	With pH and EC electrodes in 1: 2.5 soil:water suspension	
E	CaCO <sub>3</sub>		Schreiber calcimeter
F	Organic C		Turin method

This study presents data of 4 pair of forest and control plots (7 sample points) were compared near to three different settlements of the Jászság region (Tab. 2).

The area has a flat topography. The geological basis of the research area is aelic-fluvial sediments, mostly sand and silt.

*Table 2. Coordinates and land use of the investigated sample plots.*

Sample area	Number of the sample point	Land use	WGS'84 coordinates
Jászfelsőszentgyörgy	12	Poplar	47° 28' 40.5" N, 19° 46' 20.8" E
	13	Common oak	47° 28' 50.7" N, 19° 46' 25.7" E
	14	Control grassland	47° 28' 45.0 " N, 19° 46' 37.4" E
Jászberény	9	Control cropland	47° 27' 44.3" N, 19° 52' 11.6" E
	53	Black locust	47° 27' 44.8" N, 19° 52' 39.1" E
Jászfákóhalma	6	Black locust	47° 31' 45.5 " N, 20° 00' 56.3" E
	7	Control cropland	47° 31' 42.2" N, 47° 00' 54.0" E



*Figure 1 Location of monitoring plots with GW wells. The green markers are control areas, brown markers show black locust stands, orange marker shows poplar stand and the red marker shows common oak stand.*



## RESULTS AND DISCUSSION

### Total Organic Carbon content of the soil

Generally, larger organic carbon accumulation can be seen under woody, than herbaceous (control) vegetation (Figure 1, 2 and 3). The reason is that the litter material in the forest remains on the ground and continuously, slowly decomposes, and then precipitation and natural disturbance helps the organic matter to mix with the topsoil further increasing the total organic carbon content of that. In contrast, organic material of the control areas is removed from and/or plowed into the soil, where it decomposes rapidly. Due to disturbance of croplands and pastures, organic carbon content reduces, because it escapes as CO<sub>2</sub>; by comparison, such extent of human disturbance is not typical in the case of forests, as it was shown by Jobbágy and Jackson (2000) and our results also confirm the above statement.

On Figure 2, organic carbon content of the soil of poplar is less than that of the control in the depth of 0.1 m. The differences, however, are very small.

Depth profiles of total organic carbon content of controls can be very different depending on the land use. This is shown in Figure 2 (pasture), wherein organic material release of the grazing animals also increases the content of organic matter in the soil. However, the case shown in Figure 3 represents low organic carbon content, in which the variability by depth can hardly be seen. At this cropland, a substantial part of the produced organic matter (alfalfa) is continuously removed.

Since the soils of Jászberény and Jászfákóhalma have coarser texture (sand and sand with sandy loam stratification), organic carbon content of the soil is very low from 50 cm depth; the Jászfelsőszentgyörgy sample site has finer texture (loam, sandy loam, with occasional clay loam), therefore organic carbon content reduction can be seen only in the depth of 70 and 100 cm. Due to the formation of organo-mineral complex, leaching is less manifested in the Jászfelsőszentgyörgy area.

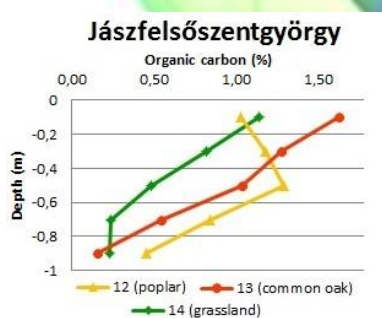


Figure 2. TOC profile of Jászfelsőszentgyörgy sample plot

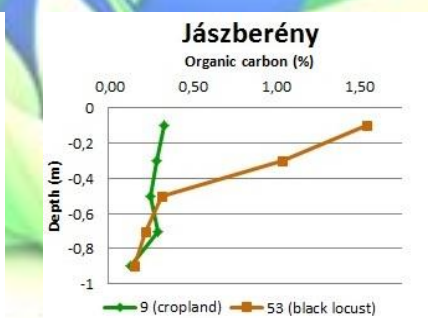


Figure 3. TOC profile of Jászberény sample plot

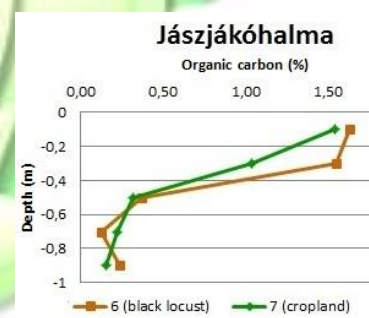


Figure 4. TOC profile of Jászfákóhalma sample plot

### CaCO<sub>3</sub> content of the soil

CaCO<sub>3</sub>, leached down by percolating soil solution from the upper soil layers, infiltrates into deeper layers, where it reaches a maximum (Fig. 5). Water table level was the shallowest at the Jászfelsőszentgyörgy sample



Figure 5.  $\text{CaCO}_3$  profile of Jászfelsőszentgyörgy



area (3.1-3.8 m). Consequently, more roots are located close to the water table, which form  $\text{CaCO}_3$ -dissolving acids.  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  dissolved in the groundwater precipitated in carbonate form under warm and dry climatic conditions, intense evaporation periods which conditions increase the  $\text{CaCO}_3$  content of the soil. The  $\text{CaCO}_3$  content in the soil of control and poplar plantation was reduced to zero in the depth of 4.5 - 5.5 m (Fig. 5).

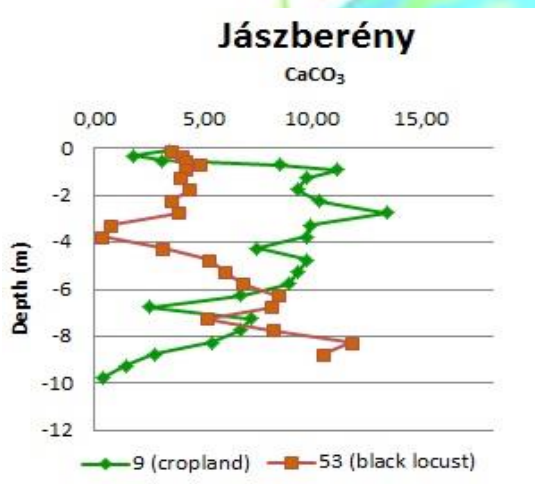


Figure 6.  $\text{CaCO}_3$  profile of Jászberény sample plot

Water table was the deepest in Jászberény, thus conditions favoured the deep leaching of  $\text{CaCO}_3$  (Figure 7).

The increase in the amount of  $\text{CaCO}_3$  is almost continuous in the soil of black locust forest under the root zone. Differences between the black locust and arable land support our initial assumptions (Fig. 6.).

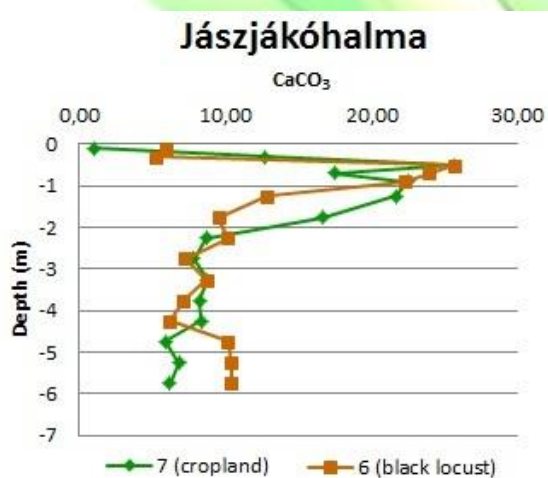


Figure 7.  $\text{CaCO}_3$  profile of Jászfákóhalma sample plot

Similarly, the leached carbonate reaches the maximum at the depth of 0.5 m, then the amount is reduced. Significant difference in the amount of  $\text{CaCO}_3$  content under the two stands cannot be observed (Fig. 7).



### Correlation between the inorganic carbon forms in the soil and groundwater

Correlation profile of the inorganic carbon form (Fig. 8) shows that a significant negative linear relationship exists between the  $\text{CaCO}_3$  content of the soil and the bicarbonate content of the groundwater. It has also been revealed, that there is negative linear relationship between the  $\text{CaCO}_3$  content of the soil and the  $\text{Ca}^{2+}$  content of the groundwater, but it is not significant. These relationships mean that, if the  $\text{CaCO}_3$  content in the soil decreases, bicarbonate and calcium content in the groundwater increases, and vice versa. The relationship between these forms of inorganic carbon suggests that the  $\text{CaCO}_3$  content of the soil dissolves and increases the concentration of these ions, and in the case of a long dry period,  $\text{CaCO}_3$  precipitates in the soil from the groundwater. These equilibrium processes are mainly regulated by the climatic factors and changes in the soil pH.

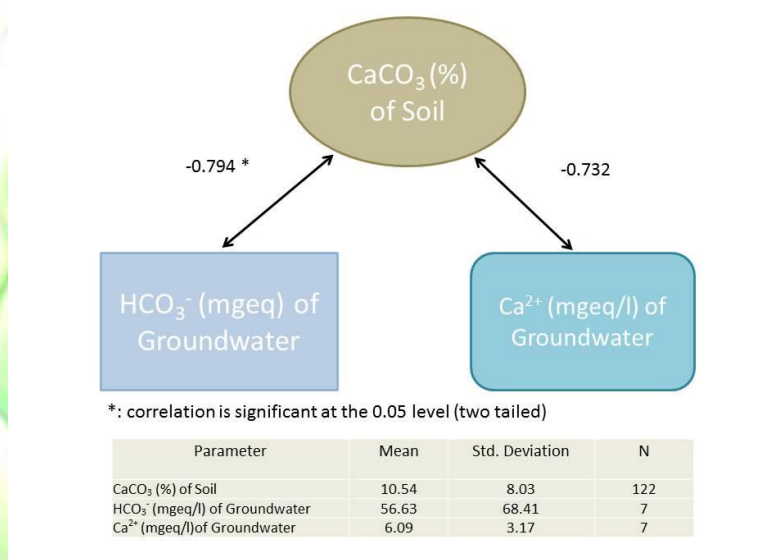


Figure 8. Correlation profile of inorganic carbon forms in the soil – groundwater system

### Fluctuation of groundwater level

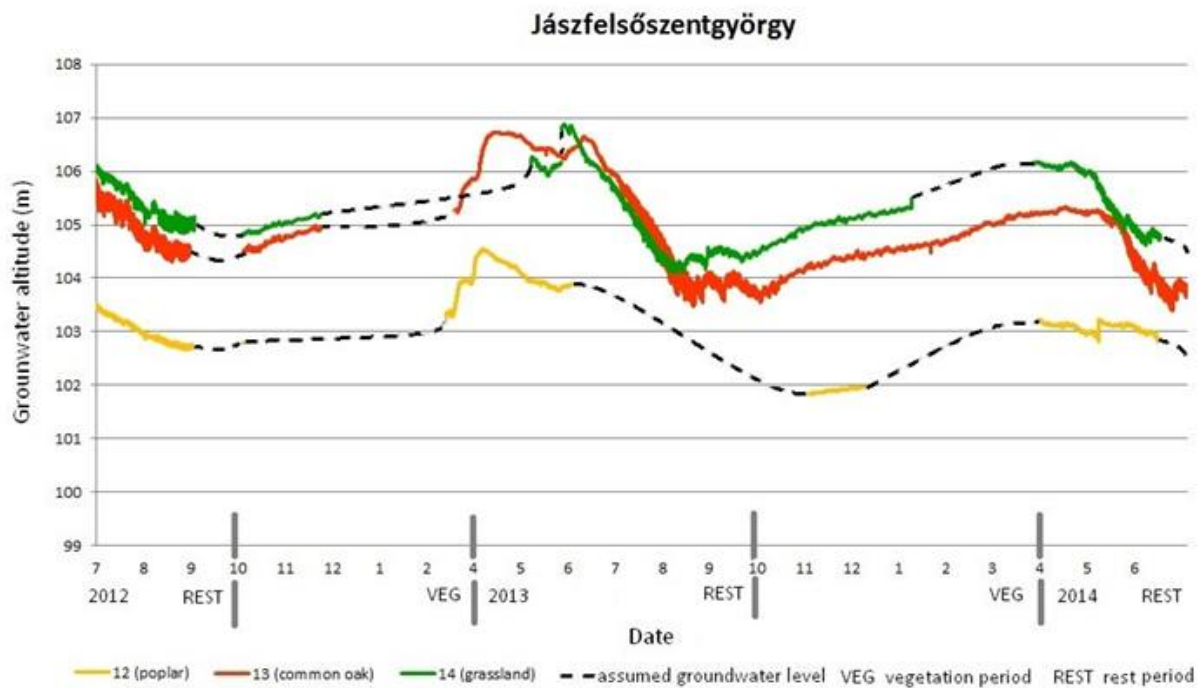
During the groundwater level monitoring, short- (daily rate) and long-term (annual rate) fluctuations in groundwater level could be identified at most of the sample plots.

A greater daily groundwater fluctuation was observed at the plots of 6, 7, 9, 12 and 14, however, this value is very small in the case of 13 and 53 plots. During the vegetation period, groundwater level decrease was typically observed under forests that can be explained by the increased evaporation of the vegetation linked to water uptake, which then cannot be fully replenished by precipitation. Groundwater level reaches its long-term minimum during this period. The process typical in the rest period is the opposite. Due to the spring snowmelt and precipitation, the groundwater level increases, in addition, replenishment keeps going on by lateral flow according to the hydraulic gradient, and reaches a maximum.

At Jászfelsőszentgyörgy, two forests and a control (grassland) areas were compared. The minimum of groundwater level in oak plantation is below that of the control, while the minimum of poplar is less than that of the oak. This is possible, because the poplar has higher water uptake, than the oak. The amplitude is similar in all three study areas, about 2.8 m. The reason of this strong effect is the shallow water table, which enables the use of water by the roots. Compared to the groundwater of the other two areas, this water table level is the shallowest, and



in comparison, stronger effects can be observed in groundwater, as more roots take up water directly from the groundwater. Due to the shallow groundwater, the peak of the curves is less pronounced, than in the Jászfákóhalma study area presented below (Fig. 9).



*Figure 9 Long-term (2012. 07.-2014. 07.) fluctuation of groundwater in Jászfelsőszentgyörgy*

At Jászberény, groundwater fluctuations of a control cropland (alfalfa) and a nearby black locust plantation were compared. Fig 10. shows that the water table in the forests continuously remains deeper than under the control area. In this area, the level of standing groundwater reaches the depth of 8 m. Based on these data it is understood that the black locust having shallow root system has not consumed groundwater directly, thus that it is trapped in the deeper layers.

Periodic changes between the rest and growing season emerge nicely on the figure. In the rest period of year 2012, heavy rainfall events are assumed on the forest area, when the amount of rainfall infiltrated into the soil more easily through the leaf litter than in the control area, and then reached the groundwater. The amplitude of the year 2013 for the black locust and alfalfa are also 1.5 m (Fig. 10).

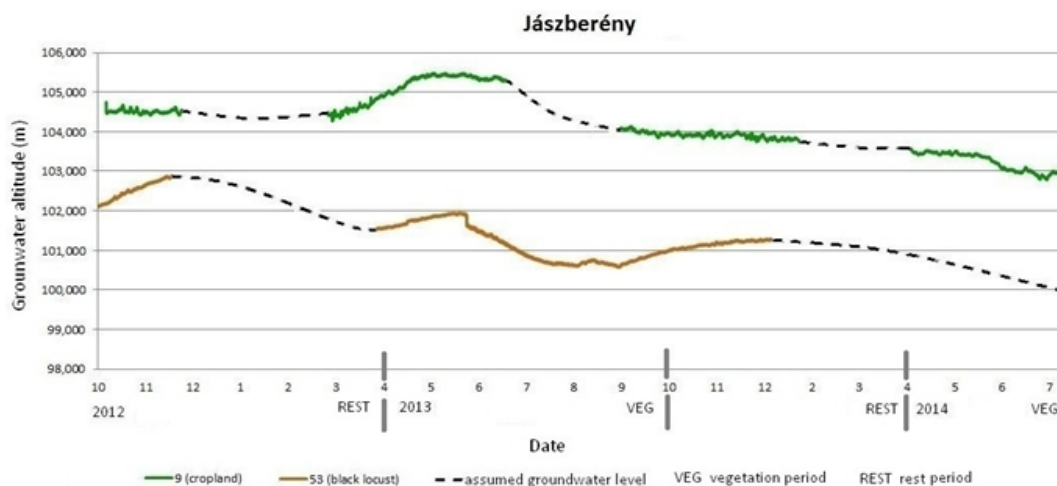


Figure 10. Long-term (2012. 10.-2014. 07.) fluctuation of groundwater in Jászberény

At Jászfákóhalma, the groundwater fluctuation of a black locust forest and the adjacent arable land were compared. Periodic fluctuations can be observed on the diagram. At the beginning of the growing season of the year 2012, a large-scale groundwater level drop occurred at the control area, within a relatively short period of time. In the year 2013, the amplitude of the groundwater fluctuation of black locust forest has reached the 2.75 m, while the same amplitude under the adjacent arable land was 1,9 m. It can be observed that there is almost 1 m difference between the amplitudes of the two areas, which shows the difference of water uptake. In addition, the minimum of groundwater level in arable land is higher than that of the woody vegetation, and the groundwater level of control area is generally higher. This is due to the shallow groundwater that is reached by the roots of trees, such as became direct consumers.

During the spring snowmelt, water table shows a peak below the forests, which is higher than that of the control area. This develops as a result of autumn-winter precipitation and the end of the winter and early spring replenishment. However, during the growing season, due to the greater water uptake of woody vegetation, groundwater level curve forms a negative peak (drop) below the similar curve of control. The groundwater level rise - caused by the infiltration - is less under the arable land. It is clearly seen that the curve representing groundwater temporal change, intersects each other twice a year systematically. Water table is higher under the cropland at the growing season, and under the forest in the rest period (Fig. 11).

## CONCLUSION

Jakab et al. 2014 have already proved that more organic carbon accumulation can be detected under the woody plant vegetation than under the control herbaceous vegetation. In the forests, litter is continuously generated and is not removed, thus decomposition of it forms a continuous supply of organic carbon in the topsoil. In contrast, on the control areas, organic material is removed each year by mowing, grazing or crop harvesting. This is demonstrated in our study, as well. Not the amount, but the depth profile of organic carbon is influenced by the soil texture.



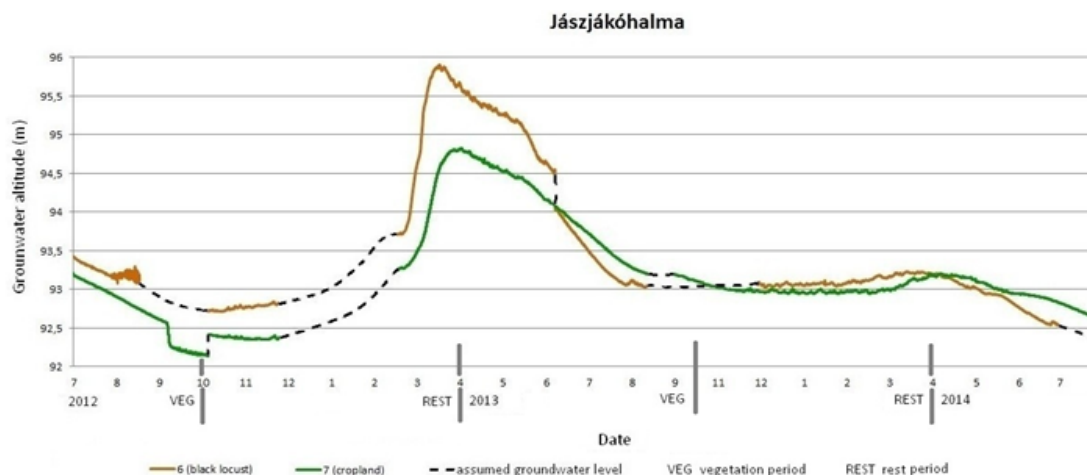


Figure 11. Long-term (2012. 10.-2014. 07.) fluctuation of groundwater in Jászfákóhalma

Close negative correlation has been shown between the calcium and bicarbonate content of groundwater and the  $\text{CaCO}_3$  content of the soil due to the equilibrium dissolution - precipitation processes occurring between soil and groundwater phase. In soils of Jászság region, - showing minor differences regarding soil texture - depth profile of  $\text{CaCO}_3$  is defined by the level and fluctuation of water table, and the composition of groundwater.

Related to the fluctuation of groundwater, the following findings were obtained:

- Water table below the forests decreased during the growing season, due to increased evaporation compared to that of control vegetation.
- Groundwater depression was detected under the forests. This result agrees with the findings of Jobbágy and Jackson (2004) and Szodfridt and Farago (1968). Jobbágy and Jackson (2004) stated that the groundwater level can be 75 cm deeper under a forest. Szodfridt and Faragó (1968) found that in shallow groundwater areas of Kiskunság, the forest vegetation generally lower the water table 50–60 cm compared to herbaceous vegetation. Considering our data on the standing groundwater levels, this value was 60 to 180 cm in the Jászság region.
- Groundwater depression showed different values in the growing and in the rest period. This phenomenon has been also revealed by Ijjász (1939). He stated, that under a forest, the water table can be detected deeper than under grassland if the trees are able to reach groundwater. The difference of the water table levels is larger in the growing season, than in the rest period.
- Water table depression, created by the plantation, levels off in the rest period, due to horizontal water flow from surrounding areas and infiltration of the precipitation from the surface during the leafless rest period.
- Out of poplar and common oak stands, examined at the same sample area, greater groundwater depression compared to the control was created by the poplar, due to the higher amount of water uptake from groundwater.
- The difference between groundwater levels in the rest and growing seasons was around 2.8 m at Jászfelsőszentgyörgy sample area. The amplitude of groundwater fluctuation was 1.5 m at Jászberény and 1.9–2.75 m at Jászfákóhalma.

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## **INVESTIGATION OF SOME EXTRACELLULAR ENZYMATIC ACTIVITIES IN THE RHIZOSPHERE OF SPRING WHEAT CULTIVATED IN SOIL MIXED WITH BIOSOLID**

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### **ABSTRACT**

There is an increasing interest in the agricultural application of biosolid obtained in wastewater treatment plants, due to the possibility of recycling valuable components; organic matter, nitrogen, phosphorus and other plant nutrients. The word biosolid is a new term used to describe municipal treatment plant solids that are tested and determined to be safe for land application. Enzyme potential activities are generally considered to be a more direct expression of soil biological activity or of the activities of specific processes of nutrient cycling and organic matter turnover, than measurements of microbial numbers. Enzyme potential activities are generally considered as direct expression of soil biological activity or of the activities of specific processes of nutrient cycling and organic matter turnover. Spring wheat plants were cultivated in acidic sandy soil treated with different rate of biosolid: 0, 30, 50, 70 and 100% (soil: biosolid, w/w) per pot. The activities of FDA, phosphatase,  $\beta$ -glucosidase and protease were measured under laboratory conditions. Results indicated that by increasing the additional rate of biosolid in the rhizosphere of spring wheat increase the potential activity of all of the tested extracellular enzymes to be maximal at 100% biosolid, the rhizosphere was in significant with the potential activity than in soil bulk. There was a significant difference between the potential activity of phosphatase in the rhizosphere of spring wheat with the activity in the soil bulk only within the applied doses (0 x 70% and 100%, 30% x 70% and 100%). Our advisors are pointed out to use the low heavy metal borne biosolid in agroecosystem every three years to prevent the bioaccumulation of heavy metals in soil or translocated to the food-chain. Therefore, by this strategy we can keep the public health-care in safety.

**Keywords:** *Biosolid, Enzyme activities, wheat, Acidic sandy soil, rhizosphere*

### **INTRODUCTION**

The word *biosolid* is a new term used to describe municipal treatment plant solids that are tested and determined to be safe for land application. The word *sludge* is a generic term that most people use to refer to some type of unprocessed waste material. There is still some interchange of these two words, but biosolid always refers to processed wastewater solids that have met specific criteria and are suitable for land application.

Soil microorganisms as one part can be sensitive biological markers and can be used to assess disturbed or contaminated soils. Microbiological properties can also serve as soil quality



indicators because after plants soil microbes are the second most important biological agent of the agricultural ecosystem. There are many indicators of soil microbiological properties including microbial biomass content, microbial diversity and activity, and enzyme activity (SIKORA et al. 1995). Each soil has a characteristic pattern of enzymes because all biochemical actions are dependent on or related to their presence. Soil enzyme assays are process level indicators and are presented as a means of determining the potential of a soil to degrade or to transform substrates. This can be useful as an indicator of how well a soil carries out important steps in different processes. Oxidoreductases, transferases and hydrolases, have been the most studied enzyme activities of soil because of their role in the oxidation and release of inorganic nutrients from organic matter. Ideally the activity of a soil should be attributable to enzymes of different origins, functioning according to their concentration and catalytic properties as expressed under the conditions of the soil micro-environment in which they are located (LADD 1978, LADD & BUTLER 1975). Enzymes in soils originate from animal, plant and microbial sources. Microorganisms supply most of the soil enzyme activity, with their large biomass, high metabolic activity and short lifetime under favourable conditions. Effect of the agroecosystem on activity of soil enzymes Soil enzyme activities are influenced by management practices because they are also related to microbial biomass which is sensitive to different treatments. The street biosolids are high in organic nitrogen, phosphorus and have significant levels of potassium and sulfate. Iron, copper, manganese, molybdenum and zinc, essential elements necessary for plant growth are also found in this material.

## MATERIALS AND METHODS

Soil sample of acidic sandy brown forest soil of low humus content was taken from non-cultivated area of Gödöllő town, Hungary. Biosolid material was received from Nyíregyháza and Regional domestic wastewater treatment plant Ltd., Nyíregyháza, Hungary. The experiments were carried out by cultivating spring wheat (*Triticum vulgare* L.) plant.

### Experimental soil-biosolid mixture

In two-kg pot capacity, the agroecosystem for plant growth was formed according to the following mixture:

Ratio of soil	Ratio of biosolid
100%	0%
70%	30%
50%	50%
30%	70%
0%	100%

The moisture content of the agroecosystem was kept constantly (approximately 60 ± 2%) throughout the 50 days as the time of cultivation.

### Greenhouse conditions

The plant-soil-biosolid agroecosystem was conducted in greenhouse under automatically setup conditions to be consisted of a 12 h day maintained with two paired day-light and warm white

fluorescent tubes at 10000 lux, day-time temperatures of 22°C, and night temperatures of 16°C. The experimental pots were watered as necessary to maintain the soil moisture content at approximately 60 ± 2% field capacity.

## METHODS

All *in vitro* investigations were carried out in the laboratories of Agricultural-, Environmental Microbiology and Soil Biotechnology, PhD School, Szent István University, Budapest, and in the greenhouse of Soil Science and Agrochemistry as well as the Central Laboratory of Szent István University, Gödöllő.

### Potential activities of some enzymes in soil amended by Biosolid

#### 1. Dehydrogenase:

Using the method of MERSI & SCHINNER (1991), 1 gram of a soil at 60% of its water field capacity is mixed with 1.5 ml of 1 M of Tris (tris(hydroxymethyl)aminomethane) buffer with pH 7 and 2 ml of substrate solution (mixture of 500 µg of 2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyltetrazoliumchloride and 2 ml of N,N-dimethylformamide) in stopper test tube, the enzyme activity was estimated by the formation of idonitrotetrazolium formazan after 2 h shaking incubation at 40°C in dark and measured spectrophotometrically at 464 nm, and expressed as µg idonitrotetrazolium formazan formed g<sup>-1</sup> soil h<sup>-1</sup>.

#### 2. Phosphatase:

Using the technique of TABATABAI (1994) 1 gram of soil sample was incubated with the substrate di-Na-p-nitrophenyl-phosphate hexahydrate and 4 ml of universal working buffer for 1 h at 37°C. After incubation 1 ml of calcium chloride solution and 4 ml of 0.5 M of sodium hydroxide were added to the incubated mixture and then 90 ml of distilled water were added. After shaking the mixture, a yellow colour filtrate was measured spectrophotometrically at 400 nm against the reagent blank. The concentration of p-nitrophenol released was assessed and expressed as µg p-nitrophenol released g<sup>-1</sup> soil h<sup>-1</sup>.

#### 3. β-glucosidase:

According to MASCIANDARO et al. (1994) by measuring the concentration of p-nitrophenol released after the soil sample mixed by the substrate and the buffer, and incubated for 1 h at 37°C. The blue coloured material is developed and spectrophotometrically measured at 578 nm, and expressed as µg p-nitrophenol released g<sup>-1</sup> soil h<sup>-1</sup>.

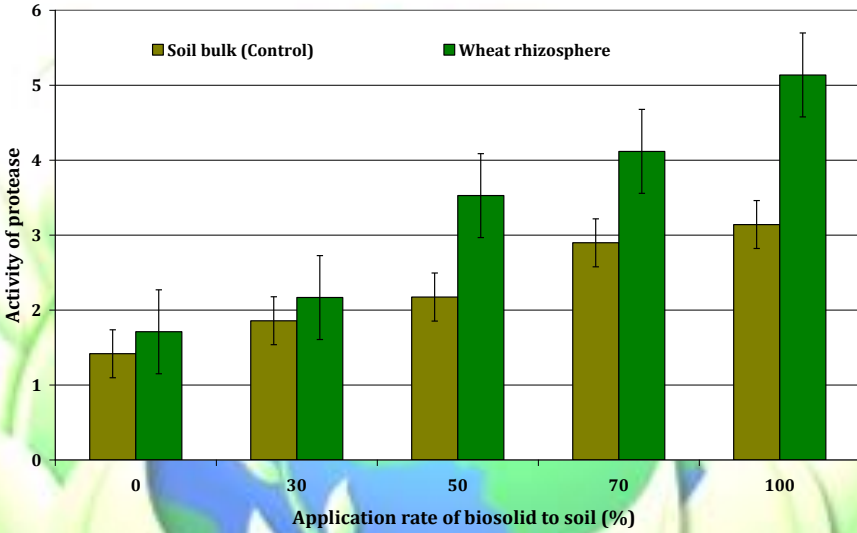
## RESULTS

### Effect of sewage sludge application on the enzymatic potential activities in treated soil rhizosphere

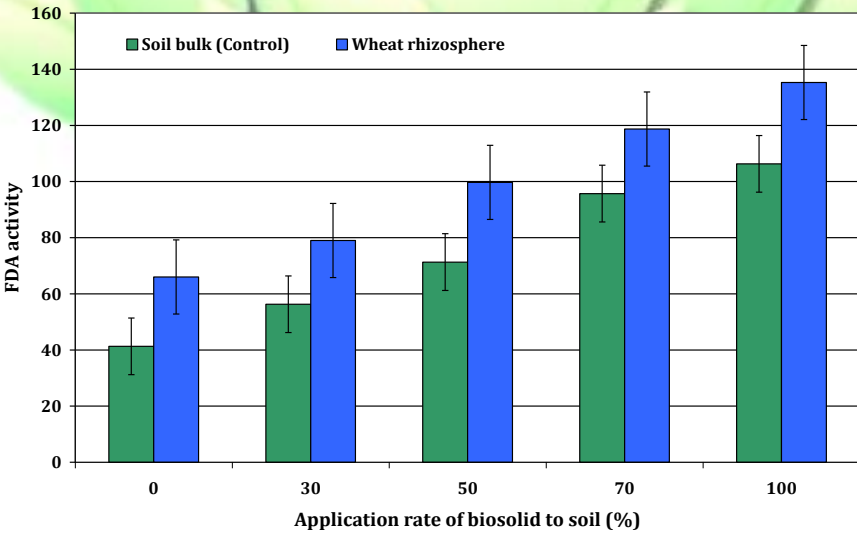
Enzyme potential activities are generally considered to be a more direct expression of soil biological activity or of the activities of specific processes of nutrient cycling and organic matter turnover, than measurements of microbial numbers. Figure 1 demonstrates that the increasing of potential activity of protease reaches the maximum at 100% sludge. Comparatively, the

potential activity of protease was at the lowest in soil bulk (control), while it was higher in the rhizosphere spring wheat. This indicated that the activity of the enzyme in the rhizospheres was in significant with the potential activity in soil bulk. These significant differences were increased by increasing the concentration of the biosolid in the pots.

Figure 2 illustrates that by increasing the additional rate of biosolid in the rhizospheres of spring wheat cause an increase in the potential activity of FDA to be maximal at 100% sludge. Comparatively, the potential activity of FDA was at the lowest in soil bulk (control), this indicated that the activity was in significant between the soil bulk and in the rhizosphere of spring wheat.



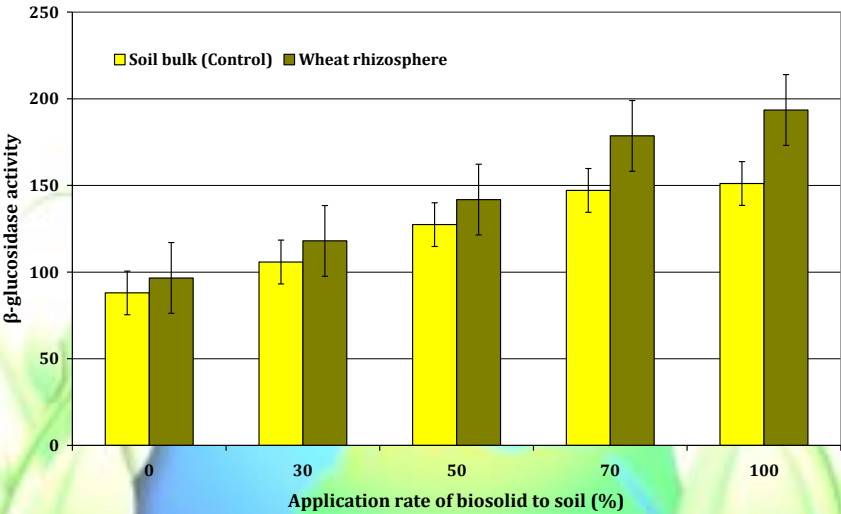
Figures 1 Effect of biosolid application on potential activity of protease in the soil bulk and rhizosphere of spring wheat



Figures 2 Effect of biosolid application on FDA activity of protease in the soil bulk and rhizosphere of spring wheat

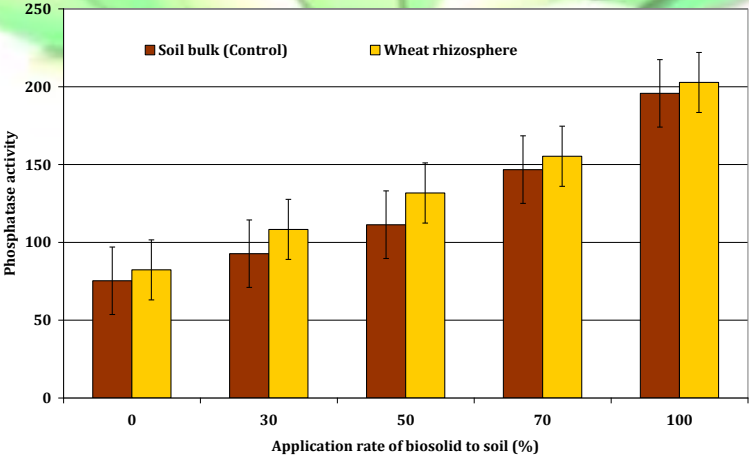


Similar results to FDA were obtained when the potential activity of  $\beta$ -glucosidase was measured. Figure 3 demonstrates that by increasing the rate of biosolid in the rhizosphere of spring wheat and the potential activity of  $\beta$ -glucosidase increased to reach the maximum activity at 100% sludge. Comparatively, there were differences in the potential activity of  $\beta$ -glucosidase within the soil bulk, and the rhizospheres of spring wheat.



Figures 3 Effect of biosolid application on  $\beta$ -glucosidase activity of protease in the soil bulk and rhizosphere of spring wheat

However, Figure 4 indicates that increasing the additional rate of biosolid in the rhizospheres of spring wheat cause an increase in the potential activity of phosphatase to reach the maximum activity at 100% sludge. Comparatively, the potential activity of phosphatase was at the lowest in soil bulk (control). This showed that there was a significant difference between the potential activity of phosphatase in the rhizospheres of spring wheat with the activity in the soil bulk only within the applied doses (0 x 70% and 100%, 30% x 70% and 100%).



Figures 4 Effect of biosolid application on phosphatase activity of protease in the soil bulk and rhizosphere of spring wheat

## DISCUSSION

### Effect of biosolid application on the enzymatic potential activities in treated soil rhizosphere

Soil enzymes play an important role in the mineralisation of organic substances and making nutrient ions available. Due to the reactions of urease and phosphates  $\text{NH}_4^+$  and  $\text{PO}_4^-$  are made available to plants from organic substances in soils (REDDY et al., 1987). The enzyme assays we described allowed a range of enzymes and a large number of samples to be assayed over a relatively short period from small quantities of soil in a less labour-intensive manner than the existing methodology.



In general, soil enzyme activity measurements are only a measure of the potential activity of a given enzyme in soil and not the *in situ* activity in the natural soil system, where activity is impaired by absorption and immobilization of enzymes by soil particles and organic matter, which differ between soils (GIANFREDA & BOLLAG, 1994). The assays that we have devised are not intended as a method for determining the actual or the maximum enzyme activities of the soil samples, as many of the enzyme assays are displaced from their optimal pH for activity and desorption from soil (QUIQUAMPOIX et al., 1993). Soil enzymes will not necessarily be at their optimal pH *in situ*, given the variation in micro-environments that exist in soil (GIANFREDA & BOLLAG, 1994). Also, the natural soil system is not saturated with enzyme substrate as it is under assay conditions. It is not necessary to create optimal activity conditions for assays in comparative studies, as long as a standard methodology used. However, it is possible to make some statistical comparisons of enzyme activities between soil types where several treatments have been used. This can be done by normalising the data into arbitrary units, for example, ranking the enzyme activities of the different treatments or considering each data point as a proportion of the data points with the highest activity.

Thus, in rhizosphere soil, there is unlikely to be much difference in the amount of enzyme secreted by the plant roots. This also supports the theory that the amount of immobilised soil enzymes is a measure of cumulative activity during the growth of plant roots and soil biochemical processes, as immobilised enzymes are relatively stable until the soil is disturbed.

For the assessment of soil perturbation, enzymatic activities and biochemical indexes have been proposed (NASEBY & LYNCH, 1997; BENDING, et al. 2000; BENITEZ et al., 2004). Nutrient availability to plant is strongly influenced by organic and inorganic amendments that usually increase the amounts of soil organic carbon, nitrogen and other nutrients. Organic matter is added to soil by incorporating plant material, animal residues, manure, sewage sludge or municipal waste. Amendments not only influence soil fertility directly, but can also affect the composition and activities of soil microorganisms.

The use of selected parameters, such as enzyme activities, organic matter, physical properties, structure and formation of humic substances, together with agronomic and chemical properties, has provided additional information about functioning and productivity of degraded soil-ecosystems under appropriate regeneration practices (NANNIPIERI, 1994; DICK, 1994; MASCIANDARO & CECCANTI, 1999).

MORENO et al. (2003) studied the effects of adding sewage sludge on enzymatic activities of a semi-arid soil contaminated with Cd or Ni in the laboratory. The activities of urease, phosphatase,  $\beta$ -glucosidase and protease-BAA were measured in soil containing concentrations of Cd or Ni in the range 0–8000 mg kg<sup>-1</sup> soil, and their inhibition was compared with those of the enzymatic activities in the same soil amended with sewage sludge and containing similar

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concentrations of the heavy metals. The inhibition was tested for three different incubation times to determine changes in the effect of the heavy metals on hydrolase activity with the time elapsed after contamination. The other two enzymes ( $\beta$ -glucosidase and protease-BAA) were less sensitive to Cd or Ni contamination, and it was more difficult to determine whether addition of sewage sludge had affected the inhibition of these enzymes by the heavy metals.

AON et al. (2001) analysed a soil recently subjected to agriculture from the El Salado river basin under no-till or conventional tillage. We sought to detect whether a pattern of interactions among microbial, biochemical and physico-chemical variables in soil exists that may be distinguished and characterised. Several microbial groups, enzymatic activities and  $O_2$  and  $CO_2$  exchange rates were monitored before planting (T0) and during the growth cycle of soybean (G. max) (T1: flowering stage; T2: pre-harvest period). Strong relationships were evidenced by correlation  $r$  ( $r^2$ ) matrices performed with several specific groups of bacteria and fungi, and soil enzymatic activities representative of main nutrient cycles (C, N, and P). A burst of biological activity was registered at T1 as could be judged through:

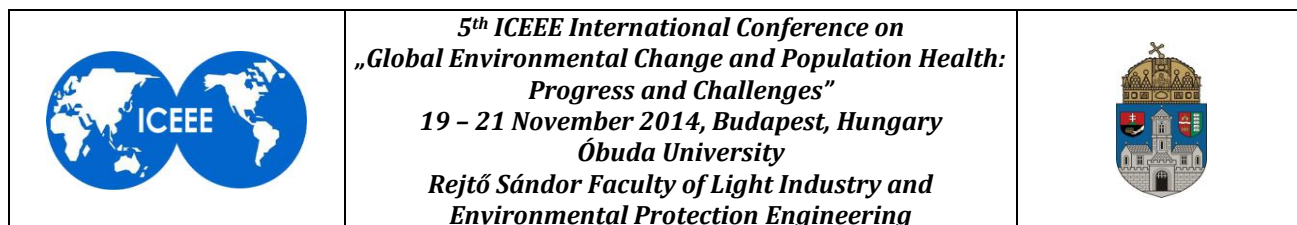
- (i) a remarkable increase in the numbers of microorganisms measured at both depths tested (D1:5-10 cm; D2:15-20 cm);
- (ii) a peak of  $O_2$  consumption; and
- (iii) a maximal gradient of activity exhibited by all enzymes tested (acid and alkaline phosphatases, dehydrogenase, FDA hydrolysis,  $\beta$ -glucosidase, urease).

Microorganisms stratified as a function of depth particularly at T0 and T2, whereas at T1 they appeared to transiently redistribute in the 5-20 cm profile unlike all enzymatic activities that showed a maximal stratification. Low respiratory quotients, RQ (0.2; RQ, defined as the ratio of  $qCO_2:qO_2$ ), were found, following an experimental method for quantifying rates of  $O_2$  consumption,  $qO_2$ , and  $CO_2$  production,  $qCO_2$ , by soil. The biodiversity of fungi increased 16% at T2 with respect to T0 along with a 37% increment in species richness. The fact that several of the variables measured were strongly linked despite season and crop presence, points to the existence of a core highly interrelate processes in soil.

KATAI (1999) found that in soil of Hajdúböszörményi, the enzymatic activity of urease and  $CO_2$ -production were increased by increases the fertiliser applied rate in triculture, while the phosphatase and catalase decreased, similarly, in monoculture, it was found that by increasing the fertiliser rate, the activities of the enzymes were decreased. But in Láptókép soil, maximum activities of catalase and phosphatase was marked at medium to high rate of fertiliser, and maximum  $CO_2$ -production was obtained at this concentration too. In the presented study, it was found that the potential activities of catalase and phosphatase as well as the  $CO_2$ -production were increased by increasing the application rate of the applied sewage sludge in the rhizospheres of spring wheat and field growing common bean.

It was expected to find an increase in activity with the addition of a large amount of organic phosphate, however, the readily available soluble from that was added would have been broken down into an inorganic form rapidly in the soil environment. Increasing available inorganic soluble phosphate is known to have an inverse effect on phosphatase production (TABATABAI, 1982; TADANO et al., 1993). Phosphomonoesterases (acid and alkaline soil phosphatases), which play a significant role in the hydrolysis of organic P compounds, occur in soils as endocellular enzymes or in a free state as well as being intimately sorbed to organic, silt, and clay colloids (LADD & BUTLER, 1975; BURNS 1982; NANNIPIERI et al., 1988). CHEN et al. (2002) confirmed that microbial and enzyme activities of phosphatase and phosphodiesterase played an important role in the mineralisation of soil organic phosphorus in the rhizosphere of radiata pine. Also, GEORGE et al. (2002) mentioned that agroforestry species enhanced the activity of acid phosphatase, while maize enhanced the activity of alkaline phosphatase. Acid phosphatase





activity increased exponentially with increasing proximity to the root mat of the agroforestry species. This suggests that agroforestry species are actively increasing rhizosphere phosphatase activity either directly by secretion or indirectly by stimulation of microbial activity and / or depletion of inorganic phosphorus. NASEBY & LYNCH (1997) studied the activities of phosphatase, and urease in soil samples. It was found that gene modified *P. fluorescens* was introduced to the soil samples it significantly increased the urease activities at 5-20 cm depth and significantly decreased the alkaline phosphatase activity.

MAWDSLEY & BURNS (1994) successfully used soil enzyme measurements to detect perturbations caused by a *Flavobacterium* spp. inoculated on to wheat seedlings, finding increased activity of  $\beta$ -glucosidase. Hydrolytic enzyme activities (phosphatase,  $\beta$ -glucosidase), and oxidoreductase activities (dehydrogenase) were used as measures of soil perturbation by BENITEZ et al. (2004).

Depending on the obtained results, we found direct strong relationships between microbial communities and dehydrogenase activities at all agroecosystem trials used in the experiment. Dehydrogenase activity can be related to the metabolic state of microbial population of the soil and we agree with the observation of GARCIA et al. (1997). CRECCHIO et al. (2004) found that by increasing the application dose of municipal soil waste compost, the organic C, total N, dehydrogenase,  $\beta$ -glucosidase, urease, nitrate reductase and phosphatase activities were increased, but there was no significant variation in the bacterial communities. Similarly, we found that by increase the application rate of sewage sludge to the soil, the enzymatic and microbial activities increased.

TAYLOR et al (2002) mentioned that knowledge of microbial numbers and activity in sub-soils is essential for understanding the transformation and down movement of natural and synthetic organics. FDA hydrolysis was used as a general indicator of soil hydrolytic activity, as it measured the activities of proteases, lipases and esterases that are all capable of cleaving the fluorogenic FDA (DICK, 1997) and our results (Figure 2) are in agreement with these results. FDA hydrolysis, like dehydrogenase activity, is regarded by some as a reliable measure of total microbial activity although, unlike dehydrogenase, these enzymes can function outside of the cell and form stable complexes with soil colloids. BORKEN et al. (2002) stated that compost waste applied to the soil increased microbial activity and biomass in the mineral soil by release of nutrients from the O-horizons to mineral soil.

The data presented in this work indicated that soil biochemical properties can be a useful tool for use as indicators of perturbations caused by microbial inoculation and other soil treatment e.g., treatment with biosolid. The results showed similar tendency to these results obtained by both techniques of the FDA and CO<sub>2</sub>-released. The dehydrogenase activity of the amended soils was significantly greater than the control soil indicating the greater metabolic activity of the microorganisms. The results demonstrated that the biological activities in different soil samples treated with different rates of biosolid were directly proportional with the amounts of fluorescein produced and CO<sub>2</sub> release. Therefore, the correlation between the CO<sub>2</sub>-release, FDA hydrolytic activities and dehydrogenase activity is occurred. A good correlation was found between FDA hydrolysis and respiration, and the decomposers activities in different environmental conditions, which was probably a reflection of the amounts of organic soil matter. No definite conclusions about the advisability of biosolid application to land could be made. There was a positive role of biosolid in improving agrochemical soil properties, but there was a negative environmental effect associated with heavy metal accumulation in soils. Our advisors are pointed out to use the low heavy metal borne biosolid in agroecosystem every three years to prevent the bioaccumulation of heavy metals in soil or translocated to the food-chain. Therefore, by this strategy we can keep the public health-care in safety.



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Óbuda University  
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Environmental Protection Engineering*



## **IMPACT OF GLOBAL ENVIRONMENTAL CHANGE ON INFECTIOUS DISEASES**

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There are many ways of environmental changes that are influencing the occurrence and range of infectious diseases in humans and animals. For instance, climate changes, including significant warming, have increased the frequency and severity of extreme weather events, and changes in the hydrological cycle are leading to widespread biotic and abiotic variations across the world. The ever increasing urbanization of human populations is creating strain on food production and tremendous burdens on health provision with subsequent socioeconomic consequences. The global environmental changes (GEC) may affect the distribution of infectious diseases. There are six major global changes: climate change, the thinning of the ozone layer, soil degradation and changes in land use, water scarcity, loss of biodiversity and a degradation of the terrestrial and aquatic ecosystems. This holistic view of the impact of GEC is welcome for two reasons: firstly, the drivers of GEC interact and their effects are therefore difficult to separate and secondly, up until now the literature has focused on single driver views, particularly on the relationship between climate change and health. Despite its name global environmental change has very different effects locally and there are large differences in the capacity of populations to protect themselves against negative health effects. To address the challenges raised by ongoing global environmental variations and their impact on infectious diseases, the major topics that will be discussed include:

- The impact of current and predicted global climate changes, globalization, urbanization and habitat loss on infectious disease dynamics in human and animal populations and wildlife and livestock across the globe.
- Predictive models to provide strategic public health responses to changing environments.
- Sociodemographic and economic factors influencing populations and their impact on the distribution and prevalence of infectious diseases.
- Policies and mechanisms of intervention to reduce the spread of infectious diseases related to global environmental changes.
- Future prospects for tackling emerging and neglected diseases.

**Keywords:** *global changes; infectious diseases; policies and mechanisms; public health responses*

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## **ECOLOGICAL AND BACTERIOLOGICAL MONITORING OF DANUBE WATER QUALITY IN BUDAPEST REGION**

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According to the global environmental changes, water quality problems of the developed and undeveloped nations such as pollution, eutrophication, toxicity development, ecosystem dysfunction, acidification from air pollution now aggravated through long standing forest fires. The urgent need for drinking water, food and recreational areas on one hand, and dangers of increasing eutrophication and pollution on the other, are problems well known in all over the world. Monitoring the environment with different systems is absolutely essential to identify human health and ecosystem hazards, to assess environmental cleanup efforts, and to prevent further degradation of the ecosystem. The objectives of this monitoring were to select the most important parameters that investigate ecological and bacteriological assessment for water quality of the main Danube River in Budapest region. The samples were collected in sterile dark bottles from four different zones between Rákóczi and Árpád Bridges from the Pest and Buda sides during June, August and October. Comparative studies were carried out during 1998, 2005, 2010, 2011, 2012 and 2013. The surface water investigated parameters were: transparency, temperature, electroconductivity, pH, BOD<sub>5</sub>, COD<sub>Mn</sub>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, as well as the bacteriological monitoring were: coliforms count, faecal streptococci, *E. coli*, *Enterococcus* sp., *Enterobacter* sp., *Pseudomonas aeruginosa*, and total aerobic mesophile heterotroph and cellulose-decomposing bacterial count at 22 and 37°C were evaluated. According to the investigated ecological parameters and on the Hungarian methods for water quality, our results demonstrate that the main Danube River water quality has improved and become unstable during the last 15 years subsequent to the diversion which could be witnessed particularly in the unfavourable oxygen saturation levels. It was found that bacteriological parameters were higher in 2012 than in 1998 and 2013. The data showed no significant differences between transparency, temperature, pH and electroconductivity in 1998, 2005 and 2010 in comparison with 2011, 2012 and 2013. With large numbers of new chemical substances entering river ecosystem, continuous monitoring systems for their detection will become increasingly important with respect to ecological impacts they produce, in addition to other toxic effects. Thus the challenges to continuous physical, chemical, biological and bacteriological monitoring will be immense. Finally the importance of integration of biological and chemical monitoring has to be emphasized.

**Keyword:** *Monitoring; Budapest; Danube River; water quality; ecological and bacteriological parameters*

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## **BIOAVAILABILITY OF CADMIUM AND LEAD IN SOIL AMENDED WITH SEWAGE SLUDGE**

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The major benefits of sewage sludge application are to increase the major plant nutrients; provision of some essential micronutrients and improve the soil physical properties. Plants take up heavy metals from soil through different reactions such as: absorption, ionic exchange, redox reactions, precipitation – dissolution, etc. It can be said that the solubility of trace elements depends on minerals in soil, soil organic matter, pH, redox potential, soil temperature and humidity. The sewage sludge application to agricultural land could affect potential availability of heavy metals. The solubility and mobility of metals throughout sludge application is controlled by organic matter and oxides that can prevent excessive heavy metals mobilisation. A pot trial was carried out to illustrate the availability of cadmium (Cd) and lead (Pb) on corn plants grown on clay loam chernozem meadow treated with urban anaerobically stabilized municipal sewage sludge. Corn plants were grown in the soils following the treatment with the sewage sludge. The addition of sewage sludge significantly increased the average dry plant biomass. The Cd and Pb uptake by corn plants generally followed the differences in metal inputs, but quantitative differences were found between heavy metals, The availability and phytotoxicity of Cd and Pb were influenced by soil properties and organic matter content and metal content in the sewage sludge as well. Furthermore, with repeated sludge applications as soil conditioner, the heavy metals may accumulate in the soil increasing the phytotoxic concentrations for crop production, although at certain concentrations the metals may be deficient for crop growth. Previous research work has shown that crop cultivation on sewage sludge treated soils can be done without contamination risk to soils or phytotoxic uptake by the crop plants. These observations were based on short-term experiments. The possible long-term heavy metal accumulation in soils and subsequent uptake by crops does pose a threat to the sustainability of sewage sludge on agricultural soils. Therefore, strict monitoring procedures are necessary and the correct management practices (e.g., controlling soil pH above 6.5 through liming). The value of sewage sludge as a soil conditioner and organofertilizer was seen in the experiments although long-term experiments under field conditions still need to be done to assess possible accumulation of heavy metals in agricultural soils.

**Key words:** *bioavailability, corn plant biomass, heavy metals, sewage sludge*

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## PROBLEMS OF SUN COLLECTORS OPERATIONAL

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### ABSTRACT

In order to efficiently solve the problems created by the deepening energy crisis affecting Europe and the world, governments cannot neglect the opportunities of using the energy produced by sun collectors. In many of the EU countries there are sun collectors producing heat energy, e.g. in 2011 in the area of EU27 (countries which belong to European Union) + Switzerland altogether 37519126 m<sup>2</sup> were operated, which are capable of producing 26.3 GWh heat energy. The energy produced by these sun collectors is utilized at the place of production. In the near future governments will have to focus more on spreading and using sun collectors. Among the complex problems of operating sun collectors, this article deals with determining the optimal tilt angle, directions of sun collectors. We evaluate the contamination of glass surface of sun collector to the produced energy. Our theoretically results are confirmed by laboratory measurements. The purpose of our work is to help users and engineers in determination of optimal operation parameters of sun collectors.

**Keywords:** heat energy, direction of sun collector, contamination of surface

### INTRODUCTION

In order that the surface of the sun collectors should be able to convert as much as possible from the energy transported by the arriving sun rays we must be familiar with the Sun-Earth movements (Duffie and Beckman, 1980). When determining the geometry of the Sun-Earth movement we tried to use the simplest formulas possible that engineers and enterprises designing the sun collectors may be able to work with. Figure 1 shows the geometric relationships of sun collectors placed on the Earth's surface.

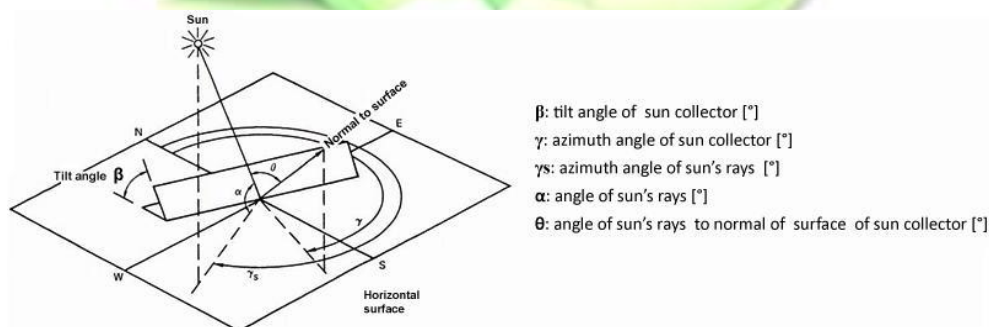


Figure 1. Relationships of the incident beam radiation and a tilted surface (Dickinson and Cheremisinooff, 1980)



The amount and intensity of the radiation arriving at the surface of the sun collector also depend on the relative position and movement of the Earth-Sun (Patkó, 2010). Figure 2 depicts the movement of the Sun and Earth in relation to each other, the so-called sun paths at 48° north longitude (Patkó, 2009).

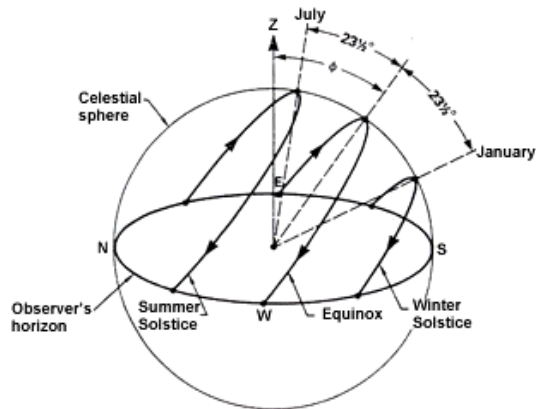


Figure 2. Visualization of the sun paths the sky (Dickinson and Cheremisinooff, 1980)

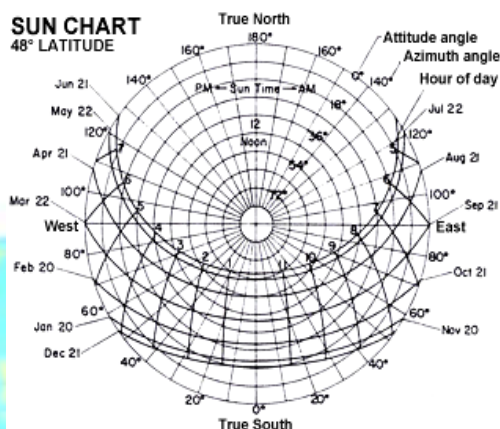


Figure 3. Sun charts (Dickinson and across Cheremisinooff 1980)

At 48° latitude of the northern hemisphere the figure shows the sun's movement at the time of the winter and summer solstice and the equinox. If we prepare the top-view picture of this figure, we get the sun chart of this northern latitude (Figure 3) (Patkó, 2009). According to the sun charts (Hand, 1978) the sun gets the closest to the sun collector placed in the centre of the figure i.e. the observation point, at the time of the summer solstice, i.e. at 12.00 June 21<sup>st</sup>. It is obvious from this figure that if the sun collector is directed in the true south direction, it gets the largest possible radiation energy. During the day the angle of the sun to the normal of the sun collector ( $\theta$ ) changes according to the passage of time (Ibrahim, 2008). If we want the sun to reach the surface of the sun collector at the most optimal angle during the day, continuous east-west sun collector adjustment must be provided. In our work with change tilt angle  $\beta$  to the horizontal surface and we determine those tilt angles ( $\beta$ ) at which, during the year, the collector will be capable of transforming the largest energy deriving from the sun. This means that the tilt angle of the ( $\beta$ ) should be modified according to the movement of the sun each day of the year.

This is technically unimaginable and impracticable; therefore in this section of our article we determine the most optimal tilt angle values at the tested geographical location (N 47.5°):

- for the whole year  
(the tilt angle of the collector ( $\beta_{\text{year}}$ ) is not modified during the year),
- seasonally  
(the tilt angle of the collector is modified according to the four seasons. Therefore four tilt angles will be defined ( $\beta_{\text{summer}}$ ,  $\beta_{\text{winter}}$ ,  $\beta_{\text{autumn}}$ ,  $\beta_{\text{spring}}$ )).

The Earth orbits the Sun in an elliptical orbit with an eccentricity of 3%. The Earth makes a full circle in a year. The Earth does not only go around the Sun but it also rotates around its own axis at a speed of one rotation per day. Its own axis is tilted at  $\delta=23.5^\circ$  from the axis of the orbit around the Sun. In this way during its orbit around the Sun, the northern hemisphere gets closer to the Sun in the summer than the southern hemisphere, and this is changed in winter. In spring and autumn the tilting of the Earth's axis ( $\delta$ ) is such that the distance of the northern



hemisphere and the southern hemisphere relative to the Sun is the same. This is shown in Figure 4.

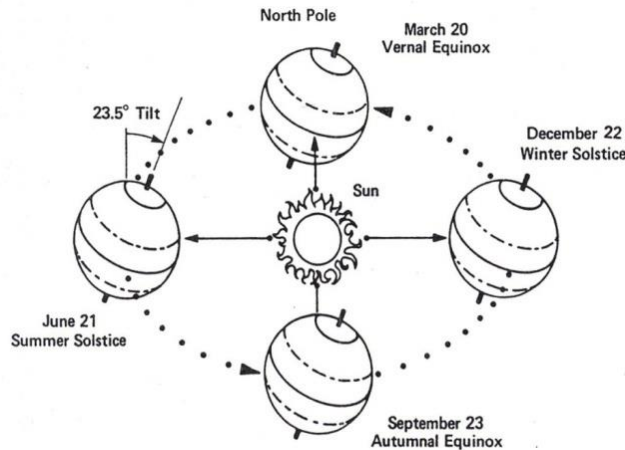


Figure 4. Diagram of the Earth's orbit around the Sun  
(Dickinson and Cheremisinooff, 1980)

On the basis of our theoretical (Patkó et al., 2013) considerations and experience we have accepted that – globally, regarding a whole year – the tilt angle of the sun collector equals the value of the northern latitude, i.e.:

- $\beta_{\text{year}} = \Phi$

so at the test site, in Budapest, (47.5° N):

- $\beta_{\text{year}} = 47.5^\circ$

According to [1]  $\beta_{\text{year}} = \Phi$  should be modified in the following way:

- $\beta_{\text{year}} = \Phi + (10^\circ \div 20^\circ)$

We disregard this assumption, proposal during our tests. The – theoretical – values of seasonal tilt angles are the following according to Figure 6.

- $\beta_{\text{summer}} = \Phi - \delta$
- $\beta_{\text{winter}} = \Phi + \delta$
- $\beta_{\text{autumn}} = \Phi$
- $\beta_{\text{spring}} = \Phi$

The tilt angles of the sun collectors at the test site, in Budapest, (47.5°N):

- $\beta_{\text{summer}} = 24^\circ$
- $\beta_{\text{winter}} = 71^\circ$
- $\beta_{\text{autumn}} = 47.5^\circ$
- $\beta_{\text{spring}} = 47.5^\circ$

We made some measurements in order to verify the correctness of the values.

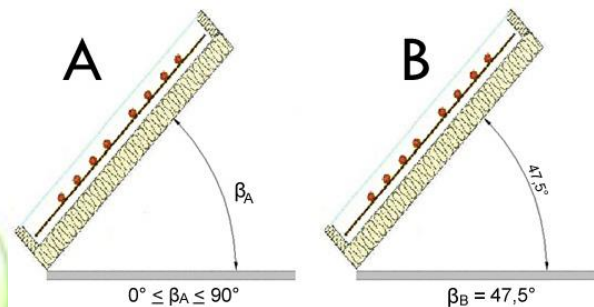
## MATERIAL AND METHODS

### Laboratory measurements

We made a series of measurements with glass covered flat collectors in order to determine the ideal collector tilt angles ( $\beta$ ) in the area of Budapest (47.5°N). The main point of the measurement is to determine the optimal tilt angles ( $\beta$ ) as a result of comparative series of measurements. We measured the thermal characteristics of two sun collectors parallel, at the



same time. We had set the tilt angle of one collector to a value – which we defined – relating to the whole year ( $\beta_{\text{year}}$ ) and we did not change that during the series of measurements. This collector was marked collector B. The tilt angle of the other collector marked A was modified according to the seasonal values defined by us ( $\beta_{\text{summer}}$ ,  $\beta_{\text{winter}}$ ,  $\beta_{\text{autumn}}$ ,  $\beta_{\text{spring}}$ ) during the measurements. Figure 5 depicts the collectors.

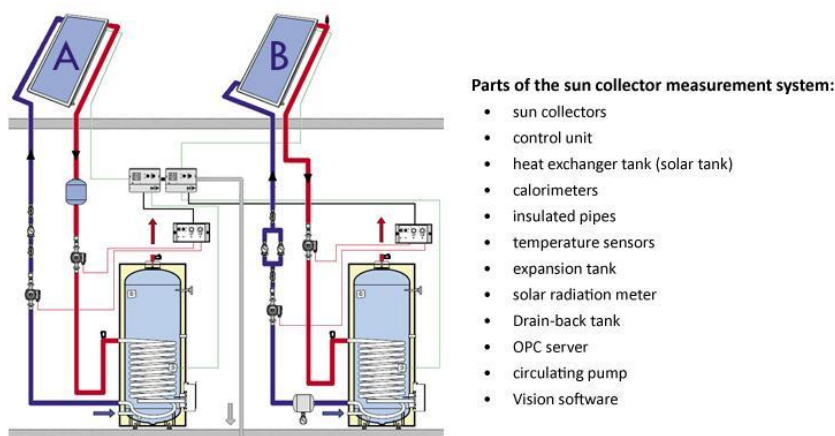


*Figure 5. Tilt angles of collectors*

During the measurements the thermal characteristics of both collectors were measured and we made our conclusions by comparing these. The measurements were made in the summer, autumn and winter of 2011. In our opinion the autumn and spring measurements – relative to each other – must produce the same result, so we did not make any measurements in spring. This conclusion is supported by Figure 6 as well.

#### **Description of the measuring equipment**

In order to confirm and support by experiments the sun collector tilt angles ( $\beta$ ) determined theoretically in the previous sections, a special measurement station was created at Óbuda University (Budapest, Hungary) and installed on the roof of the building. With the measurement equipment – which is fully automated and controlled by a computer – we were able to continuously measure the thermal characteristics of the sun collector in summer, autumn and winter. The conceptual layout of the measuring equipment is shown in Figure 6. The equipment incorporates two (2.0 m<sup>2</sup>) glass covered flat collectors (marked A and B) which were developed by us. The system has two loops. The primary loop which consists of the sun collector and the liquid heat exchanger placed in the solar tank is filled up with antifreeze liquid medium. The secondary loop utilizes the heat content of the water in the solar tank. Measurement points were established in the measuring equipment to measure the water and liquid material temperature, and the mass flow of water and liquids. In order to increase the safety and reliability of the measurements, we measured the amounts by MBUS and PLC systems. The measurements were processed by a monitoring computer and presented them on the screen by VISION system. During the measurements great care was taken to make sure the temperatures and mass flows of the medium entering the collectors – in the case of both collectors – should be equal. This was ensured by keeping the secondary loops and the tank temperatures at a constant value. The characteristics of the external atmosphere were measured by a meteorological station located on the roof and equipment measuring solar radiation, and the results were entered into the monitoring computer. Special care had to be taken of the winter measurements. The system had to be protected against freezing in a way that by the beginning of the – daily – measurement the temperature of the solar tank should not be higher than 2÷3°C. The conceptual layout of the measuring equipment is shown in Figure 6.



*Figure 6. Sun collector measurement system*

### **Measurements of optimal tilt angel ( $\beta$ )**

We set the tilt angle of collector B to  $\beta_{\text{year}} = 47.5^\circ$  and kept it at the same angle during the measurements. We set the tilt angle of collector A to three values in each season. These values are the seasonal values which we determined, i.e.:

- $\beta_{\text{summer}} = 24^\circ$
- $\beta_{\text{winter}} = 71^\circ$
- $\beta_{\text{autumn}} = 47.5^\circ$

During the measurements we measured the temperature and the mass flow of the liquids entering and leaving the sun collectors, the temperature of the solar tank, the amounts of heat carried off the solar tank as well as the data of the external atmosphere and solar radiation. During the measurements it was ensured that the temperatures and mass flows of the medium entering the collectors should be equal.

According to the previous chapters the value of entry temperatures of both sun collectors and the value of mass flows of the medium flowing through the collectors were the same during the measurements. In such cases if we want to compare the power of the collectors ( $P_A, P_B$ ). The power relation ( $R_{P_A/P_B}$ ) of the two tested collectors should – approximately – equal the relations of the exit temperatures of the collectors, which were determined in our earlier paper [14]. The determined power relations tilt angle  $\beta_A$  of collector A (with modified tilt angle) and the deviation of the calculated power relations – according to the seasons – were given in Table 1.-Table 3.

*Table 1: Summer,  $\beta_B = 47.5^\circ$*

$\beta_A$ [°]	$R_{P_A/P_B}$ [%]	Deviation
24	141	7.23
47.5	100	2.59
71	86	2.46

*Table 2: Autumn,  $\beta_B = 47.5^\circ$*

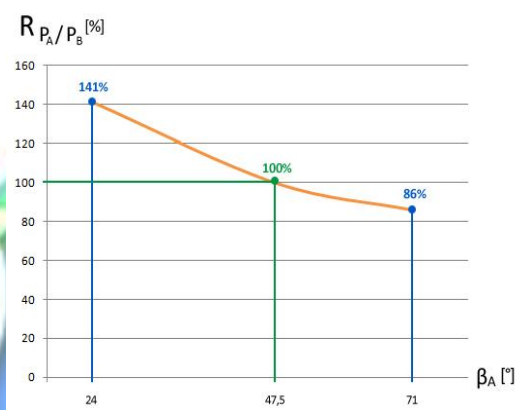
$\beta_A$ [°]	$R_{P_A/P_B}$ [%]	Deviation
24	80	1.55
47.5	100	1.83
71	81	3.37



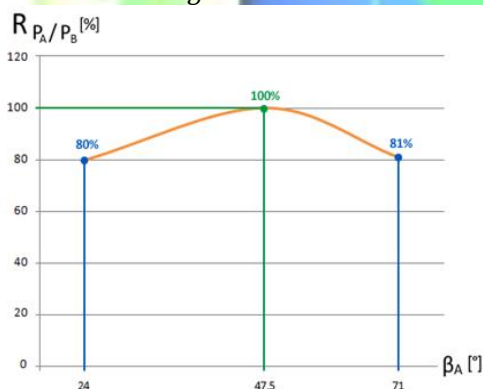
*Table 3: Winter,  $\beta_B = 47.5^\circ$*

$\beta_A$ [°]	$R_{P_A/P_B}$ [%]	Deviation
24	80	5.54
47.5	102	4.12
71	110	5.49

These diagrams shows - approximately - the  $R_{P_A/P_B}$  change of the power relation of collectors A and B at angles  $\beta_A$  and  $\beta_B = 47.5^\circ$ =constant value per season.



*Figure 7. Power relations of collectors in summer,  $\beta_B = 47.5^\circ$*



*Figure 8. Power relations of collectors in autumn,  $\beta_B = 47.5^\circ$*



*Figure 9. Power relations of collectors in winter,  $\beta_B = 47.5^\circ$*

**Measurements of infect of surface contamination**

During operation, the surface of solar collectors gets contaminated. Depositing and airborne aerosols deposit on glass surfaces and therefore reduce glass transparency, which results in reduced solar collector power. No literature has been found on the relation between surface contamination of solar collectors and power drop. It is important though to carry out experiments to explain the relation between surface contamination of solar collectors and power drop. By changing surface contamination of solar collector B the different efficiency curves at different contamination rates were determined:





$$\lambda \eta_f \left( \frac{t_s - t_a}{I} \right)$$

Where  $t_s$  is the solar collector average surface temperature,  $t_a$  is ambient temperature, and  $I$  is irradiance. To model surface contamination, carbon black was spread on the surface. In the course of measurements solar collector efficiency curves were taken at 4 different degrees of contamination: 0 g/m<sup>2</sup>, 75 g/m<sup>2</sup>, 150 g/m<sup>2</sup>, and 225 g/m<sup>2</sup>. Figure 10 shows the characteristic curves determined by measurements.

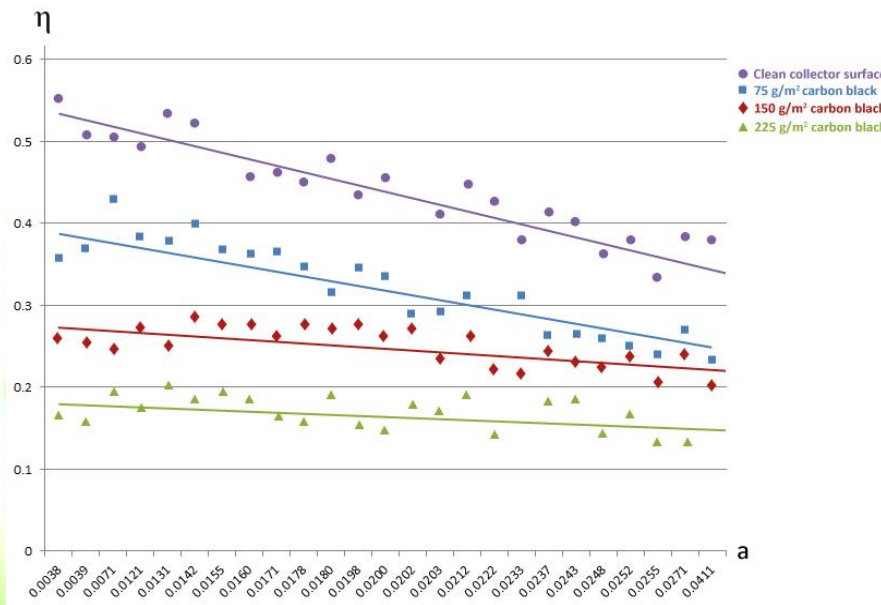


Figure.10. Relation between surface contamination and collector efficiency

According to Figure 10 it can be established that the more the surface of solar collector is contaminated the further efficiency curves are drifted toward lower efficiency value ranges. Experimental values are summarized in table 4.

Table 4: Surface contaminations and efficiency curve data

No.	Contamination [g/m <sup>2</sup> ]	Deviation R <sup>2</sup> [-]	Regression line
1	0	0.4215	$\eta = -0.0079a + 0.5147$
2	75	0.1828	$\eta = -0.0057a + 0.3917$
3	150	0.1901	$\eta = -0.0021a + 0.2749$
4	225	0.0847	$\eta = -0.0013a + 0.1808$

where:  $a : \frac{t_s - t_a}{I}$

#### Theoretical approach to the orientation of sun collectors

Orientation is of great importance in terms of solar collector performance. In the literature papers studying orientation have assumed solar collectors are faced to the true north in the South Hemisphere or the true south in the North Hemisphere. Figure 1 shows that the angle between the vertical projection of sunlight on the ground and the true north ( $\gamma_s$ ) is called the azimuth of



sun, while the angle between the vertical projection of the normal of collector surface and the true north ( $\gamma$ ) is called the azimuth of collector.  $\beta$  is tilt angle of solar panel, and  $\theta$  is the incidence angle of sunlight.

If the observer is located at or near the Equator, then the orientation of solar panels needs not to face the right direction (Calabro, 2009). Figure 1 clearly suggests that solar collectors work at optimum performance if  $\gamma = \gamma_s$  and  $\theta$  values minimum, that is  $\theta = \theta_{\min}$ .

Sun path and collector tilt angle ( $\beta$ ) also affect  $\theta$ . Theoretical considerations and findings in the literature suggest that solar collector power will decrease if panels are not oriented to the true south ( $\gamma=180^\circ$ ) in the Northern Hemisphere. According to our experiments, power at a given tilt angle ( $\beta$ ) may drop by 20-60%, depending to the rate of deviation from the true south. Considering that solar collector surface is exposed not only to direct radiation ( $I_{\text{dir}}$ ) but also diffused radiation ( $I_{\text{diff}}$ ), the total irradiation of surface is  $I_{\text{total}} = I_{\text{dir}} + I_{\text{diff}}$  (Chang, 2008). Taking Sun constant ( $1353 \text{ W/m}^2$ ) and atmospheric losses (57%) into account, the value of direct radiation is  $I_{\text{dirmax}} = 582 \text{ W/m}^2$ . Based on experimental values, diffuse radiation ( $I_{\text{diff}}$ ) is  $I_{\text{diff}} = I_{\text{dirmax}} \cdot (0.4-0.8)$ . It means that with  $\gamma=180^\circ$  and at  $\beta = \beta_{\text{opt}}$ . The irradiation solar collector surfaces are exposed to be:

$$I = I_{\text{dir}} + I_{\text{dirmax}} (0.4-0.8)$$

At  $\gamma = 90^\circ$  or  $\gamma = 270^\circ$ , or at orientation to the west or east, respectively, the irradiation solar collector surfaces are exposed to is:

$I = 0 + I_{\text{dirmax}} (0.4-0.8)$ , which results in a power drop by 20-60%. This expected drop in performance is seen in Figure 11, where  $\Delta P$  is the change in solar collector power caused by deviation in orientation.

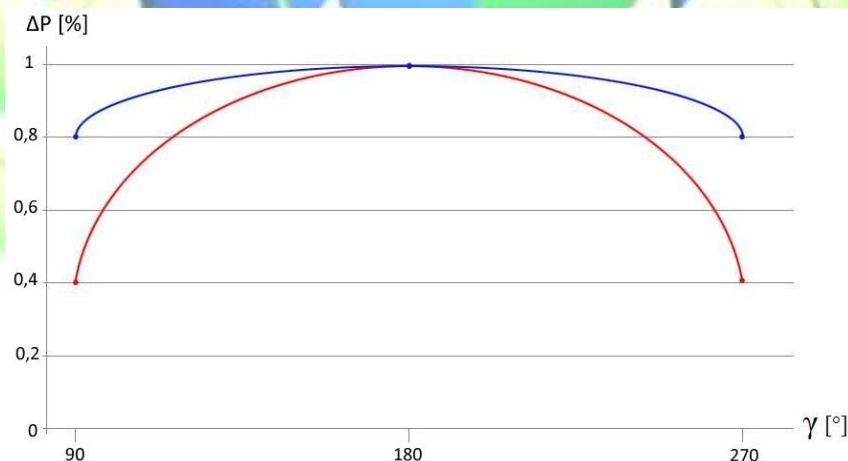


Figure 11. Optimum tilt angle ( $\beta_{\text{opt}}$ ) drop in solar collector power in function to azimuth angle ( $\gamma$ )

## CONCLUSION

Considering the efficient operation of sun collectors Óbuda University established a special measurement station capable of measuring the thermal characteristics of several sun collectors at the same time. Based on the laws of the Sun – Earth relative movement published in the specialist literature we determined the optimal tilt angle of the sun collectors at which the



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energy producing capability of the collector is optimal. In this way we determined a set-up angle for a whole year and the collector tilt angles for the four seasons (autumn, winter, spring, summer). Through laboratory measurements we confirmed our conclusions made theoretically. Our measurements made it clear that if the sun collector is not set at the right angle, the power of collector falls by up to 10-20%. Figure 7 – Figure 9 graphically depict this decrease in power due to improper tilt angles. If the tilt angle of the sun collector is not modified during the year, the power of the collector in summer – when the possibility of energy transformation is the best – is up to 20-30% less than the optimal value. In spring and autumn the operation and energy producing capability of the sun collector is optimal at this tilt angle ( $\beta = \phi = 47.5^\circ$ ). For the measurements we used a special sun collector developed by we, whose construction cost is lower compared to the commercial sun collectors available in Hungary. In the future we find it necessary to repeat our measurements under more precise circumstances, with more tilt angles and at least four collectors in parallel. We hope that those results will give us more accurate information how to modify the tilt angles of sun collectors. The effect of contamination of solar collector surface on collector performance and collector efficiency characteristic curve were determined. Based on theoretical considerations the expected drop in solar collector power was determined with collectors not facing the true south (in the northern hemisphere).

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## **GREEN PURCHASING AS A TOOL OF IMPROVING ENVIRONMENTAL PERFORMANCE – CASE STUDY OF IMPLEMENTATION IN BUSINESS COMPANY**

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### **ABSTRACT**

Many organizations worldwide are making an effort to contribute to sustainable development. One of the ways is that they use their purchasing power to choose environmentally friendly products and services. This movement is known as green purchasing. Green purchasing gives the opportunity to save materials and energy, reduce the volume of waste and pollution and help to improve environmental performance of the company. The paper provides short introduction to green purchasing, its background and principles. These basic principles are applied in the model of the small sized enterprise with the aim to demonstrate how implementation of green purchasing can increase energy savings, decrease CO<sub>2</sub> production, and can improve overall, not only environmental performance of the company. In this sense, the green purchasing can be seen as an effective tool of how companies can make practical steps to decrease their carbon footprint and contribute to greater movement to reduce negative impacts of climate changes.

**Keywords:** *green purchasing, company, environmental performance, CO<sub>2</sub> production, energy consumption*

### **INTRODUCTION**

Environmentally Preferable Purchasing (EPP) - also known as green purchasing or affirmative procurement - is the selection and acquisition of goods and services that most effectively minimize negative environmental impacts over their life cycle, from product design, development and production/provision, through product use, to the ultimate handling (i.e. recovery, recycling, re-use and/or waste disposal) of whatever remains of the product at the end of its useful lifespan.

The aim and challenge of green purchasing to integrate environmental and social considerations into the purchasing process, with the goal of reducing adverse impacts upon health, social conditions and the environment, (Rusko and Duchoň, 2007) via energy savings, efficient and effective use of natural resources, reducing the harmful impact of pollution and waste, encouraging innovations and practical expression of organization's commitment to sustainable development.

This voluntary tool of environmental policy was inspired and derived from green public procurement, which is especially used in public sector, however, authors demonstrate, that green purchasing principles can be applied in small sized enterprises and advantages of its application are significant both from environmental and economic point of view. (Chovancová, 2011)

## MATERIALS AND METHODS

Green purchasing involves identifying, selecting and purchasing products (i.e. goods and services) with significantly less adverse environmental impacts than competing products. (Rizza, 2008). Sustainable development involves using the Earth's natural resources (i.e. both renewable and non-renewable resources) to fulfil our present needs without affecting the needs of next generations. "Green Purchasing" is an important element to achieve sustainable development.

Many companies have had the perception that green means more expensive. (Kanichová, 2008) (Hrubý, 2007) (Hrazdilová Bočková and Škoda, 2014) Actually, environmentally preferable products are sometimes more expensive to purchase than alternative products. This circumstance can discourage green purchasing by consumers seeking lower costing products without significant environmental benefits. However, in many cases, green purchasing can also save money, protect staff and reduce liability (European Commission, 2011), so buying greener products does not necessarily mean paying more, especially when other cost factors are considered. The aim of this paper is to introduce green purchasing as an important tool of sustainable development and show that its implementation even in small company can contribute to significant costs reduction, and enhance human and environmental safety. In the next part of the paper the methods of analysis, comparison, induction and deduction were used.

## RESULTS AND DISCUSSION

Principles of green purchasing were applied at small sized enterprise titled PROLI Ltd. It is a private enterprise with Swiss participation dealing with the sale of industrial and office interior luminaires (IP20 fluorescent lamps, downlights, fluorescent lamps IP54 / IP65, HID lights, emergency lights) and also exterior lamps (HID lights IP54 / IP65, street lights, light sources and others) with its head office in Košice. The company has two branches in Partizánske and Bočiar. The company represents small businesses because employs eight full-time employees.

Branch office is located in the older sprawling building, which represents the major part of the storage space and the remaining part is made up of office space. Ground plan is shown in figure 1. Storage is inadequately illuminated by daylight, and therefore consumes unnecessary amounts of electricity for lighting with artificial light.

To achieve economic efficiency as well as improve energy and environmental performance, we made recommendations related to the core business of the company – light. We recommended installing the skylights in storage areas, and replace current neon tubes and halogen bulbs with LED bulbs in both storage and office parts of building.

The monthly cost of electricity consumption for lighting in the company represents a sum of approximately € 100. Table 1 describes the current state of electricity consumption of lighting in surveyed company. For the calculation we considered ten hour operation of the business six days a week.

Table 1 Current state in electricity consumption

Facility	Consumption per hour (W/h)	Operating hours per year	Consumption per year (kWh / year)
Storage lighting (neon tubes of 50-80W)	4 000	2 880	11 520
Office lighting (35 pcs halogen-45W)	1575	2 880	4 536

Total consumption	5 575	2 880	<b>16 056</b>
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Table 2 calculates selected economic and environmental characteristics of energy consumption on lighting in the company, such as energy consumption, prices and CO<sub>2</sub> production. Price of electrical energy is set according to energy producer - Východoslovenská energetika a.s. price list for SMEs. (RWE Group. 2014) CO<sub>2</sub> production is calculated in accordance with regulation no. 311/2009. It is the regulation by the Ministry of Construction and Regional Development of the Slovak Republic, which determines the amount of produced CO<sub>2</sub> in kg per kWh.

Table 2 Current economic and environmental characteristics of lightning

Facility	Consumption per year (kWh/year)	Price (€/kWh)	Total price (€)	CO <sub>2</sub> production (kg / kWh)	CO <sub>2</sub> production - total (kg/kWh)
Storage lighting (neon tubes of 50-80W)	11 520	0,0672	774,14	0,62	7 142,4
Office lighting (35 pcs halogen-45W)	4 536	0,0672	304,82	0,62	2 812,3
<b>Total</b>	<b>16 056</b>	<b>0,0672</b>	<b>1 078,96</b>	<b>0,62</b>	<b>9 954,7</b>

A significant part of the building consists of storages, which are regularly used. Whereas in the storage facilities are inadequate supply of daylight, indoor electrical lighting is necessary. Lack of daylight is caused by the high buildings in company's neighbourhood, which prevents the penetration of light through the windows of the storage. Therefore it would be appropriate to implement the skylights that bring daylight and thus reduce unnecessary energy consumption. The installation of skylights does not require building permission.

Specification of the proposed skylight studied for the enterprise:

- Type of skylight: Silver 800 instant
- Diffuser diameter: 760 mm
- Radiance: 26690 lm (replaces about 13 bulbs 58W/230V efficiency 45% = 2080 lm)
- Lighted area: 40 m<sup>2</sup>
- Length skylight: 1.11 m
- Height above surface: 5.9 m
- Light reflectivity: more than 99.97%
- Life: min 25 years
- Reduced energy consumption: 80% (impact of external lighting conditions)

Information on the dimensions of the storage:

Storage consists of four parts, each of which has the following parameters:

- Building height: 7 m
- Width of the hall: 6 m
- The length of the hall: 13.5 m
- Height of skylight above the floor: 5.9 m

Product price



To the lightning of the storage the six skylights will be necessary to install. The price is determined as follows:

- The price of skylight with all the components: € 4,508.60 (price is determined by the price list of Light way - the best bid corresponding to the requirements of purchaser)
- Assembly: € 540

Analysis of lighting in the company PROLI Ltd. showed that two-thirds of lighting is produced by neon tubes and one third by the light form halogen bulbs. We proposed to replace the original lighting by LED lighting.

LED lighting offers a 100% replacement for the classic, compact and energy efficient light bulbs. 92% of the energy is converted to light and only 8% to heat. In terms of energy efficiency it refers to the A class which represents the highest energy efficiency. LED bulbs are very efficient light sources because light bulb immediately issues not blinking light, does not contain mercury and does not issue or IR or UV radiation. There are different quality versions available in the market. In PROLI Ltd. we suggest the exchange of neon tubes and halogen bulbs for 50 pieces of LED tubes in storage and 35 pieces of LED bulbs in office. Specification of LED tubes is presented in Table. 12

Table 3 Lightning characteristics in PROLI Ltd.

	<b>50 pcs LED tubes</b>	<b>35 pcs LED bulbs</b>
Type:	T8	E 27
Input:	24 W (replaces neon tubes 80 W)	4,6 W (replaces 45W halogen lamp)
Dimension:	29x29x1200 mm	60x110x60 mm
Beam angle:	120 °	180 °
Operating life:	35 000 hours	40 000 hours
Light color:	4500 K- neutral white	6500K- daily white
Luminous flux:	2400 lm	400 lm
Led No.:	366 x	6 x 6
Dimmable:	no	no
Price per piece:	42 €	11 €
Total price:	1932 €	330 €

Installation of skylights can save 80 % of energy spent for lightning of storage, due to external light conditions. The remaining 20% of the operation time, we suggest using efficient LED tubes. Lighting of storage represents three quarters of energy consumption for lighting areas of the building. In the office part we suggest to replace 35pcs of halogen bulbs with LED bulbs.

The following table (Table 4) shows energy consumption after the installation of LED lighting and skylights. Table 5 shows the new state of economic and environmental characteristics of lightning after installation of LED lights and skylights.

Table 4 New state of energy consumption after LED lightning installation

	<b>Consumption per hour (W/h)</b>	<b>Operating hours per year</b>	<b>Consumption per year (kWh/year)</b>
Storage lightning – new	1200	576	691,2

state (50 pcs of LED tubes (24W) + skylights)	(20% of current state)		
Office lighting – new state (35 pcs of LED bulbs (4,6 W))	161	2 880	463,7
Total consumption – new state	1 154,9		

Table 5 New states of economic and environmental characteristics of lightning

Facility	Consumption per year (kWh/year)	Price (€/kWh)	Total price (€)	CO <sub>2</sub> production (kg / kWh)	CO <sub>2</sub> production – total (kg/kWh)
Storage lighting (50 pcs of LED tubes (24W))	691,2	0,0672	46,45	0,62	428,5
Office lighting (35 pcs of LED bulbs (4,6 W))	463,7	0,0672	31,16	0,62	287,5
Total	1 154,9	0,0672	77,61	0,62	716

The following chart shows a comparison of the current state of electricity consumption and CO<sub>2</sub> production of lightning, and new state after installation of LED lights and skylights. The economic and environmental improvement is remarkable.

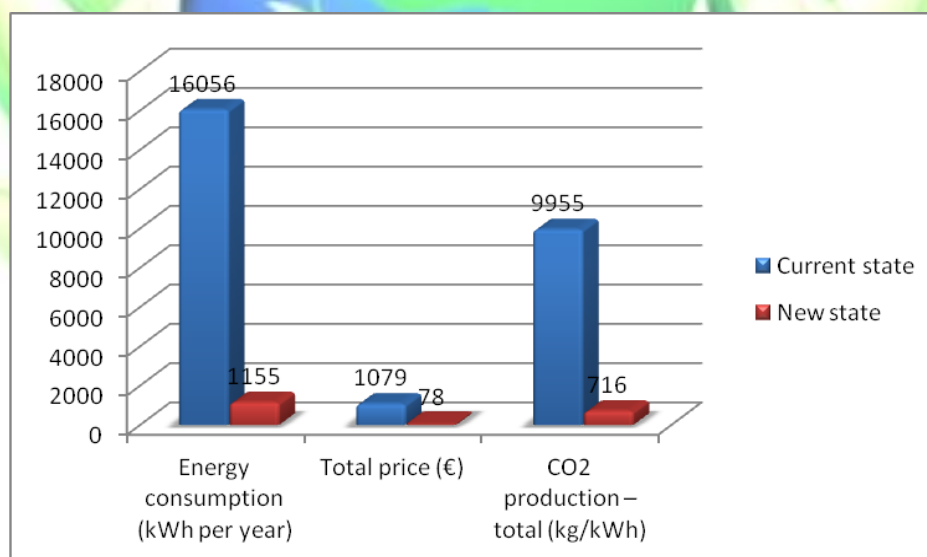


Fig. 4 Comparison of energy consumption, price and CO<sub>2</sub> production

Estimated expenses for purchasing the LED lights and skylights are 7 310 €. Annually this measure will save approximately 1001 €. Therefore we can estimate the return of investment to 9 years. From this point of view it represents a long term investment. This time can be shortened as we anticipate increase of energy prices in the future as well as long operating life of skylights and longer operating life of LED bulbs or tubes than neon tubes and halogen bulbs.

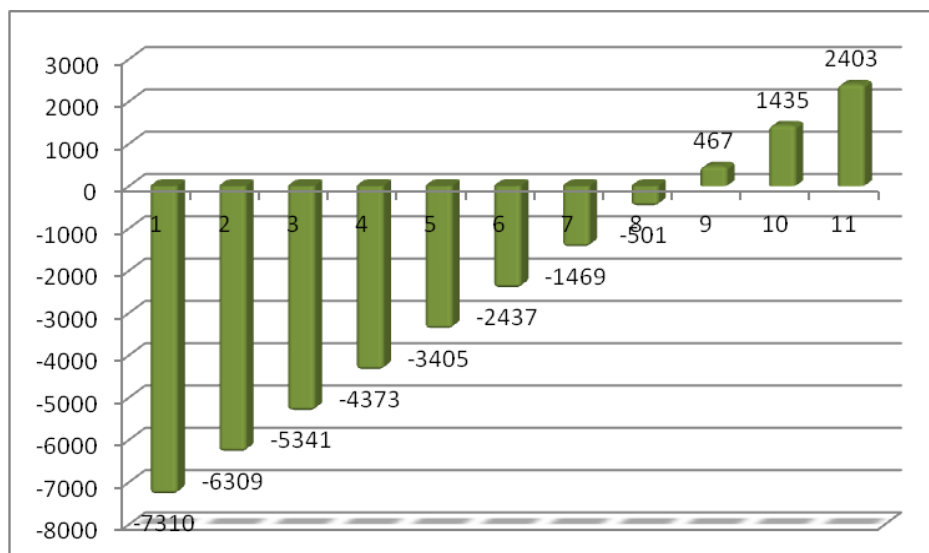


Fig. 5 Return of investment

## CONCLUSION

In presented case study we made an analysis of current state in the surveyed company. Based on realized analysis we can state that there is a space for the realization of efficient measures. The measures were focused on possibility of increasing energy efficiency of lighting in the company's building. Applying the proposed measures will result in saving electricity for lighting in the amount of 93% in comparison to the current state. Company would save annually the amount of € 968 and increase environmental efficiency due to reduction of CO<sub>2</sub> emissions production. Authors are convinced that implementation of simple principles of green purchasing can bring the win - win effect - the benefits on economic and environmental side, for every organization.

Continuous improvement and increasing scope are both desirable objectives of any green purchasing schemes. Surveyed company can continue in improving its energy efficiency and environmental performance by applying other steps of green purchasing in the future. These measures can include building insulation, or purchase of environmentally friendly all purpose cleaning products.



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## **ACUMULATION OF ZINC BY AMARANTHUS CRUENTUS PLANTS**

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The heavy metals belong to most toxic pollutants in the soil. Phytoremediation is one of most studied methods of soil purification. The aim of the project is to study the ability of amaranth plants (*Amaranthus cruentus* L.) to accumulation of zinc.

The experiment was carried out by the block method in four repetitions on 2.5 m<sup>2</sup> plots in field conditions in 2012 on the university field in Presov University in Presov (Slovakia). The Pribina and Aztec varieties of amaranth were used as experimental variants. The concentration of zinc was controlled by method of atomic absorption spectroscopy (Shimadzu AAS 7000). The content of zinc was measured in the root, aboveground part (stem+ leaves) and seeds.

The highest concentration was observed in the seeds as 0.881±0.022 mg·kg<sup>-1</sup>. Aboveground part of plants have been accumulated 0.511±0.026 mg·kg<sup>-1</sup>. The lowest content of zinc was found in the root 0.394±0.038 mg·kg<sup>-1</sup> (average value of two varieties). The content of zinc in Pribina and Aztec varieties was found 0.944±0.012 mg·kg<sup>-1</sup> and 0.818±0.032 mg·kg<sup>-1</sup>, respectively. The difference in the ability of accumulation of zinc by aboveground part of the plant and root was observed. The Pribina variety have accumulated less zinc in aboveground parts (0.414±0.021 mg·kg<sup>-1</sup>) but more in the root (0.854±0.024 mg·kg<sup>-1</sup>). The Aztec variety has shown the opposite results. The lowest content of zinc was found in the root (0.306±0.052 mg·kg<sup>-1</sup>) and highest in aboveground part (0.608±0.030 mg·kg<sup>-1</sup>).

The observed results shows ability of amaranth plants to accumulate the heavy elements, mostly in seeds.

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**Keywords:** *Amaranthus cruentus* L.; atomic absorption spectroscopy; heavy metals; phytoremediation

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## **ECOLOGICAL AND ENVIRONMENTAL LITERACY OF THE YOUNG GENERATION IN THE PROCESS OF EDUCATION FOR SUSTAINABLE DEVELOPMENT**

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### **ABSTRACT**

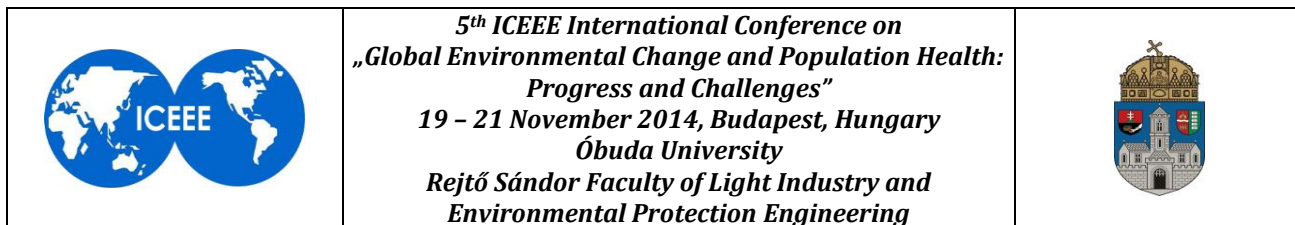
The work is focused on determination of the current state of ecological and environmental literacy of high school students with an emphasis on the current state of education and edification of sustainable development, shaping their attitudes and value orientation regarding the protection of nature and environment. The basic material for the processing of empirical research were data obtained from the primary collection through a questionnaire, which was formed by 16 open and closed questions, which were divided into three areas. The first part consisted of questions was focused on the implementation of ecological and environmental education and environmental protection, the second part was focused on the formation of attitudes, and the third was focused on the value orientation of students. The results were evaluated using mathematical and statistical methods. The results of the research showed that the significant role in the secondary school education was aimed to gaining ecological and environmental literacy science, especially biology, geography and ecology and social science subjects, especially social sciences, ethics and religious education. High school students are aware of the importance and necessity of educational activity towards nature conservation and the necessity of implementation of “environmental education” into the educational process. In matters of value orientation and attitudes towards the environment the secondary school students agree that environmental problems are indispensable to them. They are aware of the danger of environmental problems and consequences of human actions on the environment.

**Keywords:** *ecological and environmental education, sustainable development*

### **INTRODUCTION**

Principles of sustainable development are the most comprehensive and at the highest political level worded by United Nations Conference in Rio de Janeiro in 1992, which adopted Agenda 21, i.e. program of complex care of the environment of mankind in the 21st century. Agenda 21 presents opportunities to combat the devastation of land, air and water pollution, forest protection options and diversity of life forms, as well as the issue of possible negative evolution of climate on Earth. It addresses poverty, excessive consumption, health, and education as well as issues of rural and urban living. There are roles for everyone: governments, businessmen, trade unionists, scientists, teachers, indigenous people, women, youth and children. That document also states that many people do not comprehend the strong bonds between human activities and the environment because they have inaccurate and insufficient information. It is further stated that it is necessary to increase the sensitivity and commitment of people to find solutions for the environment and development issues (Demo et al., 2007; Klinda,





2001). Education can give people environmental and ethical awareness, values and attitudes, skills and behaviours necessary for sustainable development. To fulfil this, education must explain the environment not only in terms of science, but also in terms of socio-economic and in terms of human development. Primary education is the backbone of education in environmental issues and development.

Important role in this process plays an effective environmental education. It turns out that the schools need to be addressed and enforced tasks associated with the preparation for the sustainable development by a systemic approach linked with efforts to modernize the overall education on the threshold of the 21st century (Eliáš, 1994; Hilbert, 1996). The current level of environmental literacy of mankind is also reflected on the actual state of the environment. It is therefore necessary to examine its level and development opportunities. Environmental education is now part of the national educational program, which is defined as one of the seven cross-cutting themes. Environmental education as a cross-cutting theme pervades all school subjects. Its aim is to contribute to the development of pupil's personality that acquires the ability to understand, analyse and evaluate the relationship between man and his environment in the neighbourhood, while at the same time he understands the need for environmental protection worldwide. One approach to examine the effectiveness of environmental education is to measure Eco literacy of the students. Nowadays a literate man should be characterized by the ability to control information and communication technologies, work with information efficiently, master a foreign language, and to treat their environment considerably (Jakab and Kopcová, 2004 Kancír and Suchá, 2013).

The aim of the study was to determine the current state of ecological and environmental literacy of high school students with an emphasis on the current state of education and edification for sustainable development, shaping their attitudes and value orientation to the protection of nature and environment.

## **MATERIALS AND METHODS**

The basic material for the processing of empirical research were data obtained from the primary collection through a questionnaire, which was formed by 16 open and closed questions, which were divided into three areas. The first part consisted of questions focused to the implementation of ecological and environmental education and environmental protection, the second part was focused on the formation of attitudes, and the third was focused on the value orientation of students.

The results were evaluated using mathematical and statistical methods. In accordance with the aim of research, the following hypotheses were set:

D: We assume that high school students receive ecological and environmental literacy in natural science courses;

H2: We assume that in order to improve the current state of ecological and environmental literacy they require the inclusion of the environmental education courses as an optional course.

H3: We assume that secondary school students deal with environmental protection, ecological and environmental education in the school environment only;

H4: We assume that the source of information on the environmental problems of the earth and the environment is the school and the media.

**RESULTS AND DISCUSSION**

Survey attended 119 respondents - students (including 40 men and 79 women) aged 15-18 years from three selected secondary schools in Prešov. We used the method of random selection. In the first hypothesis, we assumed that high school students receive ecological and environmental literacy in science. This hypothesis, we verified on the basis of questions (Figure 1). The hypothesis was confirmed.

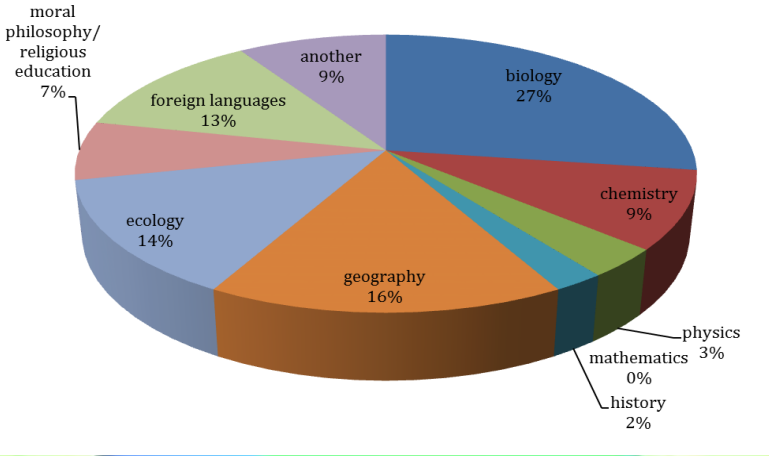


Figure 1 Which of your courses deal with environmental protection and environmental education?

In the second hypothesis, we assumed that in order to improve the current state of ecological and environmental literacy of students, they require the inclusion of the course of environmental education as an optional course. This hypothesis, we verified on the basis of questions (Figure 2). The hypothesis was rejected.



Figure 2 Should be the subject of environmental education included among the compulsory courses in high schools?

In the third hypothesis, we predicted that high school students deal with environmental protection, ecological and environmental education in the school campus only. This hypothesis we verified on the basis of question (Figure 3). The hypothesis was rejected.

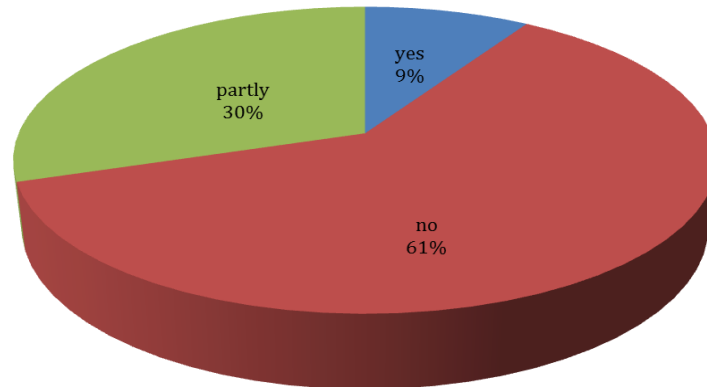


Figure 3 Do you consider the environmental protection, ecological and environmental education only at the school campus?

In the fourth hypothesis we assume that the source of information about the environmental problems of the Earth and the environment is the school and the media. This hypothesis, we verified on the basis of question (Figure 4). The hypothesis was confirmed.

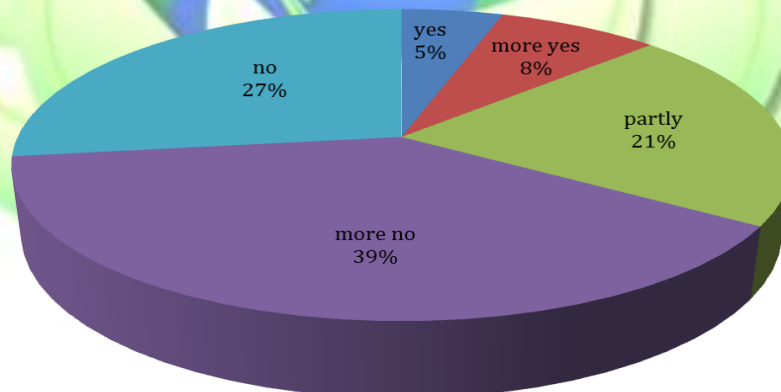


Figure 4 Do you discuss about environmental problems in your family?

The results of empirical research have shown the need for educational activity towards the care and protection of the environment requires necessity of the introduction of environmental and ecological aspects into all areas of human life, including educational process (Jozafová, 2000).





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„Global Environmental Change and Population Health:  
Progress and Challenges”  
19 – 21 November 2014, Budapest, Hungary  
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Important role in the education of secondary school aimed at obtaining ecological and environmental literacy plays especially courses such as biology, geography and ecology, and social science subjects, especially social sciences, ethics and religious education. Science subjects in accordance with the opinion of Kminiak and Pavličková (2001), have the educational function and social science subjects, have more influential, or character forming function. The aim of environmental education should be to teach pupils and students to think, present context, to perceive relationships and connections between man and his environment. High school students are aware of the importance and necessity of educational activity to nature conservation. For questions focused on value orientation and attitudes towards the environment, the secondary school students agree that environmental problems are indispensable to them (Švecová et al., 2004). They realize the danger of environmental problems and consequences of human actions on the environment. The current family in the process of bringing environmental mature personality does not play a significant role; the family has a low activity to engage in environmental conservation. The most important sources of knowledge about environmental issues among students, are the media and school (Švecová and Žákova 2007; Líšková, 2002).

## **CONCLUSION**

The results of the research showed that a significant role in the education of secondary school aimed at obtaining ecological and environmental literacy, especially biology, geography and ecology and social science subjects, especially social sciences, ethics and religious education. High school students are aware of the importance and necessity of educational activity to nature conservation and environmental education establishment remains in the educational process. In matters of value orientation and attitudes towards the environment, the secondary school students agree that environmental problems are indispensable to them. They realize the danger of environmental problems and consequences of human actions on the environment.

## **ACKNOWLEDGMENTS**

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## **NATURALNESS OF FOREST IN THE GÖDÖLLŐ HILLSIDE, HUNGARY**

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Land use and land cover change has a tremendous impact on our natural environment. On the one hand, people like nature (e.g. when they want to park their car during summer shopping underneath a nice big tree, or when they visit a lake for swimming they prefer the shade of a tree etc.), on the other hand “nature” bites: it is painful to collect fallen leaves, cut the grass, trees are blocking the view in the bend of a motorway, branches are falling on the road and making traffic dangerous etc.). Furthermore, nature provides goods and income for people so it is not easy to keep old growth forests, even in naturally protected areas. This is the reason why we analyzed former military maps from the 1770s until WWII and later CORINE Land Cover maps, to find out how the areal distribution of the forests in the Gödöllő Hillside has changed. We found that, while there were not relevant changes in the forest cover in the nature conservation areas (Gödöllő Hillside Landscape Protection District), some settlements and its urbanization processes caused tremendous changes in the natural environment, but, still, only little changes in bigger spots of the forest cover. We can conclude that the spatial distribution of the majority of the forested areas did not change in the last 200 years. The picture was too nice, and literature told us that species composition changed in a negative way and forests only look nicely on the map. We found that approx. 30% of the nature conservation area is covered by black locust that is invasive, suppress plants underneath its cover – except some couple of species – and remove soil nutrients, causing acidification. We found that besides the pressure from the community (people) and economy (e.g. forestry), there is a huge pressure on forested areas from hunters, cyclers, motorbikes, not to mention military activity. There are a huge number of people who wishes to use the natural environment, causing tremendous negative effects by noise, trampling, tree cutting etc. This last point is equally dangerous, as socio-economic approach is often neglected. Poor people tend to walk out to forest for fuel wood and carry home as much as they can by bicycle, small carts or on foot-in hand. There is a highway crossing the area where the runoff water was “elegantly” driven into the forest. The effect of runoff water from the highway has reached a point when it is causing so much degradation that endangers the highway itself. On the other hand, old trunks has been found at the forest floor, made it possible to compare present state of the trees with former trunk diameters that can be a good indicator of naturalness.

**Keywords:** *Gödöllő Hillside; forest; naturalness; historical data; maps*

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## **DELIMITATION OF VEGETATION PATCHES FOR ENVIRONMENTAL MONITORING: A QUANTITATIVE METHOD**

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### **ABSTRACT**

Vegetation is responsive to environmental changes. It has often (as in Central Europe and especially in the Carpathian Basin) a mosaic-like appearance, the patches being covered by stands of several community types. Environmental changes alter the composition and structure of these stands, causing shifts of the patch boundaries. This phenomenon can be applied in environmental monitoring. For this purpose, repeated vegetation mappings are needed. The task can be complicated however, because the patches in nature adjoin often by transition zones. Here a seeming contradiction appears: how to relate a field point to a community type, which can only develop on a certain positive area?

The proposed solving of this problem is based on determining the minimal surface where the characteristic species of a community type occur around the examined field-point. First of all, we define the minimal area of any species set at an arbitrary field-point. We assume that in the investigated area all the occurring vegetation units represented by reference stands and their (locally valid) differential species are established.

It is reasonable to consider a point more related to a community, if the differential species of this community occur on a smaller area around the point. Hence we determine the minimal area of each differential species set around the considered point and calculate the phytosociological affinity of the point to each community type  $c$  defined as  $a(P,c) = F(c)/t(c,P)$  where  $t(c,P)$  is the minimal area of differential species set  $c$  around the considered point  $P$  and  $F(c)$  denotes the mean minimal area of differential species of the community type  $c$ . If we make a vegetation map, a point will be classified to the community type to which it has the greatest affinity. If the point has the greatest affinity to two community types at once, it lies on their boundary. If we delineate the affinities as functions of the distance along a transect, the point of intersection designates the boundary.

The proposed method provides an uniform phytosociological basis for examination of transitions between several communities separated by plant species. The method's additional benefit is the possibility of statistical error estimation by calculating the standard deviation of the mean minimal area of differential species. The standard deviation can be diminished as desired by increasing the sample points in the reference stand. The outlined method was used to examine boundaries between dry grasses of Szársomlyó Mountain (South-Transdanubia).

**Keywords:** *phytosociology, community, boundary, affinity, environmental, monitoring*

### **INTRODUCTION**

Vegetation is responsive to environmental changes. It has often (as in Central Europe and especially in the Carpathian Basin) a mosaic-like appearance, the patches being covered by stands of several community types. Environmental changes alter the composition and structure

of these stands, causing shifts of the patch boundaries. This phenomenon can be applied in environmental monitoring. For this purpose, repeated vegetation mappings are needed. The task can be complicated however, because the patches in nature adjoin often by transition zones. In works of high standard the transition zone was examined on the basis of local differential species or direct gradient analysis via sample plot surveys along a transect (Matuszkiewicz 1972, van der Maarel 1976). However, also in this case the establishing of appropriate size and shape of plots seem to be extremely problematic. The conditions given by the Braun-Blanquet methodology for selection and delimitation of sample plots (relevés), i.e. physiognomic-structural and floristic homogeneity can not be fulfilled if the vegetation unforeseeably changes in space (Bagi 1991). Minimal area is also theoretically undefined in this case. Furthermore, the gradient value (e.g. van der Maarel's H-value) is only a measure of local heterogeneity, which hardly (if indeed) convincing tool to describe relations of complete plant communities.

All plant community stands have a horizontal structure, which can be reproduced by refined mapping (small plots or transect-profiles), but it do not facilitate the establishing of appropriate syntaxon. On the other hand, too big sample plots blur the spatial fine structure of the boundary. Different sizes and shapes of sample plots can give quite divergent results.

Here a seeming contradiction appears: how to relate a field point to a community type, which can only develop on a certain positive area?

Instead of surveying predetermined sample plots, the proposed solving of this problem is based on establishing the minimal surface where the characteristic species of a community type occur around the examined field-point.

## MATERIALS AND METHODS

First of all, we define the minimal area of any species set at an arbitrary field-point. Denote  $m$  the number of species in this set. For the examined point we search for the nearest individual of each species and indicate it conspicuously. The procedure is repeated in the number of species, i.e.  $m$  times. So eventually the nearest individual of each species of the set will be denoted. Now, we compose from the denoted points triangles so that each triangle leans on a side line of the previous one (Fig. 4.). The original point is considered only if it happens to get out of the polygon composed by the species. In the latter case this point will be connected to the polygon by a further triangle. If several polygons with the indicated points as their apices are possible, that of minimal area is to be chosen. In most cases this can be easily decided in the field by estimation, otherwise the areas of alternative polygons need to be determined. The area  $t$  of a polygon can be calculated as:

$$t = \frac{1}{4} \cdot \sum_{k=1}^{m-2} \sqrt{(x_k + z_k + y_k) \cdot (x_k + z_k - y_k) \cdot (y_k + x_k - z_k) \cdot (y_k - x_k + z_k)}$$

If no further triangle was necessary for the original point and

$$t = \frac{1}{4} \cdot \sum_{k=1}^{m-1} \sqrt{(x_k + z_k + y_k) \cdot (x_k + z_k - y_k) \cdot (y_k + x_k - z_k) \cdot (y_k - x_k + z_k)}$$

Otherwise here  $x_k, y_k, z_k$  are the side lengths of the  $k$ -th triangle. The summation must be performed for all triangles.





The obtained quantity we term the minimal area of the investigated species around the considered point.

Now, let us assume that in the investigated area all the occurring vegetation units represented by reference stands and their (locally valid) differential species are established. For practical purposes possibly frequent species are suitable, otherwise sometimes long distances should be also measured. For the sake of simplicity, consider two community types, A and B (the generalization to several community types is straightforward). Denote  $\alpha$  the set of differential species of community A, and  $\beta$  the set of differential species of community B. Consider e.g. the community A. We can determine the minimal area of its differential species  $\alpha$  around the considered point.

Now, we choose points at random in the typical stand of community A. For each point the minimal area of its differential species  $\alpha$  will be determined. After this we calculate the mean of these minimal areas. It can be considered as characteristic to the community A. We term this the minimal area of differential species of the community A. The same procedure is performed for the community B.

Thereupon, we can assign an arbitrary point on the investigated territory to a community type. It is reasonable to consider a point more related to a community, if the differential species of this community occur on a smaller area around the point. For this purpose we determine the minimal area of the differential species around the considered point and calculate for each community type the quantity

$$a(P,c) = F(c)/t(c,P)$$

Where  $t(c,P)$  is the minimal area of differential species set  $c$  around the considered point  $P$  and  $F(c)$  denotes the mean minimal area of differential species of the community type  $c$ .

Let us term the quantity  $a$  the phytosociological affinity of the point to the considered community type.

If we make a vegetation map, a point will be classified to the community type to which it has the greatest affinity. If the point has the greatest affinity to two community types at once, it lies on their boundary. If we delineate the affinities as functions of the distance along a transect, the point of intersection designates the boundary.

## RESULTS

The outlined method was used to examine boundaries between dry grasses of Szársomlyó Mountain (South-Transdanubia). Here a rock grassland (*Sedo sopianae-Festucetum dalmaticae* Simon 1964) border on a slope steppe (*Cleistogeni-Festucetum sulcatae* Zólyomi 1958). *Festuca dalmatica* occurs in stands of the latter too. The transition between them, and the adjacent zones constituted the subject of this examination.

The locally valid differential species were established. For the rock grassland they are as follows: *Carex liparicarpos* Gaud., *Asplenium javorkaeum* Vida, *Crupina vulgaris* Pers., *Helianthemum canum* (L.) Baumg., *Medicago minima* (L.) Grufbg., *Potentilla erecta* (L.) Rauschel, *Sedum neglectum* Ten., and for the slope steppe: *Cleistogenes serotina* (L.) Keng, *Geranium columbinum* L., *Hypericum perforatum* L., *Teucrium chamaedrys* L. Their occurrence is permanent and comparatively uniform in the related vegetation unit, while they show a significantly smaller constancy and/or abundance in others. Field-points were chosen in distances of 5 m along a transect, and the minimal area of both differential species set around each point was established. The mean minimal areas of differential species were calculated on the basis of 40-40 samples taken from typical stands of each vegetation unit. The estimated mean value for rock grassland:



3409 cm<sup>2</sup> (standard deviation: 8.62%), and for the slope steppe: 217 cm<sup>2</sup> (standard deviation: 6.17%). Thereupon the phytosociological affinity to both vegetation units was calculated around each chosen field-point.

Fig. 1 shows the results (with a logarithmic scale for the affinity). They seem to indicate, that the transition zone is a penetration complex (German: Durchdringungskomplex, Pfeiffer 1958, Dierschke 1994), rather than a continuum. Here the vegetation units alternate with each other in small mosaics, where the affinity is quite low (< 0.1) to both.

This complex could be interpreted as a form of self-organisation: in a transition setting, where both vegetation units have the same possibility to develop, the vegetation's biotic effect on the habitat plays an important role. At first small random soil differences get stronger, the positive feedback maintains the vegetation mosaic.

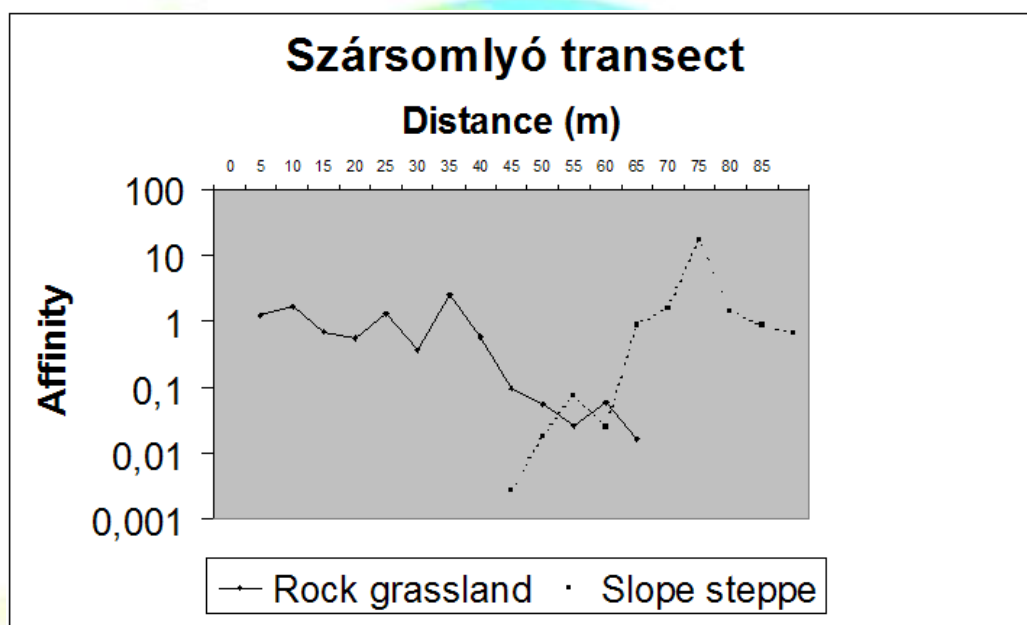


Figure 1. The change of affinity to the rock grassland association *Sedo sopianae-Festucetum dalmaticae* and to the slope steppe association *Cleistogeni-Festucetum sulcatae* along a transect on the mountain Szársomlyó, South-Transdanubia, Hungary.

Now let us see, how to apply this concept to the investigation of stand's homogeneity (Lájer 2002). One might think the matter is settled by saying that a stand is homogeneous if the affinity is constant within its boundaries. Unfortunately, this is not entirely satisfactory, because differential species are not known a priori. When we establish them, the concept of homogeneity is already used. Actually, a new approach to the minimum area problem is needed here. The minimum area of a community type is measured usually by placing out plots of the same shape (most often quadrates) but different size and noting the number of species in them. However, different shapes in general do not lead to the same result. Nobody knows a priori, what is the appropriate shape in any case.

Our concept makes it possible to estimate the minimum area by changing also the plot shape in the necessary way. To do this, we control the species number rather than the area. We start with the two species having the nearest individuals to our random point and calculate the area of their triangle taking also the chosen point into account. Thereupon we



take the next species with the nearest individual and calculate the area of the quadrangle or triangle composed by the three species and the chosen point etc. As before, the polygons with minimal area are composed. After repeating this procedure and taking the average we obtain an unambiguous (subject only to statistical uncertainty) species number – area curve (Figures 2-3), which is the exact answer to the minimum area question.

For practical purposes it is often useful to characterize this by a single number, named minimum area, which is reasonable to be chosen where the tangent of the curve takes a prescribed low value. It is remarkable that species-area curves by the outlined method become saturated at far smaller area than by the traditional quadrature method (Figures 2-3).

The procedure was also proposed in the sampling methodology of Hungarian Phytosociological Database (Lájer et al. 2007).

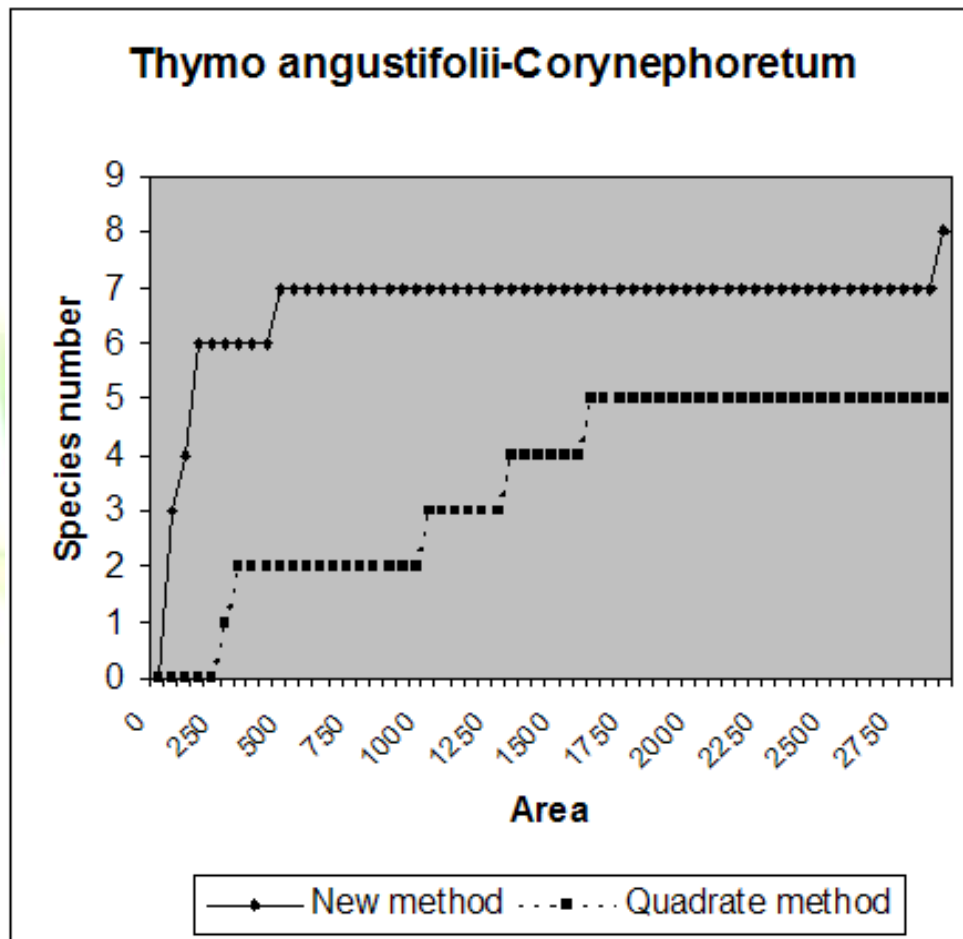


Figure 2. The species number-area curve around a point in a Grey Hair-grassland (Hegyész, South-Bakony, Hungary) surveyed by the new method (upper curve), and by the traditional quadrature method (lower curve, dashed line). Area in cm<sup>2</sup>.

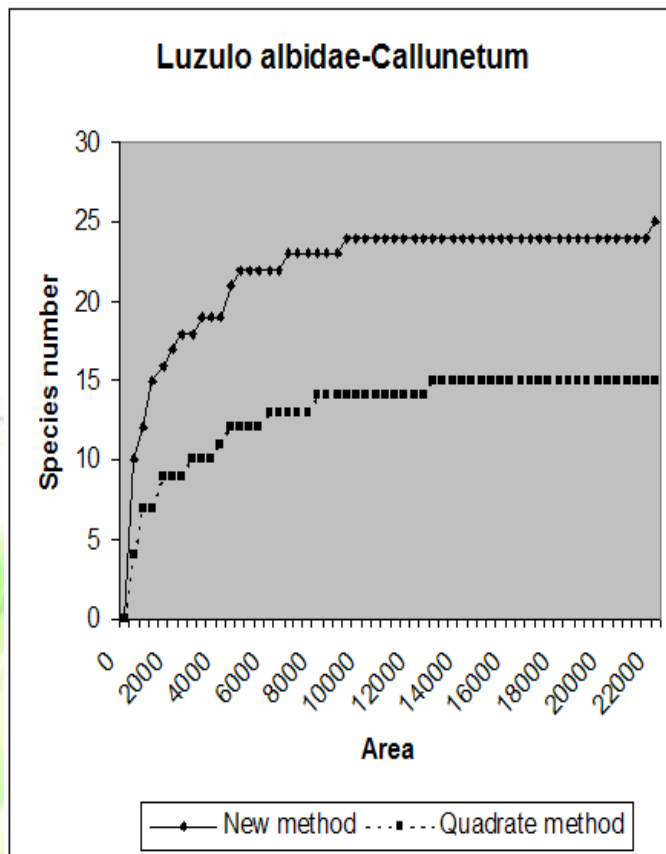


Figure 3. The species number-area curve around a point on a heath (Nyirád, Devcséri-Bakonyalja, Hungary) surveyed by the new method (upper curve), and by the traditional quadrature method (lower curve, dashed line). Area in cm<sup>2</sup>.

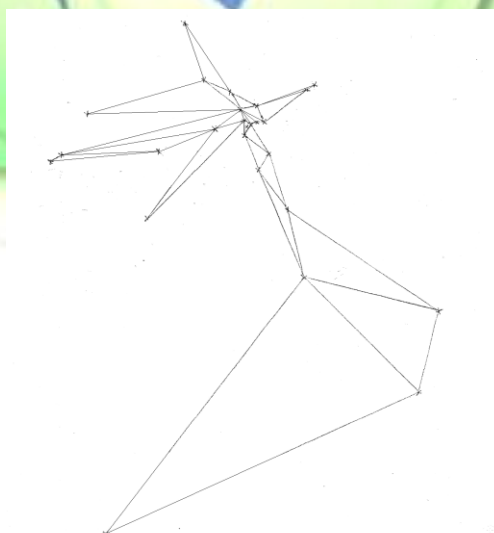


Figure 4. The minimal polygon obtained by the heath survey (Nyirád). The species on the figure from left to right:





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*Plantago lanceolata, Asperula cynanchica, Thesium linophyllum, Pseudolysimachion spicatum, Chrysopogon gryllus, Molinia coerulea subsp. hungarica, Dianthus giganteiformis subsp. pontederiae, Anthericum ramosum, Euphorbia cyparissias, Festuca rubra, Achillea pannonica, Calluna vulgaris, Carex ericetorum, Lotus corniculatus, Scabiosa canescens, Hieracium hoppeanum, Viola canina, Peucedanum oreoselinum, Anthoxanthum odoratum, Luzula campestris, Potentilla alba, Equisetum ramosissimum, Koeleria pyramidata, Hypericum perforatum, Filipendula vulgaris.*

Their order of occurrence from the marked point:

*Calluna vulgaris, Lotus corniculatus, Carex ericetorum, Hieracium hoppeanum, Peucedanum oreoselinum, Achillea pannonica, Scabiosa canescens, Euphorbia cyparissias, Anthoxanthum odoratum, Festuca rubra, Viola canina, Anthericum ramosum, Equisetum ramosissimum, Koeleria pyramidata, Molinia coerulea subsp. hungarica, Luzula campestris, Dianthus giganteiformis subsp. pontederiae, Chrysopogon gryllus, Thesium linophyllum, Asperula cynanchica, Plantago lanceolata, Potentilla alba, Filipendula vulgaris, Hypericum perforatum, Pseudolysimachion spicatum.*

## DISCUSSION

The affinity estimated in this way is subject to some statistical uncertainty because the mean minimal area of differential species of the community type is a random variable. This can be controlled however. The standard deviation of this quantity can be diminished as desired by increase of the sample points in the reference stand.

What has been said so far has also some theoretical importance. Namely, if there are reference stands and differential species, the vegetation units can be demarcated in principle with any precision.

## CONCLUSION

The proposed method provides a uniform phytosociological basis for examination of transitions between several communities separated by plant species. The method's additional benefit is the possibility of statistical error estimation by calculating the standard deviation of the mean minimal area of differential species. The standard deviation can be diminished as desired by increasing the sample points in the reference stand.

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## **GROWTH OF ALFALA IN HEAVY METAL CONTAMINATED CLAY LOAM BROWN FOREST SOIL**

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### **Abstract**

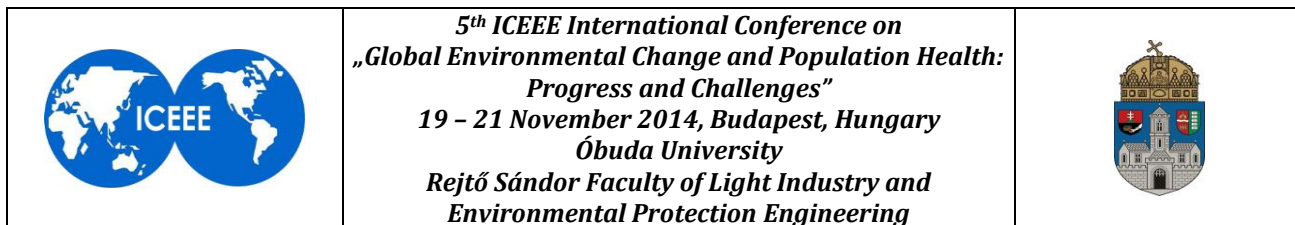
Soil contamination with heavy metals, either by natural causes or due to pollution, often has pronounced effects on the vegetation, resulting in the appearance of metallophytes, and heavy metal tolerant plants. Phytoremediation is an emerging environmental biotechnological method that promises for clean-up the environment from heavy metal pollution. The use of plant for heavy metal-polluted soil remediation is highly ecologically sound and safe technique. A laboratory experiment was conducted for 15 days in Petri dishes containing 3 layers of Whatman filter papers wetted by 50 ml of heavy metals Cd, Cu, Ni, Pb and Zn, separately at 0, 10, 20, 40, 80 to 160  $\mu\text{M}$  to determine their impacts on germination rate, root and shoot growth of surface sterilized alfalfa seeds. In vivo experiment was conducted in greenhouse, alfalfa seeds were grown for 8 weeks in plastic pot containing 2 kg of heavy metal (Cd, Cu, Ni, Pb and Zn) contaminated clay loam brown forest soil at different concentration levels (0, 10, 20, 40, 80 to 160 mg/kg). The results of in vitro experiment demonstrated that the rates of seed germination, root and shoot growth were affected by Cd, Cu, Ni and Pb metals at higher concentrations of 80 and 160  $\mu\text{M}$ . The inhibitory decreasing order of metal toxicity on seed germination was Cd > Cu > Ni > Pb > Zn. However, seed germination increased at all Zn dosages. Meanwhile, the lower concentrations of investigated metals (10 and 20  $\mu\text{M}$ ) stimulated the root and shoots length and at 10 and 20 mg/kg concentration levels increase plant biomass. It was found that alfalfa was able to grow efficiently at all Zn concentrations except at 160 mg/kg. The results showed that alfalfa able to uptake the heavy metals at the applied concentrations ranging from 10 to 160 mg/kg by various degrees. Finally, alfalfa plants demonstrated it's powerful to some extent cleanup the soil environment from heavy metals.

**Keywords:** Alfalfa plant growth parameters; heavy metals; soil contamination

### **INTRODUCTION**

Soil contamination with heavy metals, either by natural causes or due to pollution, often has pronounced effects on the vegetation, resulting in the appearance of metallophytes, and heavy metal tolerant plants. Nicholson et al. (2003) concluded that the major sources of soil heavy metals include atmospheric deposition, sewage sludge, livestock manures, inorganic fertilizers and lime, agrochemicals, irrigation water, industrial by-product 'wastes' and composts. Joshi and Luthra (2000) found that the main sources of soil heavy metal pollution are geogenic, mining and smelting, disposal of municipal industrial wastes, use of fertilizers, pesticides and fumes from automobiles. Rapid growth of urbanization as well as transportation and industries are leading to serious environmental hazards (Urban 2007). Alvarez-Ayuso (2008) mentioned that heavy metal contamination of soils derived from agricultural or industrial activities is one of the







major environmental problems in many parts of the world. Among chemical elements and compounds which are regarded as environmental pollutants, toxic metals such as Pb and Cd are the most widely spread and found around the urban agriculture areas (Mico et al. 2006, Fitamo et al. 2007). Guiweia et al. (2010) found that the concentration of Cd in the plant shoots, and the activities of catalase and ascorbate peroxidase decreased in plants from polymer-amended soil compared to an unamended control. The determination of risks dealing with the release or binding of toxic compounds in soils is a complex problem because a range of chemical, physical or biological soil properties can directly or indirectly affect these processes (Giller et al. 1998). The movements and levels of accumulation of heavy metals in a plant depend on soil type, plant and environmental factors (Alloway 1995). Deposition of metals to soil may be deleterious to crop growth and soil productivity and may also produce crops containing unacceptably high metal levels that may impact negatively on animal and human health (Nouri, 1980). The mobility of Cd and Pb metals in terms of bioavailability to plants may depend not only on the total concentration in solution but also on the speciation of the metals (Bingham et al. 1984). The speciation, adsorption and distribution of Cd in soils are governed by pH, soluble organic matter content, hydrous metal oxide content, clay content and type, presence of organic and inorganic ligands, and competition from other metal ions (Holm et al. 1995; Bingham et al. 1984). Soil pH affects the speciation and adsorption of heavy metals in soil, determining the mobility, bioavailability and toxicity of the metal.

Heavy metal uptake by plants occurs via the soil solution. Free metal ion activities are usually better indices of metal bioavailability and toxicity than are total soluble metal concentrations. As the mass of the water transpired by the plant increases, the Cu concentration in both the root and shoot increase (Cheng and Allen 2001). Vasiliadou and Dordas (2009) found that the Cd level affected the number of leaves and dry matter accumulation, and there were differences among the varying cultivars that were used. Baker and Brooks (1998) found that some native plant species were able to accumulate unusually high concentrations of potentially phytotoxic elements such as Cd, Cu, Pb, Ni and Zn from metalliferous soils. Ma et al. (2009) established that compared with the single factor pollution index (SFPI) of heavy metals calculated for the control site, the average SFPI from the sampling sites decreased in the order of Cr > Cd > Pb > Zn > Ni > Cu. There were notable negative correlations between the integral pollution index of soil heavy metals at all sampling sites and the distances from the railroad. Heavy metals interferes with several metabolic processes, causing toxicity to the plants as exhibited by reduced seed germination, root and shoots growth and phytobiomass, chlorosis, photosynthetic impairing, stunting and finally plant death (Roy et al. 2005). Plant roots participate primarily in the heavy metal cation uptake (Lasat 2002). Although heavy metal release in Germany has been decreasing in recent years (Ilyin et al. 2008), the environment still faces the problem of accumulated heavy metal deposits in soils. While some heavy metals, like Cu and Zn, are essential for plants and animals and others like Cd and Pb are toxic even at low concentrations and have no biological functions. The techniques that involve the use of living organisms include: bioremediation, phytoextraction, phytovolatilization, phytostabilization, rhizofiltration and phytoremediation (Yang et al. 2005) and are more inexpensive than chemical, mechanical or other techniques. Most metal uptake occurs in the root system, usually via absorption, where many mechanisms are available to prevent toxic effects due to the high concentration of metals in the soil and water.

Plants have shown the capacity to withstand relatively high concentration of contaminants without toxic effects. A wide range of plants can be useful in cleaning up the environment from waste hazards. The plant material may be used for non-food purposes; alternatively, it can be ashed followed by recycling the metals or disposing them in a landfill (Angel and Linacre 2005).

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Chhotu and Fulekar (2008) mentioned that the seed germination, root and shoot growth were affected by Cd, Cu, Ni, Pb and Zn metals at higher concentration of 40 and 50 ppm. However, the lower concentration of heavy metals ranging from 5 to 10 ppm doses were observed to be stimulating the root and shoot length and increase biomass of the alfalfa plant. The objective of this study was to evaluate, in vitro, the affect of various concentrations of different heavy metals on alfalfa seed germination rate, and their affects after application to clay loam brown forest soil on root/shoot growth biomass and the rate of metal uptake.

## **MATERIALS AND METHOD**

### ***Soil sampling, and soil properties***

Soil samples were collected from a depth of about 0-20 cm along uncultivated clay loam brown forest soil collected from the Gödöllő region, in Hungary. Stones and plant residues and other soil impurities were carefully removed from the soil prior to the drying process under laboratory conditions. The soil samples were screened through a 2 mm stainless steel sieve and stored in a plastic bag at room temperature until use. Concentrations of Pb, Zn, Cu, Ni and Cd were measured by atomic absorption spectrophotometer. The soil moisture content was calculated by the weight difference before and after drying at 105°C to a constant weight. The pH was measured after 30 minutes of vigorous mixed samples at 1:2.5 (Solid: distilled water ratio).

### ***Heavy metal salts***

Heavy metal solutions used in in vitro and in vivo experiments were prepared from the following heavy metal salts: Cd as Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O; Cu as CuSO<sub>4</sub>·5H<sub>2</sub>O; Ni as Ni(NO<sub>3</sub>)<sub>2</sub>; Pb as Pb(NO<sub>3</sub>)<sub>2</sub>, and Zn as Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.

### ***Laboratory experiment***

The laboratory experiment was carried out to evaluate the impacts of the various concentration levels of heavy metals Cd, Ni, Cu, Pb and Zn on alfalfa (*Medicago sativa* L.) seed germination, root and shoot length. According to Vincent (1970), alfalfa seeds were sterilized with 70% ethanol for 30 seconds followed by sterilization with 0.1% mercuric chloride for 5 min. The seeds were thoroughly washed with sterilized distilled water several times to avoid fungal contamination. To measure the effect of heavy metals on seed germination; 10 sterilized seeds were placed in large Petri dishes of 24 cm in diameter with 3 Whatman filter papers and were gotten wet with 50 ml of the following treatment solutions: 0, 10, 20, 40, 80 and 160 μM of each of Cd, Ni, Cu, Pb and Zn. The control Petri dishes were treated by distilled water. Petri dishes were sealed with Parafilm to prevent evaporation. Seeds were incubated at alternating temperatures of 25°C (16 hours) and 18°C (8 hours). The experiment was carried out by three replicates and 10 seeds were used for each treatment. Germination was counted every 3 days for 21 days. Seeds were considered to have germinated when the radical was at least 5 mm long. The germinating seedlings were harvested after 21 days and germination rate (%), shoot and root length were recorded in comparison with heavy metal free control.

### ***Greenhouse experiment***

In vivo, ten seedlings were grown in 2 Kg capacity plastic pots for studying root and shoot growth biomass and metal uptake. Soil moisture content was adjusted to about 45% of water-holding capacity with distilled water. Soil samples were treated by different concentrations: 0, 10, 20, 40, 80 and 160 mg metal/kg soil of each of Cd, Ni, Cu, Pb and Zn. The control Petri dishes were treated by distilled water.

To prevent loss of nutrients and trace elements out of the pots, plastic trays were placed under each pot and the leachate collected was put back in the respective pot. Each treatment of the plants consisted of three replicates for statistical purpose. The seedlings were set under





photoperiod of 14/10 hrs light/dark cycle and temperatures of  $26\pm 2^\circ\text{C}$  during the day and  $20\pm 2^\circ\text{C}$  during the night. The average relative humidity was recorded to be 72%. For the metal uptake study, plants were harvested after 8 weeks. The plants were then separated in to roots and shoots. The plant samples were washed with distilled water and dried in an oven at  $75^\circ\text{C}$  for 2 days and the dry weight of biomass was determined, after which these samples were stored in paper bags. The samples were considered for analysis of metal content digested with concentrated nitric acid and 30% hydrogen peroxide and then the heavy metal content was determined by an atomic absorption spectrophotometer. The experimentation layout was done in a complete randomized block design. The means of three replicates per treatment for each strain were analyzed using ANOVA to determine statistical differences among treatment and LSD at  $P = 95\%$  was calculated as well as S.D.

## RESULTS

Accumulation of heavy metal in soil after its discharge from different pollution sources increases the metal concentration in soil environments up to dangerous levels in living systems including human beings. The present study has been carried out in laboratory and greenhouse settings in pot experiments to evaluate the effects of heavy metals on seed germination and plant growth and biomass as well as root and shoot metal uptake.

### *Effect of heavy metals on seed germination*

The result of the in vitro study demonstrated a concentration dependent inhibition of the seed germination with regards to metal and alfalfa tolerance (Fig. 1). The result of this investigation indicated that Cd, Ni and Pb at 10  $\mu\text{M}$  concentration levels had very low toxic effects on seed germination while Cu at the same dose increased seed germination. At the 20 and 40  $\mu\text{M}$  concentrations of Cd, Ni and Pb reduced seed germination, while the seeds were germinated more at 10 and 20  $\mu\text{M}$  levels of Cu. The seed germination was inhibited at 80 and 160  $\mu\text{M}$  levels as compared to the control for all the four metals Cd, Ni, Pb and Cu.

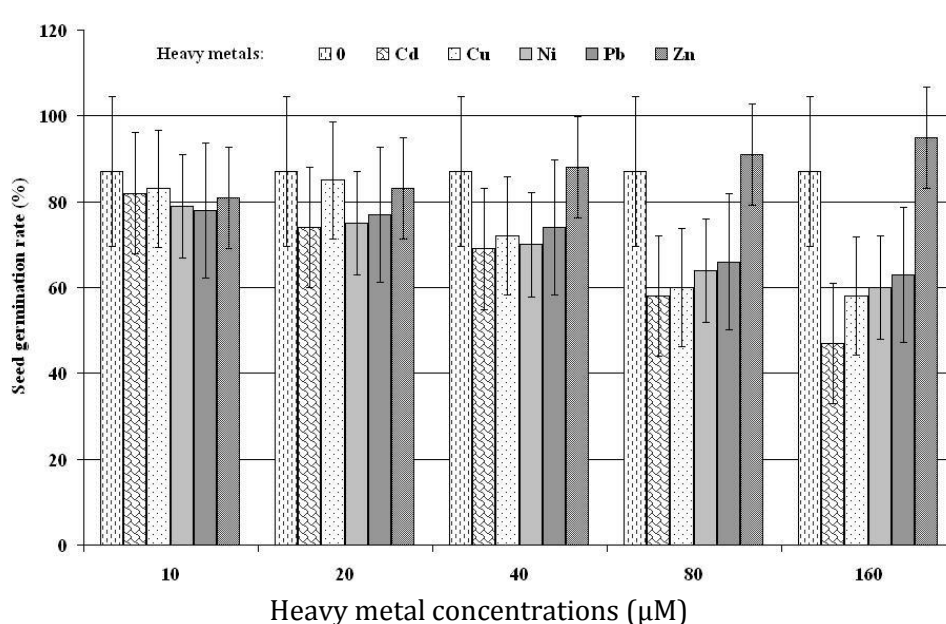


Figure 1. In vitro effects of heavy metals on alfalfa seed germination after 21 days





Delayed germination was also observed in all cases at higher (80 and 160  $\mu\text{M}$ ) concentrations. However, in the same study Zn was the only metal which did not reduce the seed germination. The decreasing order of toxicity for metals on seed germination was  $\text{Cd} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Zn}$ . However, seed germination increased at all Zn concentration levels.

#### **Effect of heavy metals on root length**

The increases in the heavy metal concentration caused a root length decrease with stunted growth of roots (Fig. 2). The dose of 10  $\mu\text{M}$  of all investigated heavy metals promoted the root length of the plants as compared to the root growth of the control plants. The heavy metals Cu, Ni, Zn and Pb at 20  $\mu\text{M}$  concentrations further increased the root growth over the control root size. However at the same dose Cd reduced the root length on comparison with the control root elongation.

The metals Cd, Ni, Cu and Pb demonstrated a concentration dependant inhibition of root growth at 40, 80 and 160  $\mu\text{M}$  levels. All Zn concentrations increased the root length in comparison to the control root length of the alfalfa plants. Root toxicity symptoms included: browning, reduced number of root hairs and growth.

In comparison to the control, plant roots were healthy and normal. The colours of the roots receiving higher heavy metals treatment (80 and 160  $\mu\text{M}$ ), except with Zn, changed gradually over time from a creamy white colour to dark brown; an indication of intense suberification. Plants treated at lower concentrations were not significantly affected by the metals. Lateral roots were observed in almost all treated samples of Zn, Cd, Cu, Pb and Ni demonstrated concentration dependant inhibition of root growth at higher concentrations.

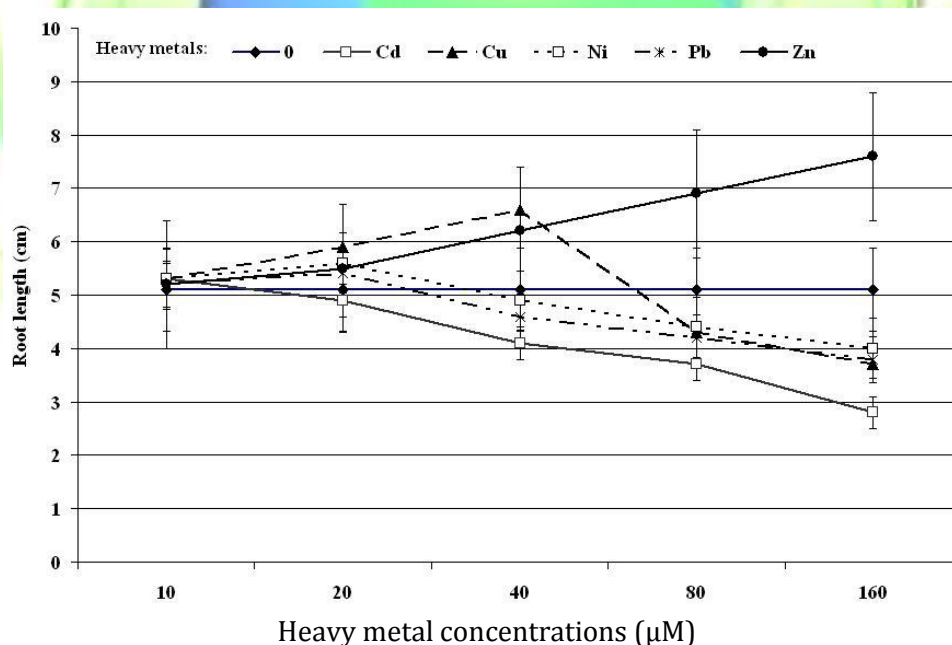


Figure 2. *In vitro* effects of heavy metals on alfalfa root length after 21 days of germination

#### **Effect of heavy metals on shoot elongation**

The impacts of heavy metals on the shoot elongation are different from their effects on root growth and length (Fig. 3). The shoot length was found slightly reduced than in the control alfalfa plants at the 10  $\mu\text{M}$  Cd level. On the other hand, the 10  $\mu\text{M}$  dose of Cu, Pb, Ni and Zn increased the shoot lengths as compared to the control treatment. These results indicate that



low concentrations of Cd, Cu, Ni and Pb have micronutrient-like effects on the alfalfa plants and all the plants appeared to be healthy.

The heavy metals Cd, Ni and Pb at 20 and 40  $\mu\text{M}$  doses reduced the shoot growth; however, Cu at the same dose increased the shoot length. When the concentration of these metals was increased to 80 and 160  $\mu\text{M}$  concentrations, the shoot length of the alfalfa plants found a concentration dependant inhibition of shoot growth as compared to the control plants. All plants grown in the soil contaminated with Zn showed increase in the shoot elongation than the plants grown in soil without Zn contamination.

### ***Effect of heavy metals on plant biomass***

The results of in vivo experiment indicated that the mean plant biomass (root and shoot dry weights) of alfalfa showed an increasing tendency as the concentrations increased from 10 to 20 for Cd, Cu and Ni. It was found that 40 mg/kg is better for plants grown in soil contaminated by Cu and Ni than in Cd-contaminated soil (Figs. 4a and 4b). The dry weights of root and shoot decreased gradually as the concentration of Cd, Cu and Ni in the soil ecosystem increased to 80 and 160 mg/kg. The plant dry weights of root and shoot yield affected by the higher concentration levels of Cd caused reduction in the plant biomass. Lead showed low effect on dry weights of roots and shoots of the plant. There was a positive effect seen in all Zn concentrations and an increase in biomass yield as compared to the control ones.

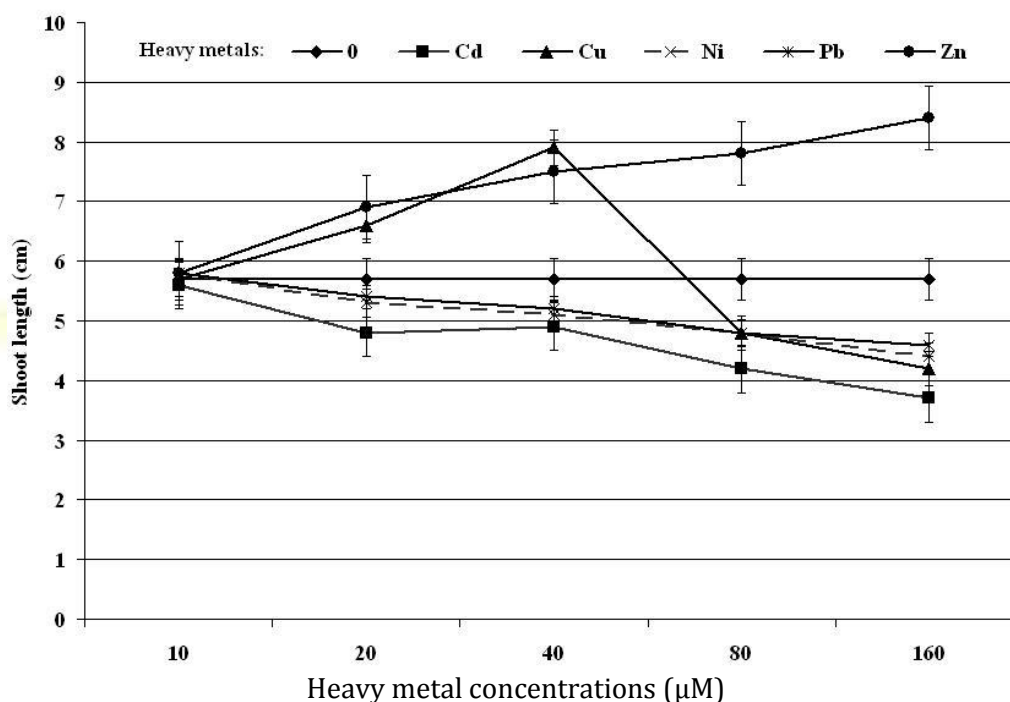


Figure 3. In vitro effects of heavy metals on alfalfa shoot length after 21 days of germination

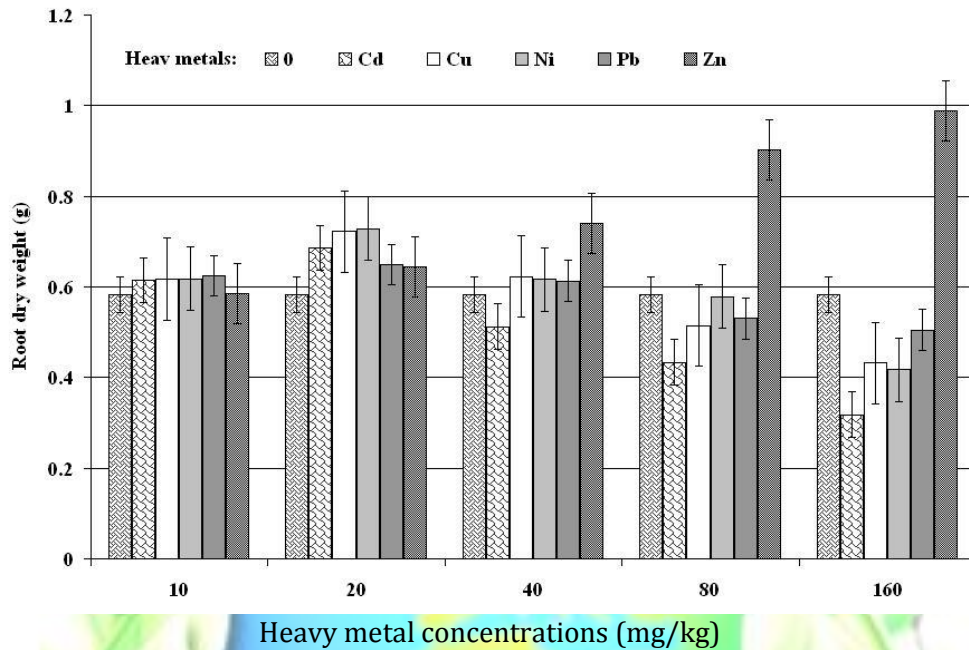


Figure 4a. In vivo effects of heavy metals on alfalfa root dry weight after 8 weeks plantation in clay loam brown forest soil

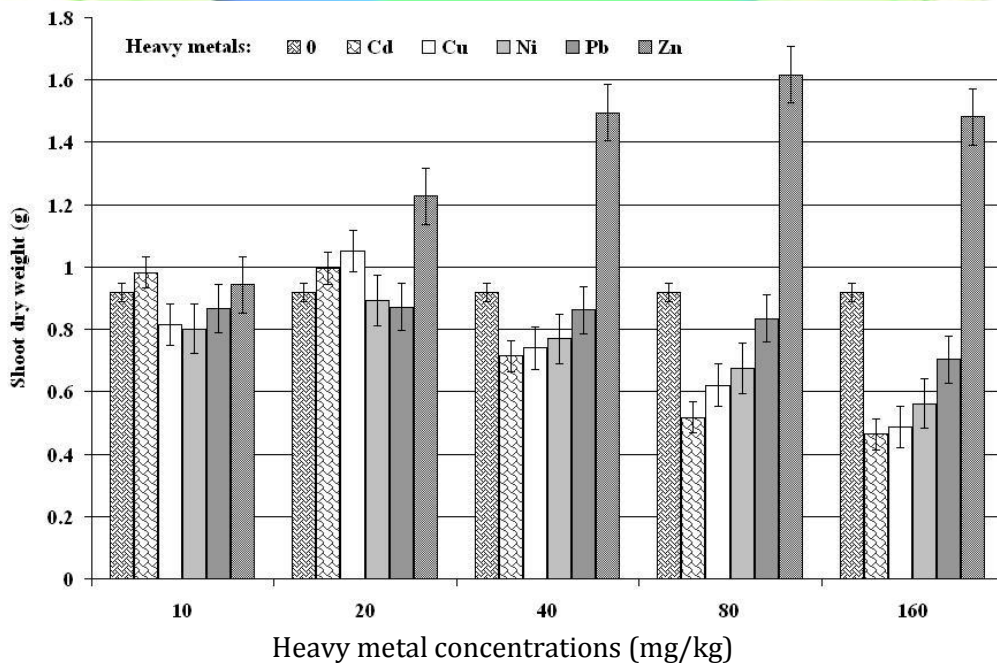


Figure 4b. In vivo effects of heavy metals on alfalfa shoot dry weight after 8 weeks plantation in clay loam brown forest soil

### Heavy metal uptake by plant roots and shoots systems

The heavy metals concentration in the plant is affected by many factors such as the metal content supplied in the soil ecosystem and the plant tissue as well as by the interaction between these factors.



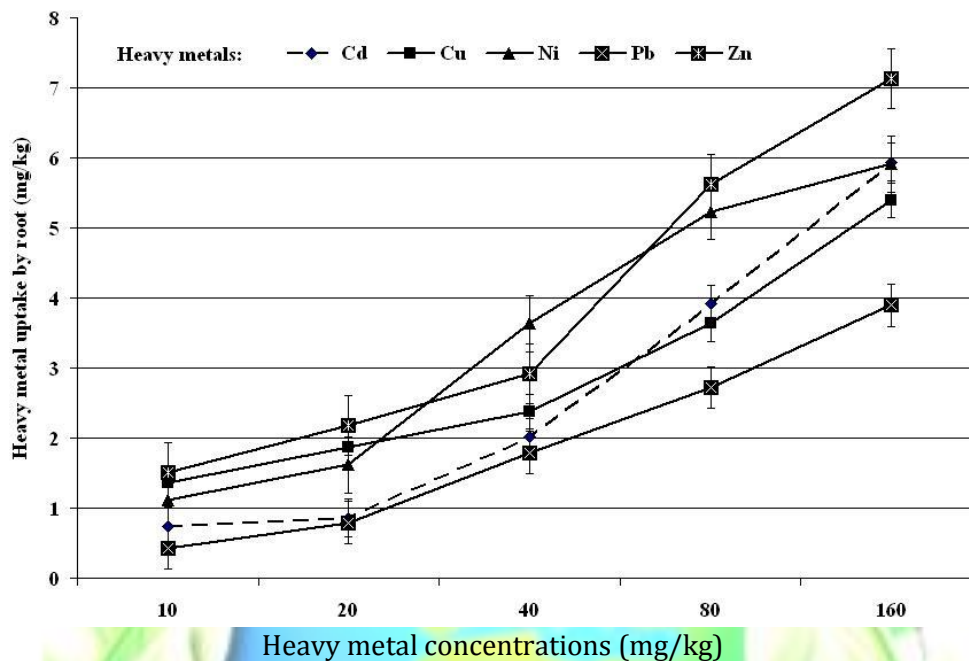


Figure 5a. Uptakes of heavy metals by alfalfa roots system after 8 weeks plantation in clay loam brown forest soil

The mean uptake of metals Cd, Ni, Pb, Cu and Zn by roots (Fig. 5a) and shoots (Fig. 5b) of alfalfa plants increased as the concentrations of these metals in the soil ecosystem increased.

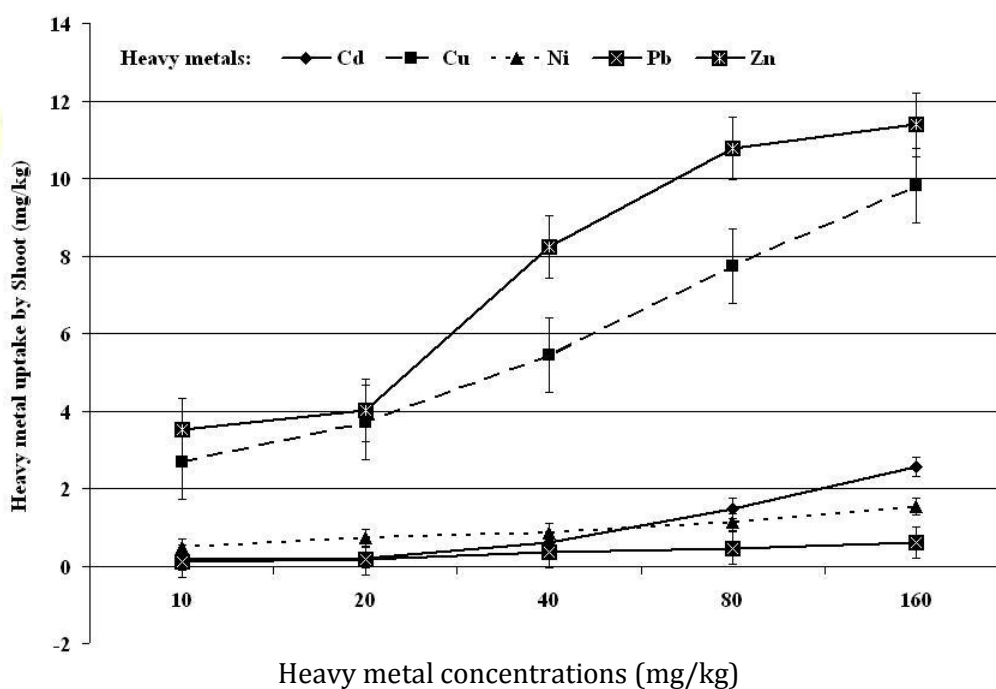


Figure 5b. Uptakes of heavy metals by alfalfa shoot system after 8 weeks plantation in clay loam brown forest soil

The results illustrated that the absorption of heavy metal by root system was directly proportional, increased by the increasing of the concentration of heavy metals. Zinc showed the highest metal uptake by root system, while Pb was the lowest metal absorbed by root system. It was found that the shoot system (Fig. 5b) accumulated Zn and Cu more Cd, Ni and Pb.

In the plants, shoots and roots, were observed to have a characteristic uptake capacity for different metals. The decreasing order of uptake of heavy metals by the alfalfa plants tissues was in the following order: Zn > Cu > Cd > Ni > Pb.

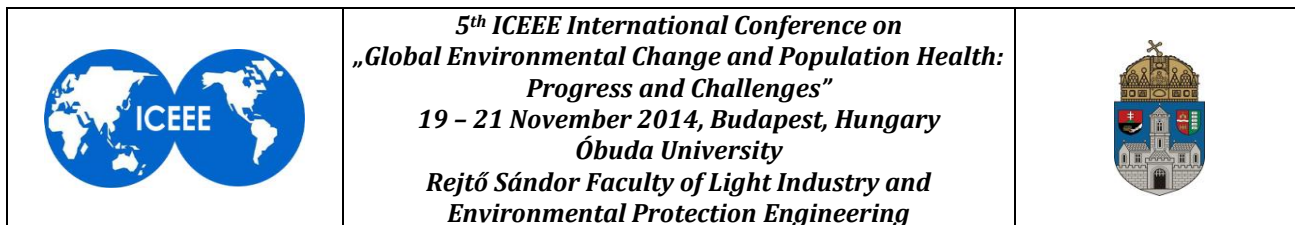
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## DISCUSSION

The results demonstrated that the concentration was dependent on the inhibition of the seed germination. To some extent, our results are in agreement with Peralta et al., (2004) who investigated alfalfa plants grown in soil at different growth stages using separate batches of Cr<sup>6+</sup> at 100 mg/l, and Cd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, or Zn<sup>2+</sup> at 500 mg/l. In his case, four days after germination, all metals except Zn<sup>2+</sup> had lethal effects on the seedlings. When applied 16 days after germination, Cr<sup>2+</sup> and Ni<sup>2+</sup> still had lethal effects on the seedlings and Cd<sup>2+</sup> and Cu<sup>2+</sup> destroyed more than 50% of the plant population. While approximately 90% of the plants exposed to Cd<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> were able to grow without apparent negative effects 20 days after germination, Cr<sup>2+</sup> and Ni<sup>2+</sup> still showed lethal effects. These results demonstrated that the tolerance of alfalfa plants to Cd, Cu and Zn was positively correlated with the age of the plants. Thus, alfalfa seedlings tolerated Zn<sup>2+</sup> at 500 mg/l at the growth stage of 4 days after germination. Alfalfa plants could be considered potentially feasible to be transplanted in uncontaminated soils where the concentrations of Cd, Cu or Zn are high enough to interfere with alfalfa seed germination.

An increase in the heavy metal concentration in the soil ecosystem caused root length decrease with stunted growth of roots. One of the explanations for roots to be more responsive to toxic metals in environment might be that roots are a specialized absorptive organ, which means that they are affected earlier and subjected to accumulation of more heavy metals than any of the other plant organs. This could be the main reason why root length is usually used as a measure for determining heavy metal tolerance of plants (Xiong 1998). According to Chaignon and Hinsinger (2003), higher concentrations of Cu can inhibit root growth before shoot growth and can accumulate in the roots without any significant increase in its content of the aerial parts. Heavy metals are found to be more toxic for root growth because they accumulate on roots and retard cell division and cell elongation. A similar conclusion was drawn by this examination in regards to results in Fig. 2. The results indicate that low concentrations of Cd, Cu, Ni and Pb have micronutrient-like impacts on the alfalfa plants. These results agreed with the observation of Chhotu and Fulekar (2008). Ormrod et al. (1986) found that Ni caused stunted and deformed growth of shoots with symptoms of chlorosis. Gyawali and Lekhak (2006) noted an 11%, 22% and 41% reduction in plant height, respectively, over the control. Generally, it was seen that degrees of inhibition of shoot and root growth started from 10 µM concentration. In this respect Peralta-Videa et al. (2004) reported that Cd affected young plants more than old plants of P.



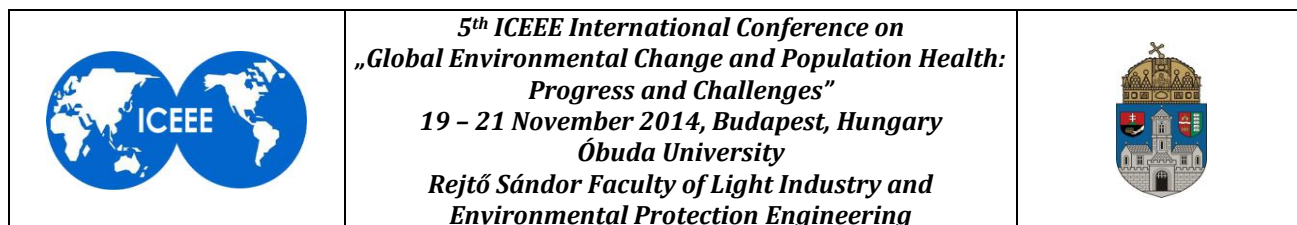
coccineus, and Cd applied to the younger plants caused a stronger reduction in growth parameters such as leaf area and fresh weight accumulation and reduced shoot growth by reducing the chlorophyll content and the activity of photosystem I.

The biomass yield affected by the higher concentrations of metals, caused reduction in the plant biomass. Higher heavy metal concentrations can affect physiology and reduce plant growth and dry biomass yield (Grifferty and Barrington 2000). Authors showed that the increased Zn concentration from 25 to 50 mg/kg had a significantly positive effect on dry biomass yield. The plant biomass may be incinerated either to reduce volume, recover energy, dispose of off-using appropriate techniques or recycled to recover valuable metals (Angel and Linacre 2005). That alfalfa produced greater biomass, which result in a higher concentration uptake of metals, was reported by Pivetz (2001). The phytotoxicity of Cd on growth and dry matter production of a number of cultivated plants have been determined by Gondek and Filipek-Mazur (2003). Our results were in agreement with those mentioned above according to our results presented in Figs 4a and 4b.

The mean uptake of Cd, Ni, Pb, Cu and Zn by alfalfa plant systems increased as the concentrations of these metals in the soil ecosystem increased. Alfalfa shoot biomass has demonstrated the ability to bind an appreciable amount of Cu, Ni, Cd, Cr, Pb and Zn from aqueous solutions (Tiemann et al. 1998). Increase in Pb uptake by alfalfa using EDTA and a plant growth promoter, was reported by Lopez et al. (2005). The large surface area of roots and their intensive penetration of soil may reduce leaching, runoff and erosion via stabilization of soil, and offer advantages for metal uptake. Most crop species tend to accumulate Cd at the highest concentrations in the root tissue, followed by leaves, then by seeds or storage organs. Several studies have demonstrated that the metal concentration in the plant tissue is a function of the heavy metals content in the growing environment (Cui et al. 2004). Cheng and Allen (2001) found that Cu uptake was linearly related to free Cu<sup>2+</sup> ion activity and was independent of total Cu concentration in solution. In Regards to the effect of Cu on alfalfa plant growth and biomass, this investigation showed similar results to Wu and Hendershot (2010) who mentioned that the accumulation and toxicity of Cu to pea roots were investigated. The root uptake of Cu and Ca varied with Ca and H activities. Calcium, H, and Cu competed for root binding with high pH and low Ca favouring more Cu uptake. Root elongation was highly sensitive to root Ca content and correlated better with root-bound Ca and Cu content than with merely dissolved Cu concentrations. A multi-element uptake model was developed to describe Cu and Ca accumulation by treating the pea roots as a collection of three biotic ligands with known site densities and proton-binding constants.

The essential elements (Cu and Zn) are required in low concentrations and hence are known as trace elements or micronutrients, whereas nonessential elements (Cd and Pb) are phytotoxic (Gerard et al. 2000). Zn is relatively mobile in soils and is the most abundant metal in the roots and shoots of contaminated plants as it is in soils. This metal is necessary as a minor nutrient and it is known that plants have special Zn transporters to absorb this metal (Zhu et al. 1999). The bioavailable of Pb is usually very low due to its strong association with organic matter, Fe-Mn oxides, clays and precipitation as carbonates, hydroxides and phosphates (Shen et al. 2002). Cadmium also is considered to be mobile in soils but is present in much smaller concentrations than Zn (Zhu et al., 1999). Moreover, many studies have demonstrated that Cd taken up by plants accumulates at higher concentrations in the roots than in the leaves (Boominathan and Doran, 2003). In addition, exudation of organic compounds by plant roots, such as organic acids, influence ion solubility and uptake (Klassen et al. 2000) through their effects on microbial activity, rhizosphere physical properties and root-growth dynamics (Yang et al. 2005). The higher concentrations heavy metals uptake by alfalfa was reported by Rehab et al. (2002). It can





be concluded that the low-doses of tested heavy metals applied, stimulated the root and shoot elongation of alfalfa plants. At higher concentrations (over 80  $\mu\text{M}$  or 80 mg/kg), Cd, Cu, Ni and Pb reduced the germination rates and phytobiomass of alfalfa plants. This study shows that heavy metals were efficiently taken up by alfalfa plants at all concentrations and the uptake was increased with the increasing concentrations in soil. Finally, the alfalfa plants, to some extent, demonstrated their potential in cleaning by removing heavy metals from the soil environment.

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## **PRODUCTION AND STRATEGIES MANAGEMENT OF WASTE IN MALANVILLE CITY (BENIN, WEST AFRICA)**

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Located in the north of Benin, Malanville city is facing to the management of waste from his population activities difficulties. In spite of the services of pre collection garbage in the city, household waste proliferates or rejected, burned or hidden in Malanville city. This study identifies and analyses the wastes management methods used and those impacts in Malanville city. The information retrieval is carried out in the libraries, the centers and the services of documentation; the observations using a grid of the 5 districts of the city made it possible to identify the most unhealthy quarters and of the investigations by questionnaires and interview guides are organized with some main leaders (2 agents of the municipality, 2 agents of NGO "BETHESDA", 5 agents of health and 1 agent of the service of hygiene) and in 189 households selected with Schwartz (1995) in Malanville city. The data (demographic, wastes statistics, affections ...) collected are treated and analyzed with PEIR model. It reveals that Malanville city endures the insufficiency of solid waste points regrouping, the lack of the disposal site and the treatment of those wastes. From that, only 12% of surveyed households subscribe to the service pre waste collection, over 18% of households surveyed incinerate their solid waste, 10% burrow it into the soil and 60% discharge it into nature. About the liquid waste, due to the lack of waste water infrastructures in the city, most households dump their wastewater into being home, on roads, in nature, and nearly 50% of respondents defecate in nature. This kind of waste management causes the pollution of environment especially water resources used and the development of the hydrous diseases such as malaria (65.92%), acute respiratory infections (16.47%), in the city. The same management system of the household garbage is found in other localities of Benin and in the world. It is essential that the local and municipality authorities and the actors in collaboration with the population of the Malanville city develop and instigate recycling and the transformation of waste into compost for the agricultural production and energy for domestic lighting.

***Key words:** Benin; Malanville city; waste management; water resources pollution; water borne diseases*

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## EXAMINATION OF AIR-SOURCE HEAT PUMP AND POSSIBILITY OF ITS SEPARATION FROM NATIONAL ELECTRICITY NETWORK

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### ABSTRACT

The examined heat pump is used for making domestic hot water and air condition. Decreasing energy resources of the Earth and enhanced energy consumption are typical of our life. However, one of the basic conditions to survive is that the amount of the energy used every day should be reduced. The energy used to air-condition a room and the possible use of secondary energies generated by the air-conditioning is studied in the research. The heat energy distracted by a heat pump out of the room is not let outside as heat loss, but it is used for making domestic hot water. The efficiency of the heat pump is examined with varied air parameters inside. About 0.3 kW electric power taken by heat pump from national electricity network. Heat pump can be separated from united electrical network by solar energy system, this article shows solution for this method too.

**Keywords:** Heat pump, air-conditioning, effectiveness, coefficient of performance (COP), domestic hot water supply, solar energy system.

### INTRODUCTION

In general, the purpose of air-conditioning is to generate temperature lower than the ambient temperature and keeping it constant inside the room to air-condition [8]. In practice, heat pumps driven by an electric compressor are generally used. The ratio of the heat energy egressed by the heat pump and the energy taken from the electric supply for driving the compressor (and the fans) is called the coefficient of performance of the cycle. The higher the coefficient of performance of a heat pump is the more economic it is, it varies between 2 and 5 according to the structure of the heat pump, the ambient temperature outside and the way of application. See the schematic diagram of a heat pump in Figure 1.

The following relation can be described between the energies in Figure 1:

$$Q_h = Q_c + W \quad (1)$$

where:

- |       |   |     |
|-------|---|-----|
| $Q_c$ | the heat distracted from the room                   | [], |
| $Q_h$ | the quantity of heat egressed to the hot water tank | [], |
| $W$   | electric energy taken by the heat pump              | [], |

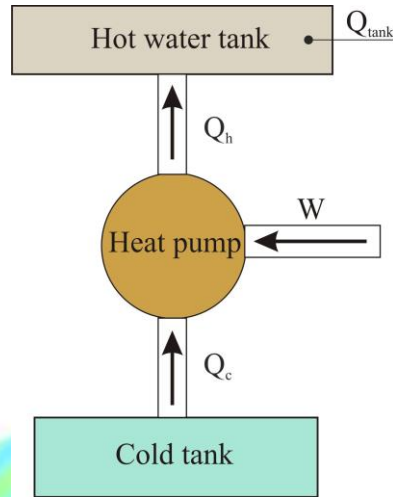


Figure 1 Schematic diagram of a heat pump

Theoretical coefficient of performance of the heat pump [1-6]:

$$COP = \frac{Q_h}{W} = \frac{Q_c + W}{W} \quad (2)$$

where:

COP coefficient of performance of the heat pump [-].

The heat energy stored in the hot water tank of the heat pump as hot water:

$$Q_{\text{tank}} = m_w c_w \Delta T_w \quad (3)$$

where:

$Q_{\text{tank}}$  heat energy stored in a hot water tank [J],

$m_w$  mass of the heated water [kg],

$c_w$  specific heat of the water,  $\left[ \frac{\text{kJ}}{\text{kg} \cdot \text{C}} \right]$ ,

$\Delta T_w$  difference of the mean temperature at the bottom and on the top of the water tank [ $^{\circ}\text{C}$ ].

As a result of the losses of the system:

$$Q_h > Q_{\text{tank}} \quad (4)$$

The heat loss on the condenser side:

$$Q_{\text{loss}} = Q_h - Q_{\text{tank}} \quad (5)$$

where:

$Q_{\text{loss}}$  loss generated in the heat exchanger (condenser) [J].

Thus the relation of the actual and theoretical coefficients of performance can be written on the operation of the heat pump, using relation (3):

$$COP > COP_{\text{actual}} = \frac{Q_{\text{tank}}}{W} = \frac{m_w c_w \Delta T_w}{W} \quad (6)$$





The heat pump system is a cycle that consists of two heat exchangers (evaporator, condenser), a compressor and a butterfly valve [7]. Each element is joined by a pipe filled with transfer medium. The operation of the heat pump is illustrated in Figure 2.

- 1 The compressor condenses the gaseous transfer medium (R134a) using electric energy (which heats) and circulates it in the system permanently.
- 2 The heat of the hot gas inside the fan-coil unit - through a water heat exchanger - is used for making hot water, while the medium cools down, precipitate and turned into fluid again.
- 3 The liquid medium flows to a space of bigger cross section, through an expansion valve, to the evaporator. The pressure declined hereby makes the medium, which expands and strongly cools accordingly, gaseous again.
- 4 By utilizing hundreds of cubic meters of air sucked through the evaporator, heat is distracted from the surroundings, which makes the air cool down in the room. Then this hotter vapor is condensed again starting from the first step.

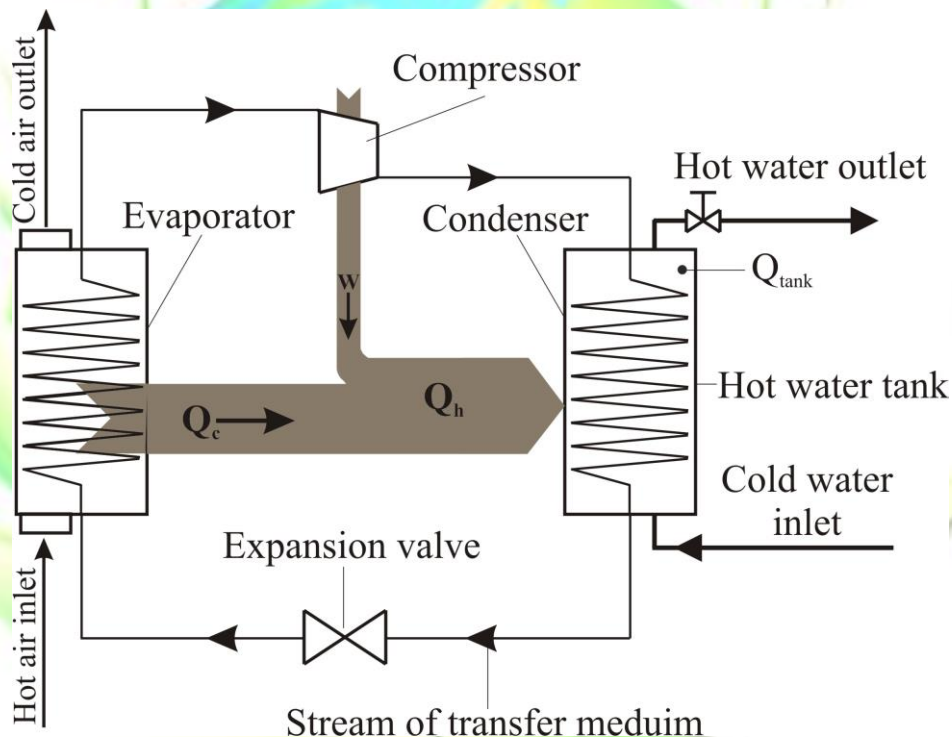


Figure 2 Working process of the heat pump cycle

Heat pumps are heat engines of reverse operation. The thermodynamic cycle can be followed on the temperature-entropy ( $T$ - $s$ ) diagram (Figure 3). The process starts from point 1, where the medium at  $P_i$  pressure and  $T_i$  temperature occurs as saturated vapor. Processes 1 and 2 are adiabatic compressions that happen in the compressor. Normally, this change of state is indicated in the diagram as a vertical line (isentropic compression), but in reality the change of state is irreversible, entropy permanently increases, thus the curve slightly bends to the right. Processes 2 to 5 happen in the condenser: processes 2 and 3 are the distraction of overheating heat, in point 3 the vapor reaches saturated state at pressure  $P_f$ . In processes 3 and 4 the temperature does not change, more and more vapor precipitates and the liquid state emerges in point 4. Processes 4 and 5 in the condenser is the possible after-cooling of the fluid medium,



then processes 5 and 6 is the thermodynamic process, which results in sudden fall of the pressure, at the end of which the medium expands to  $P_f$  pressure and  $T_f$  temperature, the liquid partly (approximately half of it) evaporates suddenly and the medium turns into wet, vapor state. This is an isenthalpic process, i.e. during the process the enthalpy does not change. Finally, in processes 6-1, the medium takes heat in the evaporator from the space to cool at permanent temperature and pressure, while the moisture content of the vapor declines gradually. Then the medium returns to the starting point of the cycle, to state 1, and the process starts again. Naturally, all mentioned above apply to an ideal medium, the processes rather differ in deed [10].

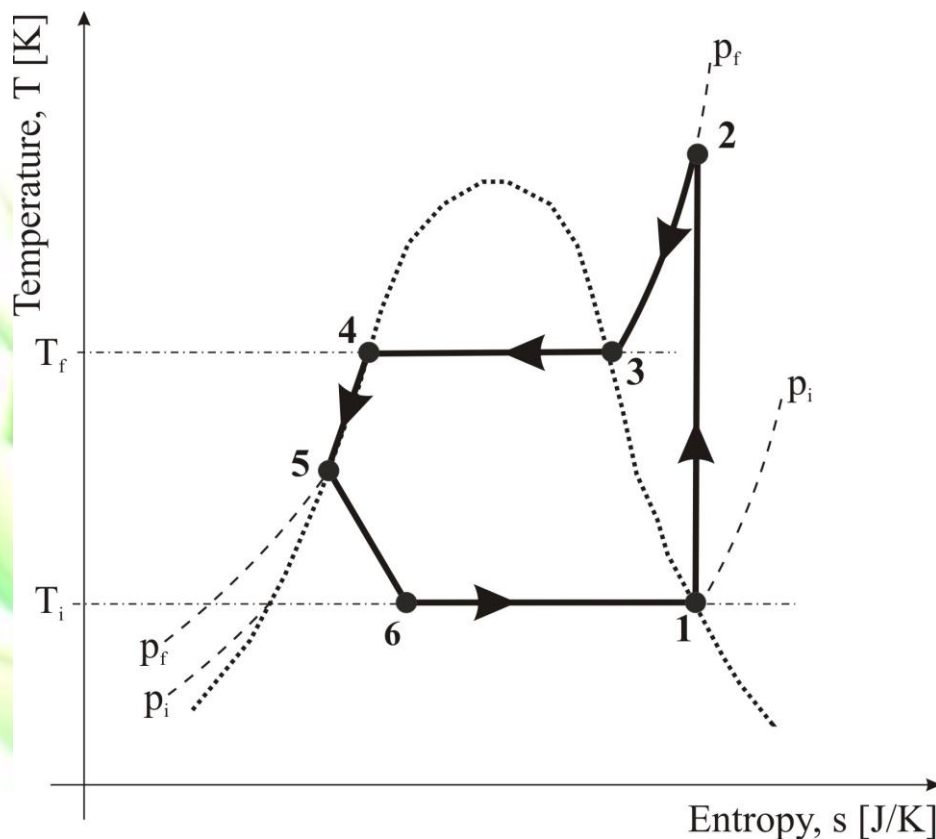


Figure 3 Cycle of the vapor-compression refrigerator on the temperature-entropy diagram

## MATERIALS AND METHODS

A heat pump installed in one of the rooms of the site of Óbuda University in Doberdó Street is examined focusing on the economy of air-conditioning. The examination is performed depending on the measuring order illustrated on Figure 4.

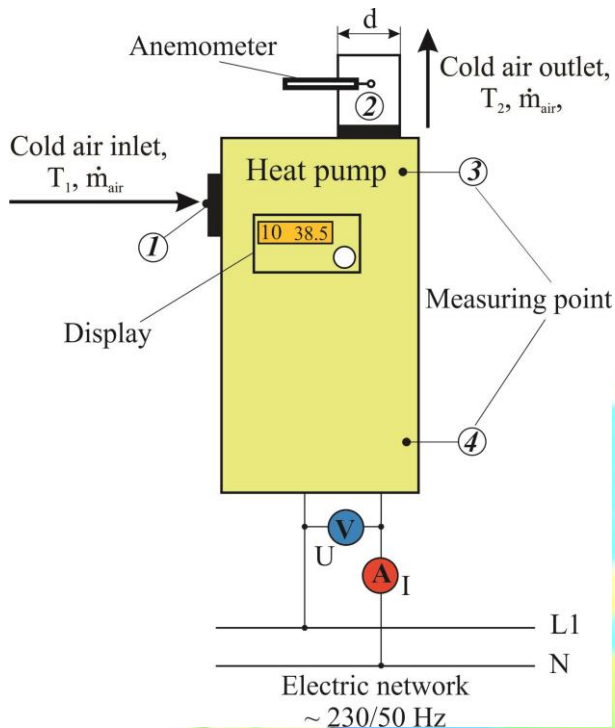


Figure 4 Measuring order of a heat pump

The measuring system consists of the following main elements:

- air-water heat pump to examine,
- anemometer type testo 435,
- ammeter and voltmeter,
- thermometers built in the heat pump.

## RESULTS

The temperatures of the air let in and out of the pump are measured at the measuring points 1 and 2 as illustrated on Figure 4. At point 2 the air flows out of the pump through a pipe end of 160 mm diameter. The speed of the air let out of the pump is measured with an anemometer type testo 435, the average of which is:  $v_{\text{air}} = 3.3 \text{ ms}^{-1}$ . During the time of warming up ( $t = 242 \text{ min} \approx 4 \text{ h}$ ) the volume flow rate of the air blown out is  $237.6 \text{ m}^3\text{h}^{-1}$ . The outgoing values relating to the measuring time are illustrated in Microsoft Excel. Afterwards, the trend lines are defined by using regression, indicating the determinant coefficients  $R^2$ .



Table I  
Temperature measuring results

Measuring time, t [min]	Inlet air temperature, $T_1$ [°C]	Outlet air temperature, $T_2$ [°C]	Hot water temperature up, $T_3$ [°C]	Hot water temperature down, $T_4$ [°C]
0	24.2	22.5	26.9	26.4
5	24.2	17	27	26.4
10	23.5	13.2	27.6	26.4
15	23.1	12.5	28.2	26.4
30	22.6	12.1	30	26.4
45	22.5	11.4	31.6	26.5
60	22.4	11.1	33.2	26.5
75	22.3	10.9	34.7	26.6
105	22.2	10.9	37.5	26.7
135	22.2	11.1	40.3	27
165	22	11.1	43.1	27.4
195	21.8	11.2	45.8	27.9
225	21.7	11.3	48.5	28.5
242	21.7	11.2	50	29.8

Figures 5 and 6 illustrate the inlet and outlet temperatures of air listed in Table I.

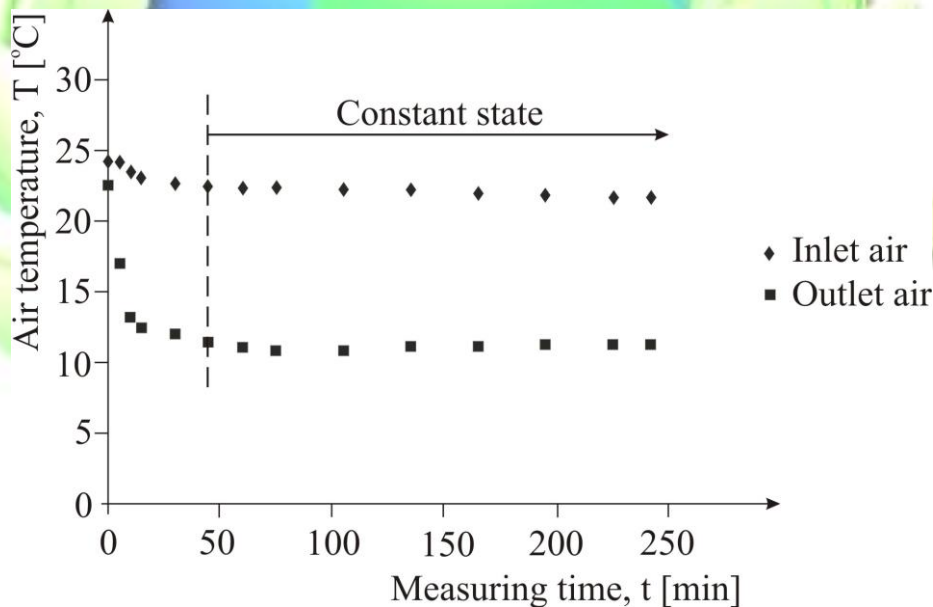


Figure 5 The temperatures of inlet and outlet air during the operation of the heat pump

Figure 6 indicates the regressive approach of the air let in and out, also marking the determinant coefficients.

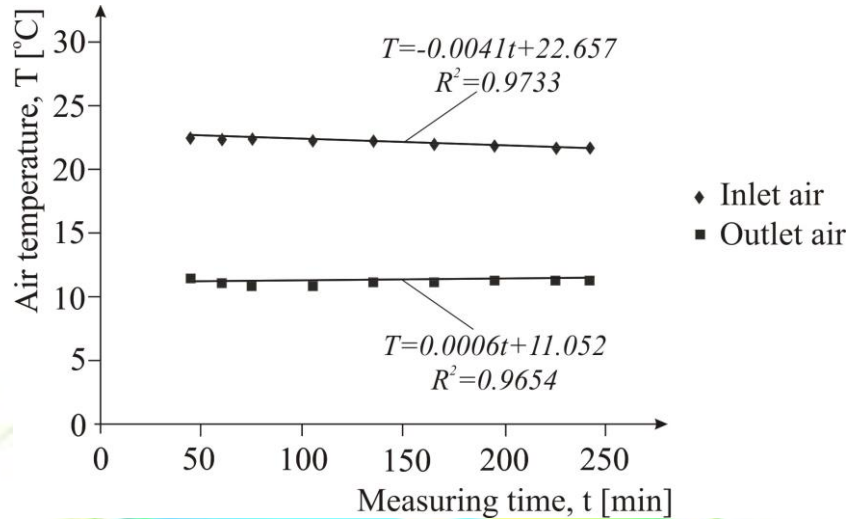


Figure 6 The temperatures and regression of inlet and outlet air in the constant state

At measuring point 3 in Figure 4, the temperature is measured at the top of the hot water tank, and at point 4, the temperature is measured at the bottom of the tank. Table I contains the measuring results. Figure 7 shows the temperatures of the hot water tank.

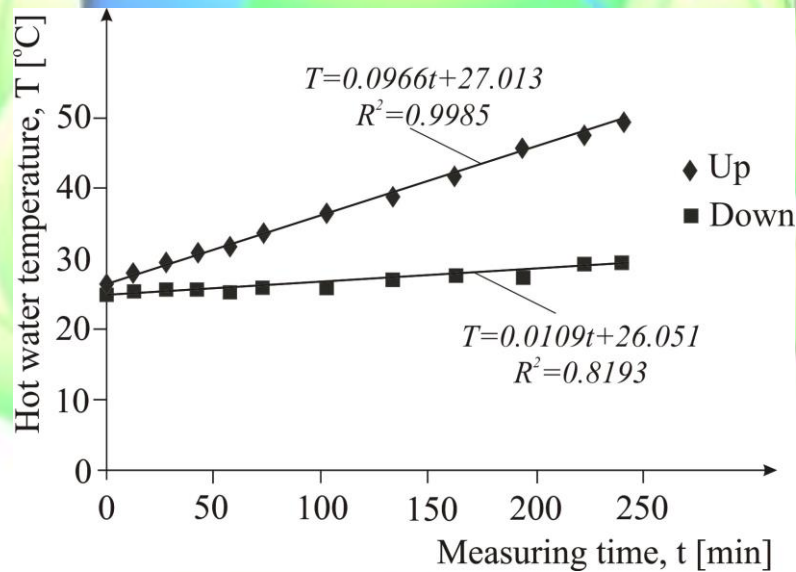


Figure 7 The temperatures of the hot water tank up and down

Figure 8 indicates the temperatures of the evaporator.

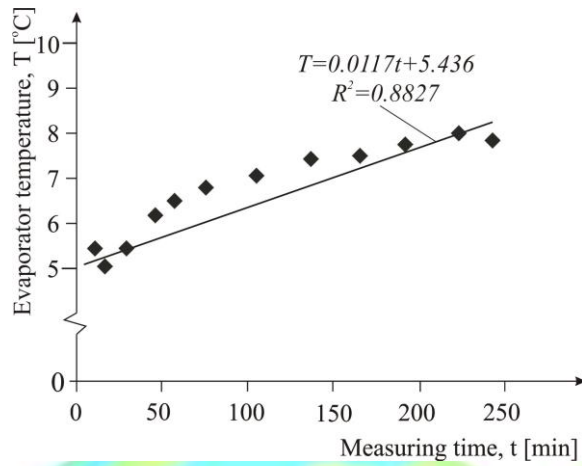


Figure 8 Temperature ranges of the evaporator

Figure 9 presents the current consumption of the heat pump with constantly  $U = 224$  V alternating voltage, the graph indicates increasing current consumption. The value of the power factor during the operation of the heat pump is  $\cos \varphi = 0.9$ .

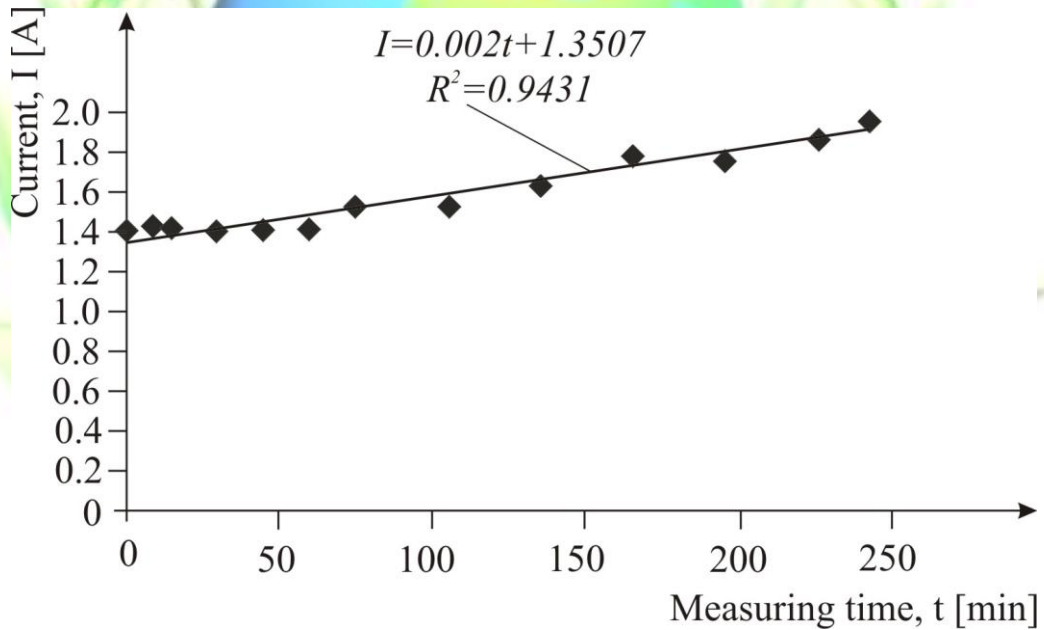


Figure 9 Current consumption of the heat pump

Rewriting relation (6) to performances:

$$COP_{actual} = \frac{Q_{\text{tank}}}{W} = \frac{P_{\text{tank}} \cdot t}{P_e \cdot t} = \frac{P_{\text{tank}}}{P_e} \quad (7)$$

where:

$P_{\text{tank}}$  heat power of the hot water tank [kW],





$P_e$  electric power taken by the heat pump [kW].

Taken electric power based on the measured data:

$$P_e = U\bar{I} \cos \varphi = 224 \cdot 1.53 \cdot 0.9 = 308.5 \text{ W} \approx 0.3 \text{ kW}. \quad (8)$$

where:

$U$  effective value of the alternating voltage [V],

$\bar{I}$  average of the measured currents (based on the data of Figure 9).

Volume flow rate of the inlet and outlet air:

$$\dot{V}_{air} = A\bar{v}_{air} = \frac{d^2\pi}{4}\bar{v}_{air} = \frac{0.16^2\pi}{2} \cdot 3.3 = 0.02 \cdot 3.3 = 0.066 \text{ m}^3/\text{s} = 237.6 \text{ m}^3/\text{h}. \quad (9)$$

where:

$A$  cross section of the and air pipe end in and out [m<sup>2</sup>],

$d$  diameter of the air pipe end in and out (Figure 4) [m],

$\bar{v}_{air}$  the average speed of the air outlet in the cross section out [m/s].

The mass flow of the inlet air:

$$\dot{m}_{air} = \dot{V}_{air}\rho_{air} = 0.066 \cdot 1.2 = 0.0792 \approx 0.08 \text{ kg/s} = 288 \text{ kg/h}. \quad (10)$$

here:

$\rho_{air}$  density of the air [kg/m<sup>3</sup>].

Heat power extracted from the air:

$$\dot{Q}_c = \dot{m}_{air}c_{air}\Delta T_{air} = \dot{m}_{air} \cdot c_{air} (\bar{T}_1 - \bar{T}_2) = 0.08 \cdot 1 \cdot (22.6 - 11) = 0.928 \approx 0.93 \text{ kW}. \quad (11)$$

where:

$c_{air}$  specific heat of the air at constant pressure  $\left[ \frac{\text{kJ}}{\text{kg}^\circ\text{C}} \right]$ ,

$\Delta T_{air}$  difference of the mean temperatures of the inlet and outlet air [°C].

Quantity of the heat of the hot water based on (3) and Figure 10:

$$Q_{\text{tank}} = m_w c_w (\bar{T}_{34f} - \bar{T}_{34i}) = 290 \cdot 4.2 (40.0 - 26.65) = 16260.3 \text{ kJ} \approx 16.26 \text{ MJ}. \quad (12)$$

where:

$\bar{T}_{34i}$  the mean temperature of the water tank at the beginning of measuring [°C],

$\bar{T}_{34f}$  the mean temperature of the water tank at the end of measuring [°C].

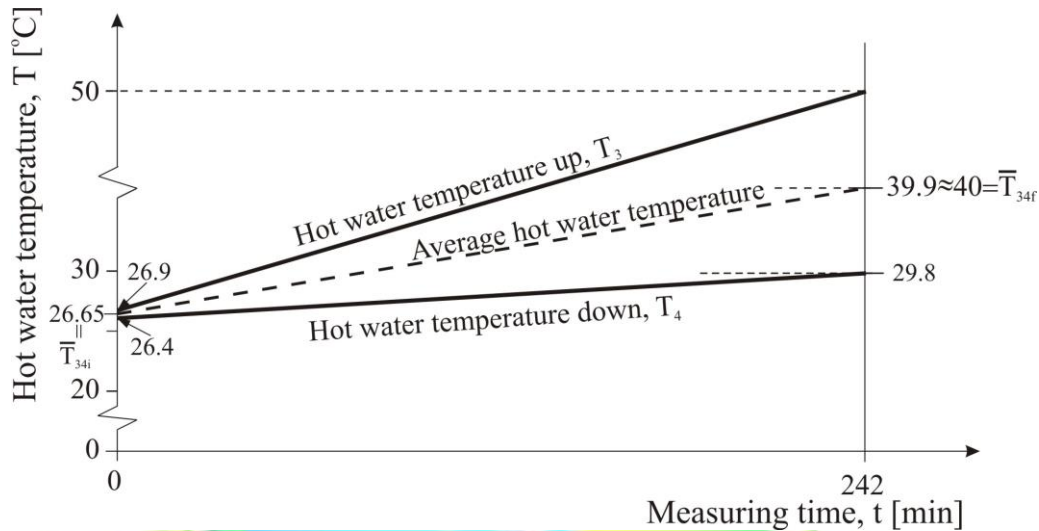


Figure 10 Temperature ranges of the hot water tank depending on measuring time

Heat power:

$$P_{\text{tank}} = \dot{Q}_{\text{tank}} = \frac{Q_{\text{tank}}}{t} = \frac{16.26 \cdot 10^6}{14.52 \cdot 10^3} = 1.119 \approx 1.12 \text{ kW}. \quad (13)$$

where:

t measuring time (warming up time) [s].

Applying this factor the result is relation (7), i.e. the actual coefficient of performance of the heat pump:

$$COP_{\text{actual}} = \frac{P_{\text{tank}}}{P_e} = \frac{1.12}{0.3} = 3.73 \approx 3.7. \quad (14)$$

## CONCLUSION

The value of the coefficient of performance, while examining the heat pump energetically, is  $COP = 3.7$ , which corresponds to the value defined in the technical literature.

At present, concerning air intake air conditioners, the heat energy taken from the space to air-condition is generally let outside the room. In our research a system is established that enables the heat energy that has been managed as loss so far, to be utilized for making domestic hot water. This energy decreases the amount of electricity taken for making domestic hot water. Thus the efficiency of the system (air-conditioning and making domestic hot water), having been examined, is nearly 100%.

The time of the static return of investment of the system may be defined by the following relation [9].

$$\text{Time of return of investment} = \frac{\text{Invested sum of money}}{\text{Savings annually}}. \quad (15)$$

Return of investment of this system may be expected within 5 years.

On the effect of more intensive radiation of the sun the temperature of the air is increasing. On this effect the warmer feed-water produced by solar collector and connected to the inlet arm for cold water of the heat pump increases the efficiency of the heat pump.

The production of the electricity of the solar panel system is also increasing while the electricity supply of the heat pump is rendered. The air-water heat pump working in this way is an effective device for energy production. The theoretical scheme of its realization is shown in Figure 11.

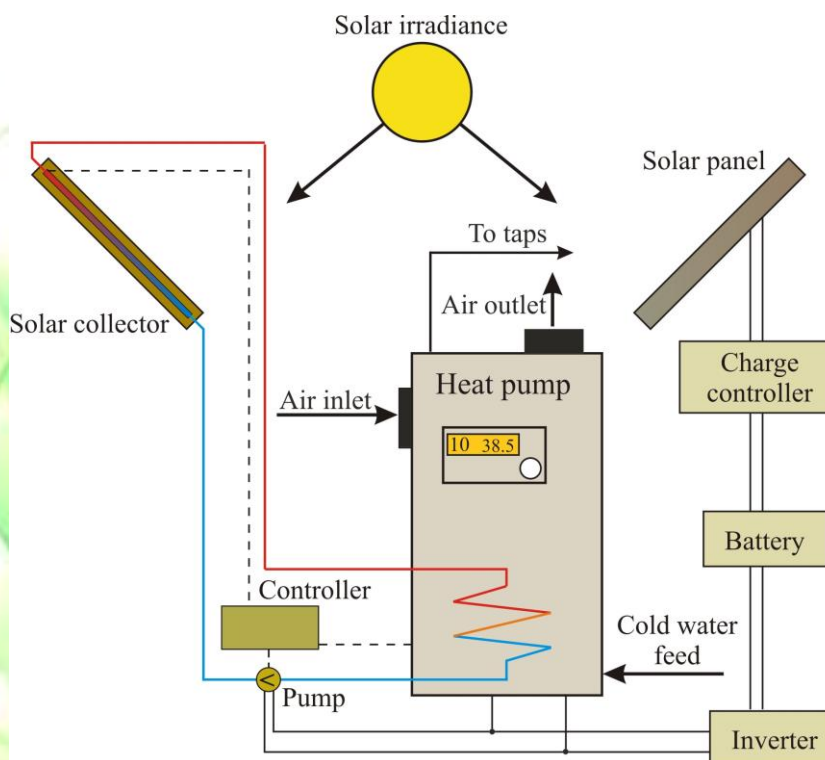


Figure 11 Used of solar energy system

This makes possible the disconnection from the national mains. Thus the supply of energy (domestic hot water, air conditioning) and the electricity of a family house can be realized from renewable energy-sources.

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## **CURRENT WASTE MANAGEMENT IN THE SLOVAK REPUBLIC**

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### **ABSTRACT**

Waste is generated everywhere and in nearly every human activity. If it had not been treated properly, then the company would waste overflowed. Therefore, it is important to inform people how to properly handle waste: how to properly recover, sort or use waste to produce other products. If we want to reduce the amount of municipal waste, therefore we must not forget the acquisition, processing and provision of information on waste

The aim of this paper is to define the current methods of waste treatment in the EU. The main role in waste management is to minimize the quantity at disposal in landfills and recovery of useful components. Limit on quantity of waste entails a reduction in waste management costs, less pollution and reduce noise associated with the collection and transport of waste. These requirements leads to best suits introduction and implementation of separate collection.

***Keywords:** waste, Slovak Republic, waste management, municipal waste*

### **INTRODUCTION**

Today's modern period can be characterized very consumerist lifestyle, which is associated on one side with the overexploitation of natural resources and on the other hand, with the formation of a large amount of unneeded of waste. The biggest problem we currently include is environmental pollution, and especially the production of waste. With a large increase in production is growing production of non-biodegradable waste. Precisely for this reason the most important tasks of today's society is the separation of waste.

### **MATERIALS AND METHODS**



We used several methods that have served us in analysing the problems of waste management in Slovakia. Methods used were divided into two groups:

- Theoretical,
- Empirical.

Among the theoretical methods include:

- Abstraction
- Analysis, synthesis,
- Comparison.

We gathered data from the literature mainly domestic, but also from Waste Act and Waste Management Program. All these collected information has been processed into the tables, figures and also in the text in this paper.

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## RESULTS

Industrialized society is increasingly faced with the concept of waste. Municipal and industrial wastes are still produced in large quantities and in addition to the main question of the total volume of waste is growing faster problem of their impact on the environment. The environment is not only undermined by wastes, but are often also emissions from the waste disposal becoming increasingly harmful to the environment. The current problem of rapid environmental degradation is related to the fundamental issues that need to be addressed. Those associated with waste reduction, recycling usable with the active components of waste and at the same time thus ecologically and economically acceptable methods of waste disposal (Strhan, 2000).

The concept of waste is as defined in the Waste Act § 2 ods.1 as a movable property, which the holder discards or intends to discard or is required to discard. Waste is defined in two respects: in as a subjective thing, which the holder discards of discretion, or from an objective point of view, if the holder of the waste requires the law to get rid of certain movable property (Act no. 233/2001 ECR.).

Waste is defined as Council Directive 75/442 / EEC on waste as any substance or object which the holder is deferred or postponed their wishes under the rules applicable national laws (Council Directive 75/442 / EEC on was

Waste arises in every human activity, the consumer and the manufacturing sector. Its accumulation is a major intervention in the environment, since it contains substances that often threaten environmental components (water quality, soil or air). Proper disposal and management of waste is becoming an important issue as well as the provision of basic living needs of humanity. Waste occurs in three states, in solid, liquid and gaseous. In principle we can waste divided into two types:

1. Natural waste which is generated in the cycle of natural substances,
2. Waste which nature cannot dispose, and therefore most of the significant problem for society (Takáčová, 2011).

The place of origin wastes divided into two groups, municipal and industrial. Municipal waste is waste from households, resulting in the municipality the activities of natural or legal persons, other than waste arising in the performance of activities constituting the objects of the legal person. Waste from households is considered a waste of real estate used by individuals for their individual recreation, for example of cottages or parking. Furthermore, household waste is waste generated in the municipality for cleaning of public roads and spaces, which are municipal property, and also the maintenance of public green areas. Industrial waste is produced by industry and technology. Many of them are the most threatening in human health and the environment and also are very dangerous because they emit toxic pollutants that can contaminate drinking water or food (Act no. 233/2001 ECR.).

Waste management is a relatively new industry, which directly relates to all stages of production, but also the consumer cycle, from raw material extraction, production, transportation, consumption of products to their destruction. Waste Management Act defines. 233/2001 ECR. as a: "Waste management is action to prevent and minimize waste generation and reducing environmental hazards and waste management in accordance with this Act." This is a targeted activity, so as to prevent impact and limited his work. Waste management action should be thought out, conceptually and organizationally ensured in various areas of social and economic life (Strhan, 2000).



Figure 1 shows the basic activities and various concepts of waste management into a logical sequence, but the individual activities can build on each other, complement or influence.

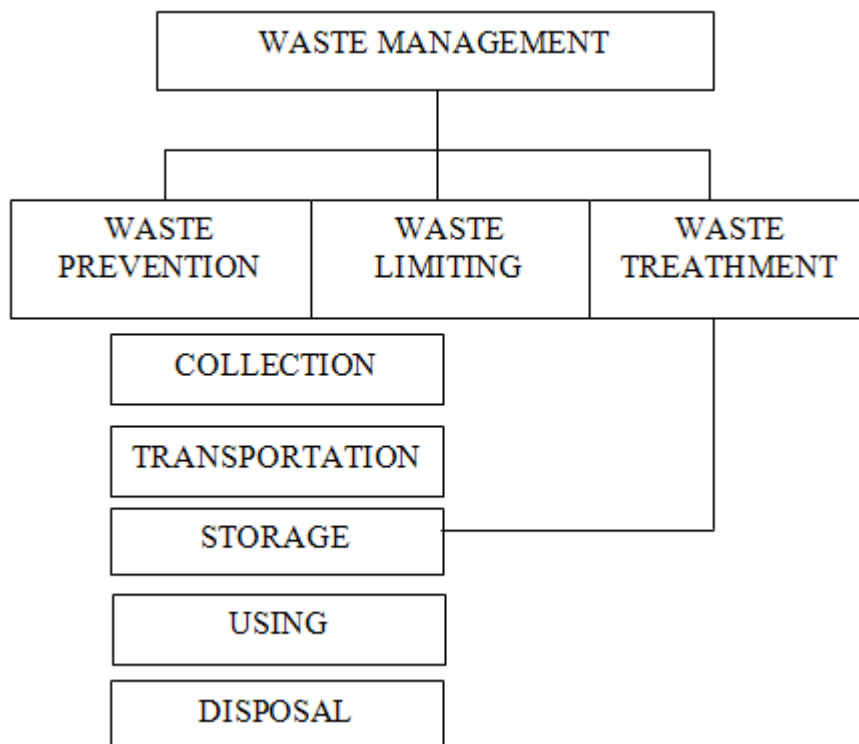


Figure 1 Basic activity in waste management

Source: own processing according to STRHAN, R. – KOLLÁR, V. – KAČEŇÁK, I. (2005)

Globally, the waste management is created from factors, which reflect mainly the level of utilization of raw material inputs and environmental care. Waste management methods in the Slovak Republic are (Figure 2):

- Waste prevention and restriction of his work - a set of measures, which exclude the formation and accumulation of waste in the production or consumption. This can be achieved by changing technology, little-waste and non-waste technology.
- Handling and collection of waste - respect of any waste management, and its temporary collection before further processing.
- Shipments of waste - the waste movement.
- Storage of waste - of waste location between activities when dealing with him at the time, which is necessary for organizational, operational or transportation reasons.
- Preparation and use of waste - a change in the physical, biological or chemical characteristics of the waste by means of cutting, pressing, packaging and so on and subsequently obtained from waste secondary materials.
- Disposal of waste - is actually handling it in order to avoid or reduce harmful effects on the environment. These are the landfill, incineration or neutralization.

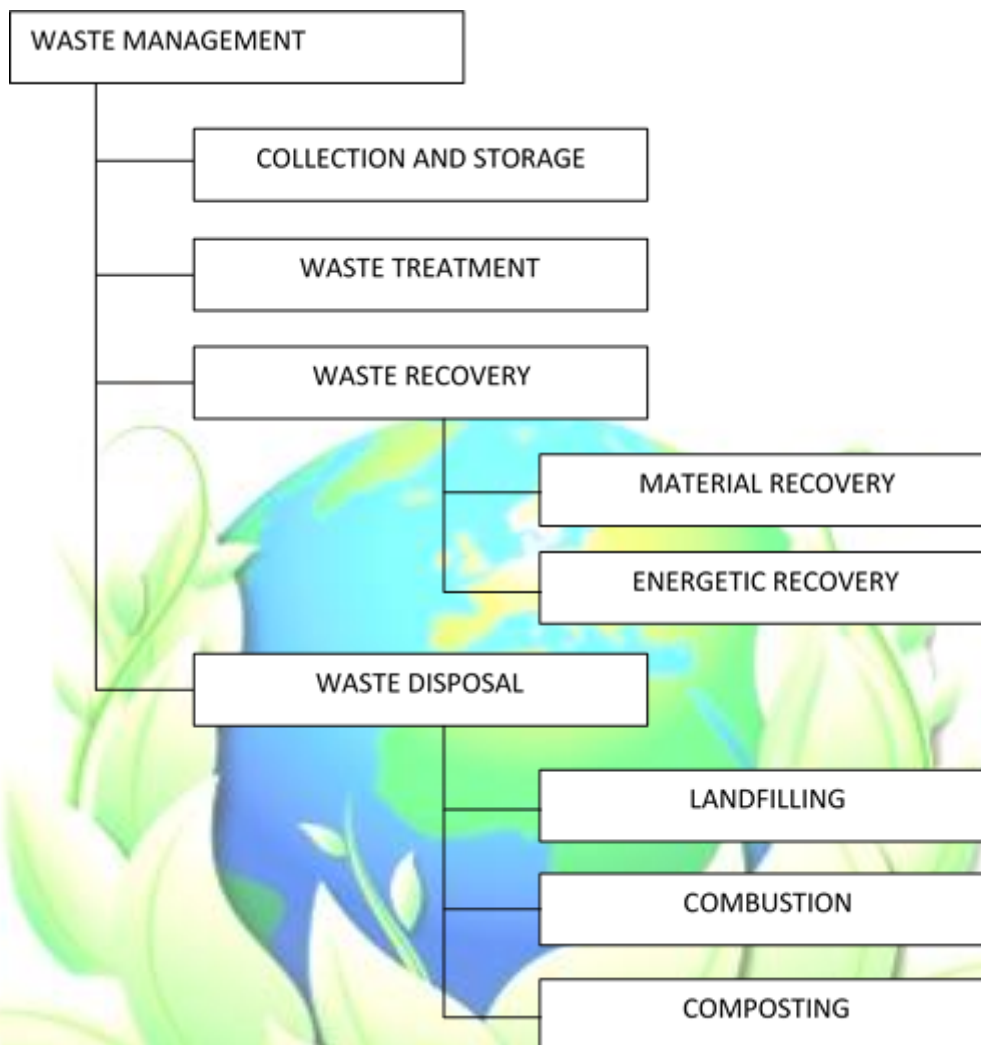


Figure 1 Current waste management methods in Slovakia  
Source: own processing

For successful waste management must have adequate information system of waste management. Functioning system for monitoring of treatment and management waste is a very effective tool for the producer of the waste, but also for those, who treat them to adhere to the rules laid down in accordance with applicable standards (Strhan, 2000).

### **Current State of the Waste Management in the Slovak Republic and in the EU**

A very important document in waste management area is the European Parliament and Council Directive 2008/98 / EC of 19 November 2008 on waste and repealing. Directive of the European Parliament and Council Directive 2006/12 / EC on waste establishes a legal framework for waste management in the Community. It defines basic concepts such as waste, recovery and disposal waste. It then sets out the basic requirements for waste management, in particular the obligation of establishments and undertakings carrying out any waste management activities have a permit or be registered, and the obligation of all member states to



draw up waste management. The Directive lays down the main principles such as the obligation to handle waste in a way that does not adversely affect the environment and human health, or support the application of the waste hierarchy, in accordance with the principle that the cost of waste disposal to bear its holder or producer of the product from which the waste came (Council Directive 2008/98 / EC on waste).

Next important documentation in waste management is a Waste Management Program of the Slovak Republic (SR POH) for 2011-2015 issued by the Ministry of Environment for a period of five years and approved by the Government. Waste Management Program is a strategic document on waste management, which has been prepared in accordance with the requirements of sustainable growth and its contents the requirements set out in the legislative regulations of the SR and the EU. Waste Management Program for the years 2011 - 2015 is the fourth in order of Waste Management Program. The basic starting point for developing a WMP SR is the Waste Act and the Decree of Ministry of the Environment. 283/2001 Z. z. on implementing certain provisions of the Waste Act, as amended.

WMP programs are being developed at three levels:

- National level,
- Regional level,
- At the level of individual waste producers and municipalities.

Binding portion of WMP SR is a binding document for decision-making activities government bodies. Sets targets for waste management by 2015 and in general proposes measures to achieve the objectives. Binding part also deals with the responsibility to implement the proposed measures. Each regional office is required to prepare programs of regions based on the objectives and measures set out in this document.

The guide section deals with the improvement of the collection and selective collection of waste and the need to build a certain recovery installations.

The main objective of waste management by 2015 is to minimize the negative effects of the generation and management of waste on human health and the environment and reducing the use of resources. The main objectives are the practical application of the waste hierarchy, namely:

- Prevention,
- Preparing waste for reuse
- Recycling,
- Other recovery,
- Disposal.

The strategic objective of WMP SR is diverting waste from landfill, resp. reduce the amount of waste going to landfill. To achieve this objective is needed:

1. Introduce a variety of measures to prevent waste, promote reuse of products and reduce the hazardous properties of products
2. Implement related systems of waste management in the area,
3. Promote the use of materials obtained from recycled waste to produce products and improve their market conditions, increase the rate of energy recovery of waste (Mračko, 2012).

Landfill has a low initial cost, use of biogas and can be opened in a relatively short time. The disadvantage of landfill is public resistance, loss of raw materials, a high risk of groundwater contamination but also self-ignition (Takáčová, 2011).

Table 1 show that in Slovakia was in 2012 recorded 118 landfills. Most internal waste landfills in the Nitra and Košice. Only one such region has a landfill. Conversely, up to 15 landfills



waste, non-hazardous me just Prešov region, which is the highest of all regions. Žilina Region does not have any one landfill for dangerous waste. Kosice region has 3 landfills for dangerous waste. Most landfills of any type has Nitra region - 19. The next is Prešov region with 17 of landfills. Žilina Region and Banská Bystrica region have the every one 16 landfills. Of the total number of landfills in the Slovak Republic 90 landfills of waste are non-dangerous.

Table 1 The landfills in Slovakia

SR	LANDFILLS INTERNAL WASTE	LANDFILL WASTE, NON-HAZARDOUS	LANDFILLS FOR HAZARDOUS WASTE	THE TOTAL NUMBER OF LANDFILLS
BRATISLAVA	2	7	2	11
TRNAVA	2	7	1	10
TRENČÍN	2	11	1	14
NITRA	3	14	2	19
ŽILINA	2	14	0	16
BANSKÁ BYSTRICA	2	13	1	16
PREŠOV	1	15	1	17
KOŠICE	3	9	3	15
<b>SR</b>	<b>17</b>	<b>90</b>	<b>11</b>	<b>118</b>

Source: own processing according to <<http://www.enviroportal.sk>>

Data are collected annually on the state of waste management in Slovakia. They are used while a number of indicators, particularly the amount of waste per capita, and the amount of recovered waste collecting network density and the like. The average municipal waste production in 2012 was at 323.76 kg per capita, which is a decrease compared to 2011 by almost 50 kg. Taking into account the different regions, and most municipal waste produced in the region of Banská Bystrica - more than 340 kg waste produced and at least east of Slovakia, only slightly more than 266 kg / inhabitant / year.

Table 2 shows that, the total amount of municipal waste since 2010 is decreasing, which is a positive development for the future. Since 2008 is increasing the amount of waste, that is recovered. In 2012, it reached up to 25.53%. Most uses energy recovery, 9.38% before composting and material recovery of municipal waste. Most waste is disposed of by landfilling. In 2012 it was over 99% of waste. The good thing is that the amount of collected waste dropped by 2012 to 0.1% of the total municipal waste.

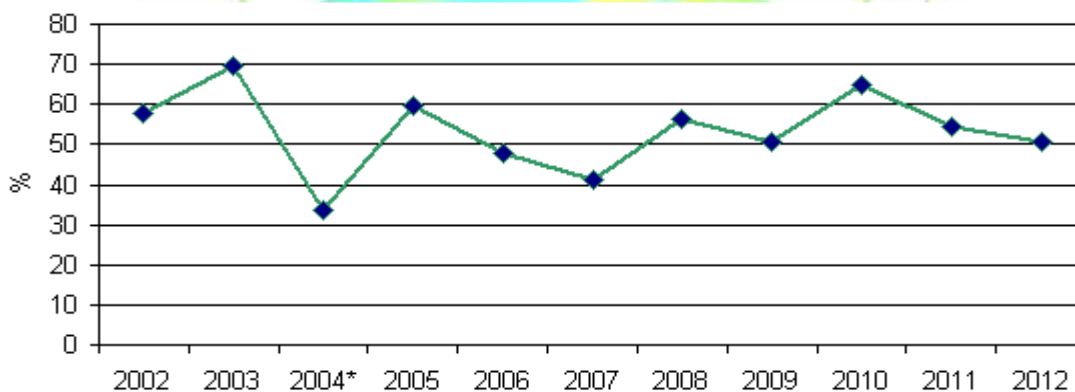
Table 2 Municipal waste arising

	2008	2009	2010	2011	2012
Amount Of Municipal Waste (T)	1 772	1 745	1 808	1 766	1 747
Amount Of Municipal Waste Per Capita (Kg)	327,5	321,8	331,1	372,4	323,76
The Amount Of Recovered Municipal Waste Per Capita (Kg)	58,3	52	66,8	78,3	82,65
Material Recovery (%)	2,4	2,7	3,6	4,3	5,88
Energy Recovery (%)	8,9	6,8	9,5	10,3	9,38
Composting Recovery (%)	4,5	5,1	5	5,7	7,01

Another Method Of Recovery (%)	2	1,6	2	3,7	3,26
Total (%)	17,8	16,2	20,1	24	25,53
Landfill Disposal (%)	76,2	80,8	78,1	74,7	99,64
Disposal By Incineration (%)	0	0,2	0,7	0,2	0,29
Another Method Of Disposal (%)	0,1	0,2	0,5	0,5	0,06
Collected (%)	5,9	2,7	0,7	0,6	0,1

Source: own processing

Figure 3 shows the rate of recovery of waste without municipal waste in % from 2002 to 2012. This recovery has variable character. The percentage ranges from 35% in 2004 to 70% in 2003. Last three years has a falling character and is about 50%, which, given the direction of waste management in Slovakia, can be considered positive.



**Figure 3 Rate of waste recovery in Slovakia**

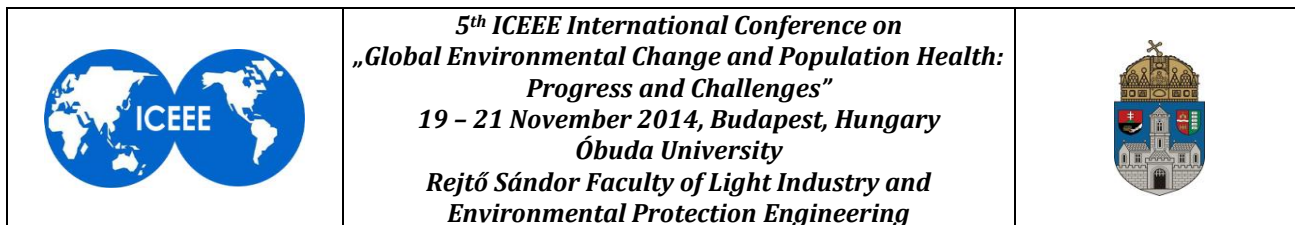
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According to Eurostat data, in 2011, produced an average of 503 kg of municipal waste per capita. In comparison with 2001, it's about 17 kg more. Municipal waste was treated in different ways. 37% had been stored in landfills, 23% of waste was incinerated, 25% of municipal waste is recycled and 15% composted waste is appreciated.

The total amount of municipal waste across the EU varies. Most waste produced in Denmark, 718 kg per capita. The next are Luxembourg and Cyprus, who have more than 600 kg of waste. Hungary, Bulgaria, Croatia, Slovenia, Czech Republic, Slovakia, Romania, Lithuania and Estonia produce less than 400 kg of municipal waste per capita.

According to Eurostat data, the method of waste recovery in different countries varies considerably. In 2011 had the highest proportion of municipal waste in landfills in Romania (99%), Bulgaria (94%) and Malta (92%). Countries that have incinerate waste most are Denmark (54%), Sweden (51%), Belgium (42%) with the Netherlands and Luxembourg (38%). Recycling as a way of recovery of municipal waste is the most used in Germany (45%), Ireland (37%) and Belgium (36%). Composting is the most devoted Austria (34%), the Netherlands (28%) and Belgium with Luxembourg (20%).

Overall, we can evaluate the recovery rate of waste in Slovakia since 2010 rising. It is a positive indication, but we should try to appreciate even more waste. Compared with countries



in the European Union, Slovakia is ranked fourth in the amount of waste generated. This trend can be sustained remains.

Amount of waste continues to increase, so it needs to be recovered in any way. Separation of waste is introduced in most of the Slovak Republic and gradually the company begins to pay recycling.

## DISCUSSION

Our society annually produces more waste. Therefore, it is the place to be interested in what happens with things that are no longer required for us and become worthless waste. Is the number of ways of waste disposal? When working with waste is most important to prevent its occurrence, minimize its use or reuse the same purpose. Waste treatment options are shown in Figure 2. The first step is the collection of waste and its storage. Followed by the transport of waste and recovery, which is activity leading to the use of physical, biological or chemical properties. Recovery either know the material, which uses wastes as secondary raw material for the production of useful product reclaim, recovery or recycling, and energy recovery, which uses waste to produce energy. This is followed by disposal of waste, which costs them so that it does not damage the environment or endangering people. The main conclusions of the experimental work should be presented. The contribution of the work to the scientific community and its economic implications should be emphasized.

## CONCLUSION

Nowadays in Slovakia as well as in the world it deals with waste in several ways. The oldest, cheapest, but also the most widely used method of waste management is our landfill. Other ways of waste management are as incineration, composting, separation and recycling. Slovakia is the most widely used method of processing waste landfill.

Slovak Republic issued several regulations on waste. In its legislative provides a register of waste handling, waste management program declares and publishes Waste Catalogue. The main regulations issued by the Ministry of the Environment is an Act of the waste 233/2001 Col.

The total amount of municipal waste is decreasing, which is a positive development for the future. In Slovakia are about 120 landfills and this is a most popular way of waste management. Amount of waste continues to increase, so it needs to be recovered in any way. Waste separation as a way of proper waste management is introduced in most territories of the Slovak Republic.

## ACKNOWLEDGMENTS

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## **ENVIRONMENTALLY FRIENDLY LASER CLEANING OF MATERIALS**

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### **ABSTRACT**

The contribution deals with environmentally friendly laser cleaning of various types of materials. The aim of this contribution is to present the new abilities of cleaning of materials in the future. There are mentioned and compared various material cleaning methods from classic ones to progressive ones and their influence on the environment. Laser cleaning is one of the newest progressive methods of the material cleaning. The results of this technology were recently tested and shown in the Department of Process and Environmental Engineering, Faculty of Mechanical Engineering, Technical University of Kosice together with the firm Trumpf Slovakia s.r.o.

The laser cleaning technology can be used in the various fields of industry, in the production sphere, in the renovation of products and materials and also minimised the influence of harmful impact on the environment.

**Keywords:** *material, laser cleaning, environmentally friendly technology*

### **INTRODUCTION**

In various branches of industries we must lubricate metal materials, their surfaces, components. Equally, the important role as lubrication is also degreasing and scouring of these metal surfaces. Degreasing of metal materials in the mechanical industry is an important technology for cleaning materials to further processing or as a finishing treatment of surfaces, or is used in the maintenance of machinery parts, tools and the like. By degreasing of metal surfaces not only removes lubricant from surfaces, but also cleans mechanical particles of dust, abrasion and others. With the continuously deteriorating of environment, it is necessary to use such degreasing technologies of materials that have no negative impacts on the environment. Also the environment protection is encompassed by standards and decrees of REACH.[1]

### **CLEANING TECHNOLOGY OF MATERIALS**

Cleaning technology of materials should be clear and shortly we can divide the decreasing of materials according to various methods of degreasing as [3]:

- Mechanical cleaning technologies - by W) technologies, [2],
- Chemical technologies [4]:
  - degreasing in organic or inorganic solvents,
  - degreasing in alkali solution,
  - degreasing by detergents,
  - emulsion degreasing,
  - degreasing by steam/ vapour,

- Progressive cleaning technologies – ultrasonic cleaning technology (together with degreasing in solvents or water)
  - dry ice cleaning technology, [5], [6], [7]
  - laser cleaning.

### CHEMICAL CLEANING DEGREASING TECHNOLOGY

The degreasing of metal materials by chemical method belongs to the oldest method of the degreasing. This technology requires the using of various degreasers, chemicals, which are very dangerous for the environment both in terms of storage of new and pure chemicals, their utilisation and at the storage of the chemicals. Chemical degreasing is performed most often by using of degreasing machines. Their classification and examples are as follows [3], [4]:

- Tub and wettable immersion degreasing machine (degreasing washing machine,
- Continuous Spray degreaser machine (grate),
- The chamber Degreaser Spray Machine (grate),
- Transition tunnel device,
- Carousel spray degreasing machines and others.

### CLEANING BY DRY ICE CLEANING TECHNOLOGY

Dry ice blast cleaning utilizes a unique combination of forces to powerfully lift surface contaminants without causing of damage or creating harmful secondary waste. Similar to sand, bead and soda blasting, dry ice blast cleaning prepares and cleans material surfaces by using a medium accelerated in a pressurized air stream. In the Figure 1 is shown the principle of dry ice blast cleaning [5], [6]:

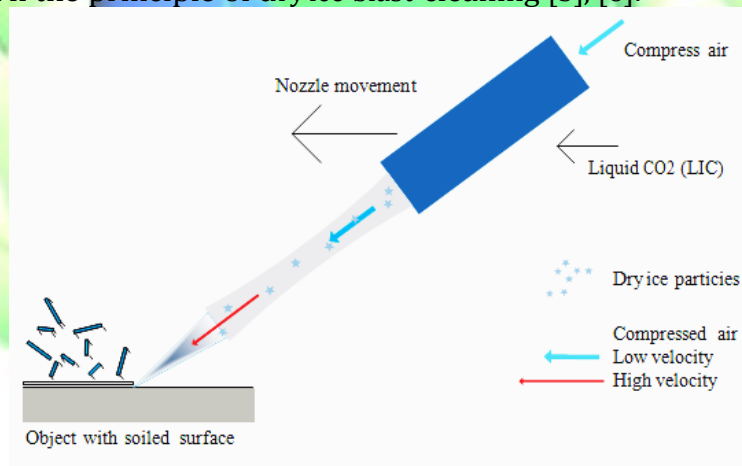


Figure 1 The principle of dry ice blast cleaning [6]

Dry ice blast cleaning offers comprehensive cleaning benefits over traditional methods, and can save up to 80% over current cleaning costs. Technical arguments against classic blasting technologies are [6]:

- A method is significantly faster and more efficient compared to any other cleaning system,
- Non-abrasive cleaning: absolutely no wear to cleaned surfaces, increasing the life of moulds, machinery and production equipment,
- Guarantee of the high quality finish to manufactured products,
- Ecological and economical dry ice leaves no trace and does not any additional



- waste to be processed,
- significant increase in productivity due to reduced production stops resulting from cleaning without disassembly or reassembly or cooling down.

In the Figure 2 and Figure 3 is the result of dry ice cleaning of the extrusion screws at the plastic production.



Figure 2 The extrusion screws before [7]      Figure 3 The extrusion screws after [7]

In the Table 1 is shown the comparison of blasting technologies according to environmental requirements.

Table 1 Blasting technologies according to environmental requirements [7]

CLEANING METHOD	NO SECONDARY	NON-CONDUCTIVE	NON-TOXIC	NON-ABRASIVE
Dry Ice Blasting	•	•	•	•
Sand Blasting*		•	•	
Soda Blasting*		•	•	
Water Blasting*			•	•
Hand Tools	•		•	
Solvents/Chemicals				•

\* Upon contact, traditional blasting materials become contaminated when used to clean hazardous substances and objects. These blasting materials are also then classified as toxic waste and require appropriate safe disposal.

## LASER CLEANING

Laser cleaning is a valuable addition toolbox as it offers a highly selective, reliable and precise method of removing layers of corrosion, pollution, unwanted paint and other surface coatings.

Developed over the last 10 years, the innovative laser cleaning systems combine power and versatility, with the lowest operating cost of all industrial cleaning methods. They offer a safe cleaning method and are environmentally friendly, using no water or chemicals and producing



no effluent. Primarily used for industrial cleaning and surface treatment, renovation and paint removal applications they also remove contaminants, production residue and coatings without damaging the substrate. Metallic and reflective surfaces are ideal although other substrates can be addressed. Laser cleaning systems offer an extremely high level of control and precision. Laser cleaning systems are currently in use in the automobile, aerospace, bakery, food, electronics, restoration and other industries.

### **THERMAL BEHAVIOUR OF THE LASER CLEANING PROCESS**

The cleaning surface reflects laser energy and is minimally affected, however, any contaminants on the surface absorb the laser energy and are quickly vaporized, with any fumes or particulates removed by an in-built filter.

When a laser beam irradiates on the material surface, it may be considered that energy flows in only one direction in a semi- infinite body.

The depth the laser energy penetrated into the material surface is constrained by the duration of the laser irradiation. Increasing ir- radiation time will allow the laser energy to penetrate deeper so as to raise the material substrate temperature. In the Figure 4 is shown the dependence of increase of surface temperature under different laser irradiation conditions.

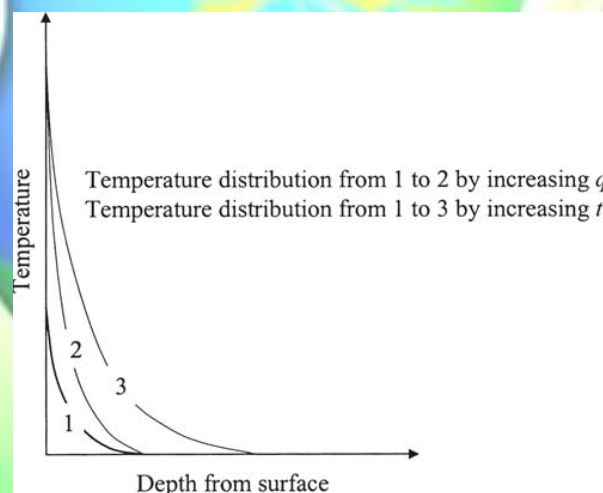


Figure 4 Increase of surface temperature under different laser irradiation conditions, where:  $q$  - laser power flux absorbed by the tested material,  $t$  - the time after laser irradiation begins [8]

Figure 4 illustrates the different effects of laser power flux and irradiation duration on the temperature elevation in the material. For the purpose of laser cleaning, higher surface temperatures are desirable for the removal of machining debris. However, the elevation of temperature under the wheel surface may damage the wheel structure, which should be prevented. Therefore, high power flux and short irradiation laser pulses are likely to be optimum for laser cleaning purposes. [8]

The cleaning of material surface stops when the contaminant is consumed, and consequently there is a minimal heat build-up, avoiding the microscopic roughening and cracking of metal surfaces that can be present when using traditional cleaning methods. [9]

In the Figure 6 is shown the principle of the laser cleaning technology.

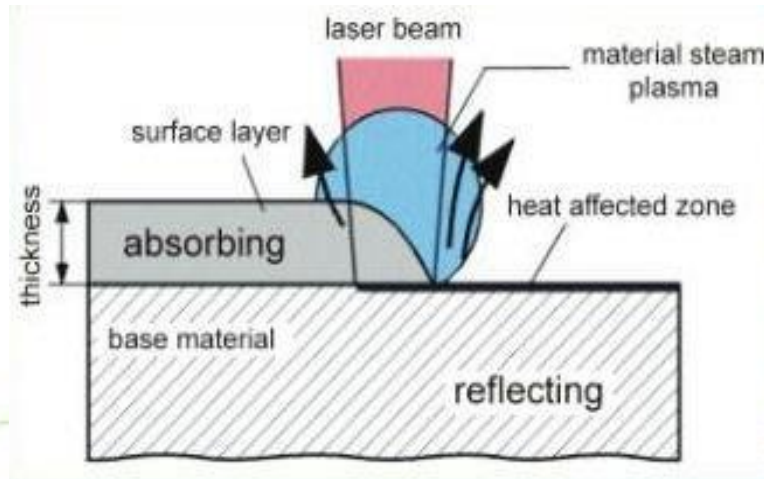


Figure 5 The principle of the laser cleaning technology [9]

The technology steps can be summarized in the following points: [8]

- Powerful, very short, rapid and moving laser pulses produce micro-plasma bursts, shockwaves and thermal pressure resulting in sublimation and ejection of the target material.
- A focused laser beam precisely vaporizes the target coating or contaminant.
- Process optimization of the laser beam produces maximum reaction with the target material for speed while, at the same time, does so safely and without harm to the base material.
- Metal surfaces are well-suited for many laser cleaning applications. Optimized beam settings will not metallurgically change or damage the laser treated surface. That depends on the focus position of the work piece, Figure 6

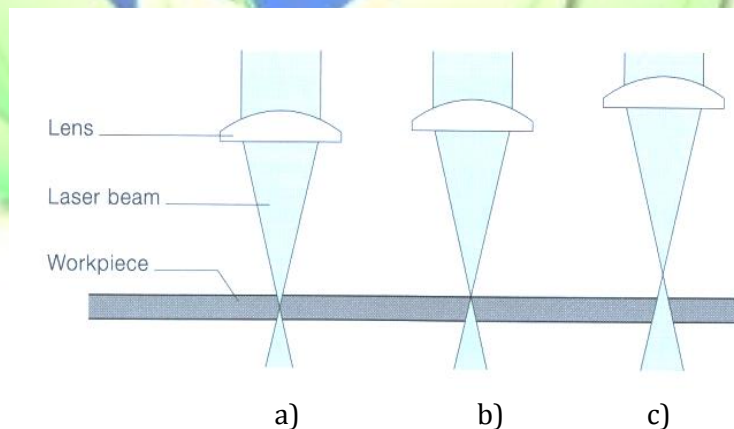


Figure 6 The focus position of laser beam: a) in the workpiece, b) on the surface, c) above the part [11]

- Only the coating, residue or oxide targeted for removal is affected as the laser beam is precisely adjusted not to react with the underlying metal surface.
- Laser beam power density is accurately and easily adjusted to achieve cleaning results

**Technology and environmental benefits** of laser cleaning technology are [8], [9], [10]:





- Fast set-up
- Easy to operate
- Quiet
- No clean-up
- Leaves no residue
- Highly reliable
- Easy to automate
- Low operating costs
- Virtually maintenance-free
- No consumable media - no abrasives, chemicals, solvents
- Green process - no pollution
- Laser beam settings are precisely adjustable to optimize process speed and gentleness

**Laser ablation applications are following [8], [9], [10]:**

- Mould cleaning,
- Surface Preparation,
- Removal of coatings and release agents,
- Weld and joining pre-treatment,
- Removal of oil and grease,
- Oxide removal,
- Paint removal,
- Surface cleaning,
- Gluing pre-treatment,
- Tool cleaning,
- Baking tray cleaning,
- Use of mirror attachment to work on complex shapes
- Historic Restoration.

In the Figure 7 to Figure 10 are shown the examples results of laser cleaning.



Figure 7 Tooth before and after  
Laser cleaning [8]



Figure 8 Brake pads before and  
after laser cleaning.[9]



Figure 9 Cleaning of an injection mould [10]

Lasers have been successfully used to clean prehistoric artefacts, sculptures and monuments, while preserving patina, fine surface detail and important surface coatings, [12]

### EXPERIMENTAL TESTING AND VERIFICATION OF LASER CLEANING TECHNOLOGY

The realisation of the first experimental testing was made in the cooperation with the firm Trumpf, Slovakia s.r.o. Materials used for the experiments were:

- a) Steel sheet (deep-drawn steel sheet KOSMALT 190), table: 100x50 mm, thickness: 2 mm, according to standard STN 038737
- b) Synthetic lubrications with various properties (various viscosity):
  1. **Berutox M21 EPK 420**, temperature range: -5°C to + 200 ~ + 220°C, viscosity of the basic oil: 490 mm<sup>2</sup>.s<sup>-1</sup>, at the temperature t = 40°C [13]
  2. **Berutox M 21 KN**, temperature range: -5°C to + 200 ~ + 220°C, viscosity of the basic oil: 490 mm<sup>2</sup>.s<sup>-1</sup>, at the temperature 40 °C [ 14]
  3. **Beruplex LI-EP 2**, temperature range: -30°C to + 150°C [15]

There were used 5 tested pieces for each experiment. Figure 10 shows the dimensions and tested pieces.

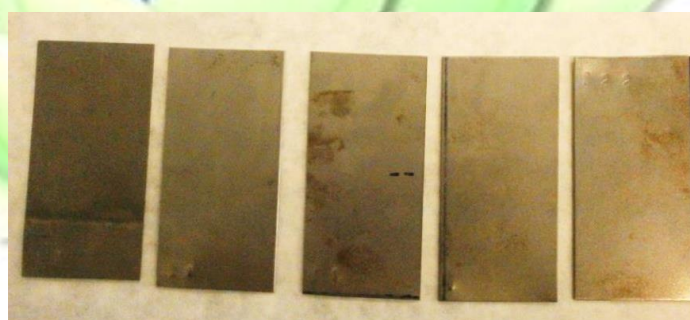
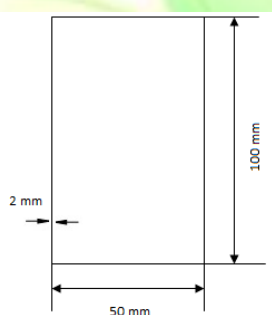


Figure 10 Rectangular profile of deep-drawn sheet KOSMALT 190

After degreasing with technical white gasoline, the tested samples were weighed on laboratory scales MS, METTLER TOLEDO. The lubricants were applied by a paintbrush and were weighed again. The decreasing of tested samples by laser cleaning were experimentally provided on the laser compact machine TruMarkStation 5000, with the least power, to not do an effect on the surface layer of the metal by hardening. There was used the “c” type of focus position of laser beam as it is shown in the Figure 6. The condition of the laser parameters are shown in the Table. The example of testing and workplace is shown in the Figure 11.

Table 2 Testing parameters of laser beam at the degreasing of testing sample

beam source	TruMark 6130
Optics	F 163
wavelength $\lambda$	1604 $\mu\text{m}$
The speed of the laser beam v	1000 mm/s
frequency	50 kHz
defocus	1,5 mm



Figure 11 The example of laser cleaning – position of the sample

After laser cleaning, the tested samples were weighted again and were found the weight loss of tested samples. The weighted values of the tested samples are shown in the Table 3.

Table 31 Examples of the values of the tested samples cleaned by laser beam – sample U1-U5

Sample	weight			
	Degreased sample by white gasoline	Sample + lubrication	Degreased sample by laser	Used lubricant
1	53,189	53,607	53,505	Berutox M 21 EPK 420
2	52,029	53,074	52,77	Berutox M 21 KN
3	53,972	55,518	54,593	Beruplex LI-EP2
4	52,577	53,661	52,598	Berutox M 21 KN

The results after first planned experiment, where the laser beam passed only once through the surface sample during the laser cleaning,, are shown in the Figure 12 to Figure 21.





Figure 12 The sample after laser cleaning  
Lubricant Berutox M 21 EPK 420

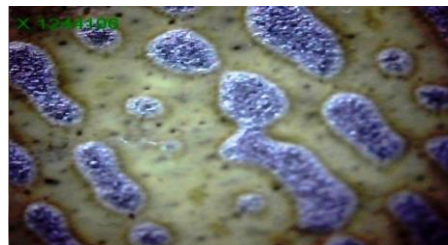


Figure 13 Detail of degreasing of  
lubricant by USB microscope



Figure 14 Tested sample before (light field) and after laser decreasing (dark field), lubricant  
Berutox M 21 KN



Figure 15 The sample after laser cleaning  
lubricant Berutox M 21 KN

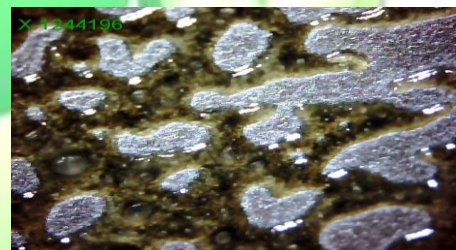


Figure 16 Detail of degreasing of  
lubricant by USB microscope



Figure 17 The sample after laser cleaning,  
lubricant Beruplex LI-EP2

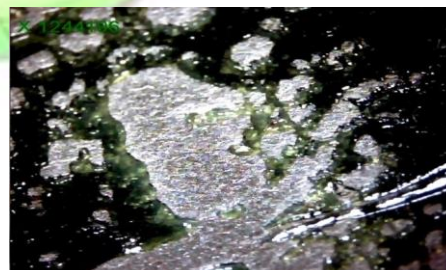


Figure 18 Detail of degreasing of  
lubricant by USB microscope

The results of the comparison of the chosen tested samples weighted on the laboratory scales and cleaned by laser beam are shown in the Figure 19.

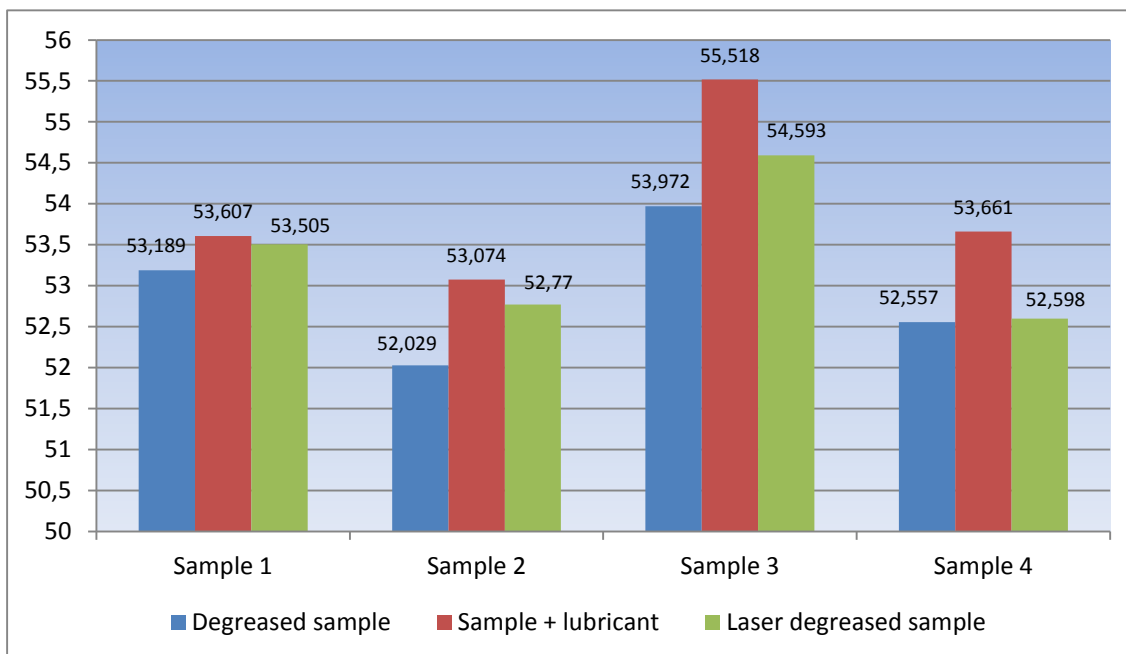


Figure 19 Degreasing of tested sample by laser beam, sample 1 – Berutox M 21 EPK 420, sample 2 – Berutox M 21 KN, sample 3 – Beruplex LI-EP 2, sample 4 – Berutox M 21 KN

## CONCLUSION

Due to the ongoing problem of environmental degradation, we try to find ways to minimize these negative factors. The engineering industry as a whole is greatly contributes to environmental degradation. That is why we try and look for the ways how to minimize the impact on the environment. One of these ways was to try decrease of the material without the using of chemicals.

In cooperation with TRUMF Slovakia s.r.o., we tested and verified the possibility of cleaning of the samples with a laser beam (with the compact machine TruMark 5000) for the first time.

From the experiments, we can make a conclusion after visual control that during the laser cleaning tests of the samples No. 4, they reached the best results .The samples were greased by the lubricant BERUTOX M 21 KN, and on the other hand the worst results were reached with the samples No.1, which were greased by the lubricant Berutox M 21 EPK 420.

## Acknowledgement

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## **ENVIRONMENTAL LIFE CYCLE ASSESSMENTS FOR WATER TREATMENT PROCESSES AN ALGERIAN CASE STUDY OF AN URBAN WATER CYCLE**

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### **ABSTRACT**

The environmental performance of wastewater treatment plant (WWTP) is still poorly evaluated. Comprehensive and reliable method is needed to guide policy makers on the environment. A literature review showed that, Life Cycle Analysis (LCA) has been tested to address this problem and it appeared as an essential tool to study the environmental impacts of wastewater treatment plant (WWTP).

In our study the evaluation method used is the life cycle assessment (LCA) for the determination and evaluation of potential impact of wastewater treatment plant (WWTP of Medea), Algeria.

LCA requires both the identification and quantification of materials and energy used in all stages of the product's life, when the inventory information is acquired, it will be then interpreted into the form of potential impact Eco-indicators'99 towards study areas covered by LCA, using the SimaPro 7.1 software for wastewater treatment process is necessary to discover the weaknesses in the water treatment process in order for it to be further improved ensuring quality life. SimaPro. 7.1 conceived by PréConsultant is used for the determination of various categories of impacts generated by the WWTP.

As this research is still in its development stage. Inventory data from wastewater treatment process are still being collected from each plant involved. The experimental results show that the WWTP of Médéa (Oued Lahrech). by its energy consumption, solid rejections (sludge), and especially liquids (water) do not take part in deterioration of the environment (plants: fruit and vegetables) and animals.

**Keywords:** *Life cycle assessment (LCA), Environment, wastewater treatment process, Potable water, Simapro 7.1*

### **INTRODUCTION**

Facing the increase of environmental concern in the water treatment field, researchers need decisive decision support tools to assess environmental performances of industrial and urban wastewater, ADEME (1999). A sets of treatment flowsheets can be built and therefore the overall impact on environment wastewater systems is more difficult to assess. That situation explains the need for rigorous methods to evaluate and compare environmental performances of wastewater treatment plants. They have to be multicriteria-based because many impacts are concerned: toxicity and ecotoxicity of treated water and sludge, energy consumption, greenhouse effect, eutrophication, etc. Life Cycle Assessment (LCA) is a “cradle-to-grave” approach which evaluates several potential environmental impacts, as those listed above, of a product, a process or a service. To ensure a credible evaluation and comparison, methodological rules have to be followed which are developed within the framework of the ISO 14040 standards

ISO 14040 (1997), ISO 14041 (1998) and ISO 14042 (2000). LCA is divided in four stages that can be summarized as follows Guinée et al. (2002) and Renou et al. (2008):

- Goal and scope definition
- Life cycle inventory (LCI)
- Life Cycle Impact Assessment (LCIA)
- Interpretation: results

A lot of papers have been conducted and published concerning the use of the LCA as an assessment methodology for WWTP or for potable water treatment plant. But in Algeria few works have been conducted to this field using LCA methodology, In spite of the big number of WWTP, Boureghda et al., (2013). The goal of the present work is to evaluate the influence of the selected impact assessment method on the LCA outcome in the case of wastewater treatment (Medea's WWTP). In the first part the methodology of Life Cycle Assessment is applied to an urban wastewater treatment plant for carbon and nutrient removal, including sludge treatment and recycling.

## MATERIALS AND METHODS

The wastewater treatment plant (WWTP) is located at Medea (Oued Lahrech) about 100 km from the capital of Algeria. It is designed to treat domestic sewage from the city of Medea and its surroundings villages (Figure 1). WWTP of Medea uses activated sludge collected in a conventional aeration process that ensures a very good efficiency in reducing the Biochemical Oxygen Demand (BOD).



Figure 1: Satellite view of the STEP of Medea, coordinates: 36 ° 14 '04.10 "N; W 2 ° 45' 29.44" E

1. Mechanical treatment which includes coarse and fine grids (50mm / 25mm), grit removal (aerated) / oiling.
2. Biological treatment (prolonged low load aeration) consists of two units, each equipped with an aeration tank and clarifier and a sludge pumping station and return in excess.
3. Decanter.
4. Sludge treatment using thickeners and drying beds (dehydration)
5. Chlorination tank.





(a)

(b)

(c)

Figure 2: Mechanical pre-treatment steps: a) oil separator sand trap. b) Rake coarse. c) Rake coarse fines



Figure 3: Biological Treatment, aeration basin



Figure 4: Decanter





Figure 5: tertiary treatment, (a) sludge drying bed (pool chlorination)

## RESULTS AND DISCUSSION

The functional flow in our case is based on wastewater, which is a liter of wastewater to treat arriving at the station for a year. Emissions of treatment plants are very dependent on local criteria such as wastewater quality (high influence of industrial streams, combined rain and sewage networks), operation, pollutants dispersion, etc. If some of these pollutants are analyzed to check conformity to regulations on treated water or sludge, others are not measured on a routine basis. Missing data can be replaced by information from literature. However, their degree of relevance with respect to the site under study will affect the accuracy of the results.

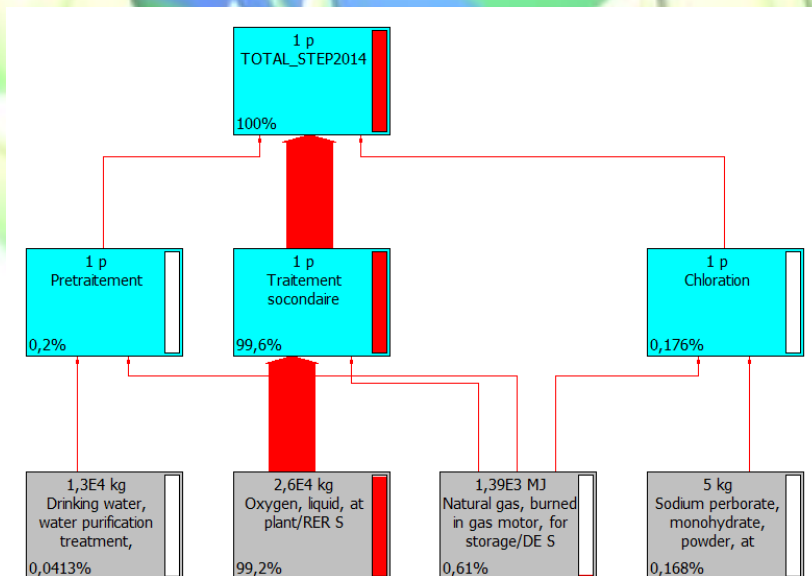


Figure 6: LCA flowchart of Medea WWTP



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## CONCLUSION

For impacts like acidification, eutrophication, greenhouse gas emission or resource depletion, the choice of one of the other impact assessment methods available in LCA software (SimaPro 7.1) is not a critical issue as the results they provide are similar. However, finding a way to take into account local river eutrophication in the assessment, would be also helpful. further work is necessary on human and ecosystem health indicators to make researchers fully confident as the current impact assessment methods do not converge toward similar results. It would be very useful for urban wastewater treatment specialists if specific information related to wastewater treatment and re-use such as pathogens and Pharmaceuticals and Personal Care Products (PPCPs) could be introduced in databases.

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## **GEOINFORMATICS FOR DELINEATION AND ESTIMATION OF SALT AFFECTED SOILS**

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Geoinformatics is the application of information technology for study and management of earth resources. Soil and water are the two indispensable natural resources of the earth. Salt affected soils pose a severe threat to the sustainability and health of the soil. A study was carried out in Gohana block of Haryana, India to monitor the effect of groundwater on the salt accumulation of soils with the objective to prepare soil map on 1:50,000 scale. Salt affected area of the block was estimated by Indian remote sensing satellite (IRS) using LISS-III data. It was observed that 2.41% area of the block is found to be salt affected. The soils were categorised into moderately and strongly salt affected. The area under moderately and strongly salt affected was 412 and 468 hectares, respectively, out of the 36,448 hectares total area of block. Soil maps based on electrical conductivity ( $EC_e$ ) of the soil extract, pH and exchangeable sodium percentage (ESP) were prepared in ArcGIS software. Therefore, remote sensing and GIS techniques are found to be an important tool for delineation and estimation of salt affected soils.

*Keywords: Geoinformatics; sustainability; salt affected soils; LISS-III;  $EC_e$ ; pH; ESP; ArcGIS; remote sensing; delineation; estimation*

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## **ANALYSIS OF MATERIAL POTENTIAL END-OF-LIFE PHOTOVOLTAIC PANELS IN SLOVAK REPUBLIC**

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### **ABSTRACT**

Solar power is one of the fastest growing sources of renewable power in the world today. The word “photovoltaic” is a combination of two words “photo”, meaning light, and “voltaic”, meaning electricity. Therefore photovoltaic technology, the scientific term used to describe solar energy, involves the generation of electricity from light. During the last years rapidly increased the number of photovoltaic sources in Slovak republic. By the increasing numbers of photovoltaic sources also increased the numbers of installed photovoltaic panels in Slovak republic. Photovoltaic panels contents valuable materials. These valuable materials will become interesting at the life end of photovoltaic panels.

*Keywords: photovoltaic panels, materials, solar energy, recycling*

### **INTRODUCTION**

A solar power generating system works no different than a conventional power plant. However, there is one important difference, no harm is done to the environment during their lifetime by burning coal, oil, natural gas or by splitting uranium to produce energy. It generates power solely from the energy from the sun. But after the finishing the period of lifetime is necessary environmental disposal of the elements belongs to solar energy sources. One of the most used and important element is photovoltaic panel.

### **CHARACTERISTICS OF PHOTOVOLTAIC PANELS**

Photovoltaic panels represent a renewable source of energy by enabling the direct conversion or solar radiation into current electricity. The solar cells is the elementary building block of the photovoltaic technology. There are several types of solar cells. More than 90% of the solar cells currently produced worldwide consist of crystalline silicon cells. The second most utilised solar cell material with increased market share is cadmium telluride. It enables thin film cells which can be produced with lower costs than silicon based solar cells [4].

Types of photovoltaic cells:

- 1st generation – crystalline silicon,
- 2nd generation – thin film (cadmium telluride),
- 3rd generation – concentrators of photovoltaic.

### **PHOTOVOLTAIC IN SLOVAK REPUBLIC**

Until the year 2007 very little attention has been given to photovoltaic so far. Up to 2007 the total installed power in Slovakia was only 20 kW. This was primarily a consequence of the fact that photovoltaic was seen as an expensive and if at all a very long term option, and

therefore not included in the Slovak energy policy. As the future Slovak economy strongly depends on the availability of energy at an acceptable price and low environmental impact, the Slovak energy policy is part of the national economic strategy of the Slovak Republic to ensure maximum economic growth while retaining sustainable development. In recent years there has been a constant increase in coverage of energy demands from renewable energy sources. One of the most widely used renewable energy was dendromass (Martinka et al, 2014), but in the last years also solar energy. With an average solar irradiation of between 1100 and 1150 kWh/m<sup>2</sup>/yr (higher than in Germany (around 1000 kWh/m<sup>2</sup>/yr)), PV solar energy can give a considerable contribution to the future Slovak electricity production. The direction, chosen by the Slovak government to set up a feed in tariff with an annual cap and a relatively high tariff, allowing newcomers in the field to include a risk surcharge in their system price and other forms of support [6].

These measures in the last years increased the installed power of photovoltaic plants. At the end of year 2012 was installed overall power of photovoltaic power plants 543 MW as shown table 1.

Tab. 1 Producer of electric energy by the Photovoltaic solar systems in the Slovak republic

Number of producers	Installed power	Overall installed power
<b>1182</b>	<b>≤ 0,1 MW</b>	<b>41 MW</b>
<b>81</b>	<b>0,1 – 0,9 MW</b>	<b>49 MW</b>
<b>370</b>	<b>&gt; 0,9 MW</b>	<b>453 MW</b>
	<b>Overall</b>	<b>543 MW</b>

For comparison summary installed capacity of hydropower plants in Slovak republic is 1652 MW, which is approximately 30% of the total installed capacity of Slovak power plants (fig. 1) (Zbojovský et al., 2012, Hladký et al., 2006).

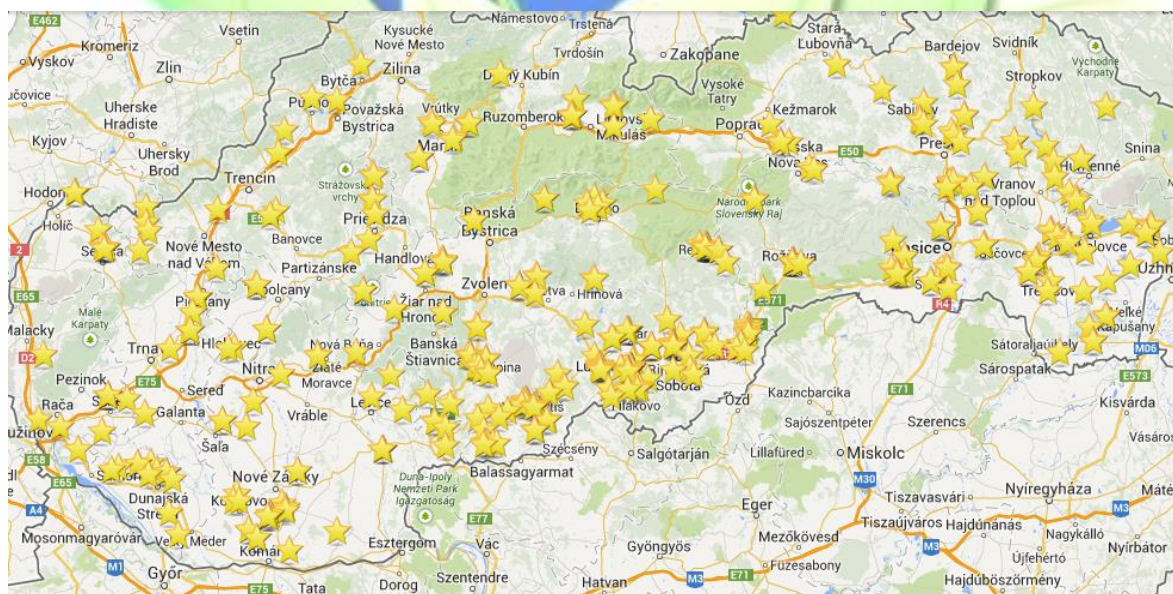
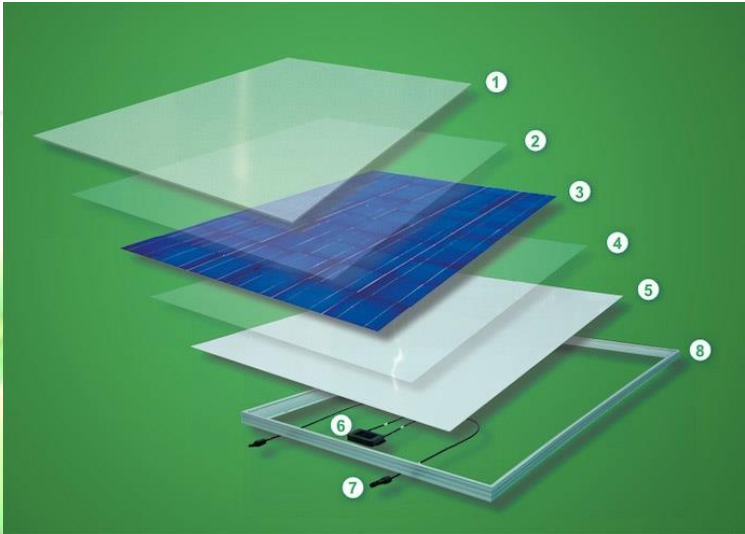


Fig. 1 Map of Photovoltaic solar electric power plant in Slovak republic with power > 100 kW [7]



**MATERIAL COMPOSITION OF PHOTOVOLTAIC PANELS**

The solar cell is the elementary building block of the photovoltaic technology. Solar cells are made of semiconductor materials, such as silicon, exhibiting the photovoltaic effect. There are several types of solar cells. However, more than 90% of the solar cells currently produced worldwide consist of wafer-based crystalline silicon cells [4]. The second most utilized solar cell material, with an increasing market share, is cadmium telluride. Basic elements of photovoltaic panels presents fig. 2.



1- glass, 2 – EVA film, 3 – solar cells, 4 – EVA film, 5 – PVF layer, 6 – isolations, 7 – contact box, 8 - frame

Fig. 2 Basic parts of photovoltaic panel

For the knowledge of material composition of photovoltaic cells was realised experimental dismantling by using regular mechanical tools. Result of dismantling and material composition of dismantled photovoltaic panels shows tab. 2.



Table 2 Result of dismantling of photovoltaic panel

Material	Weight percentage [%]
Glass	74
Aluminium	12
Solar cells	4
Other material (EVA, back sheet, silicon)	1
Other components including metals	9

**RESULTS**

The amount of photovoltaic panels placed on the market in Slovak republic and also EU has been rising sharply in the last years, and is expected to strongly grow in the coming years. Photovoltaic panel recycling is currently not economically viable because waste volumes generated are too small. Significant volumes of end-of-life photovoltaic panels will only begin to appear in 2027 or 2032. According to material composition of photovoltaic panels, their weight



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and installed numbers of panel in Slovak republic we can predict volume waste from photovoltaic panels. Between the year 2027-2032 will finish the lifetime of Solar photovoltaic plants built in last few years. Nowadays is installed power photovoltaic solar plant about 550 MW. It means more than 2 000 000 installed photovoltaic panels. Average weight of photovoltaic panels is 20 kg, it means 40 000 – 50 000 tons waste of photovoltaic panels. During next year is necessary to develop new recycling and recovery technologies of photovoltaic panels.

## **DISCUSSION ABOUT RECYCLING AND RECOVERY OF PHOTOVOLTAIC PANELS**

Treatment and recycling procedures for photovoltaic panels are similar to recycling for LCDs, screen glass, mirrors, windscreens, other laminated glass, and gas discharge lamps, due to their large portion of glass.

Despite their higher energy intensity for production, it is cheaper to use virgin raw materials in photovoltaic panel production. While this remains true for silicon-based panels due to the abundant supply of silicon as a raw material, more potential economic incentives exist for CIS, CIGS, and CdTe panels due to the rarity of indium, tellurium, and other rare metals, particularly in comparison to expected future growth in the photovoltaic industry and the resulting exponential increase in raw material demand [3].

While a number of treatment and recycling processes are under development globally for photovoltaic panels, there are currently only two treatment and recycling methods developed specifically for PV panels which have been tested and put into operation:

Deutsche Solar's process which is predominantly used for crystalline silicon panels, and First Solar's process (currently operational in the United States, Germany, and Malaysia) which is primarily used for CdTe panels [3].

## **CONCLUSION**

Including photovoltaic panels in the WEEE Directive reduces the potential negative environmental impacts of improper disposal and generates economic benefits. Limiting the quantity of photovoltaic panels improperly disposed of has the positive environmental impacts of avoiding lead and cadmium leaching and avoiding potential resource loss due to non-recovery of valuable conventional resources and rare metals in photovoltaic panels. Important factor of the collection and recycling of photovoltaic panels is if residential and commercially used photovoltaic panel will be included by the directive of EU.

In 2012 new directive of EU was approved. Directive 2012/19/EU on waste of electrical and electronic equipment include photovoltaic panels [4]. According new directive photovoltaic panels was included into category 4, consumer equipment and photovoltaic panels. It means new responsibility of producers and importers of photovoltaic panels.

## **ACKNOWLEDGMENTS**

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## **THE IMPACT OF ACID MINE WATER ON THE BIO AVAILABILITY OF HEAVY METALS IN THE ABANDONED MINING DEPOSITS IN THE TOWN SMOLNIK**

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### **ABSTRACT**

Acid mine drainage (AMD) has been in the interest of researchers all over the world as it presents an especially dangerous type of mine water. Acid mine drainage is formed predominantly in deposits with pyrite (ore, non-ore, coal) and it can mobilize exceptionally high concentrations of toxic metals. The paper covers the most important iron ore area in Eastern Slovakia. It presents environmental problems related to mining in this environmentally loaded area, with special focus on acid mine drainage presence research and on the possibilities of eliminating its impact on the environment.

***Keywords:** acid mine drainage – AMD, heavy metals, mine deposit*

### **INTRODUCTION**

Removing the after-effects of mining activities presents an important environmental issue of the present. One of the greatest problems to be tackled is the impact of acid mine drainage on the environment. Due to oxidation and other chemical processes, mine waters with high level of mineralization by low pH (as low as 3) are generated in flooded mine areas, in refuse piles and setting pits. This acid mine drainage contaminates the environment, the groundwater; it causes soil degradation and can also cause decomposition of other minerals that can be the source of other toxic elements.

Chemical weathering of sulfides may be characterized as a series of geochemically and microbially induced reactions whereby contaminants are released into the hydrological cycle and become mobile and therefore bioaccessible. The result of weathering of such minerals as sphalerite, galenite, chalcopyrite or arsenopyrite is the release of mainly metal ions into the environment. Acidity is primarily released by weathering of pyrite by air oxygen and water, or by solutions containing dissolved oxygen. In surface conditions this is followed by precipitation of iron-oxyhydroxides. They are generally named ochres, because they are very well visible as yellow to brown films on solid surfaces of sources from where mine water flows. The released metal ions, acidity and ochre formation - all these products present environmentally unacceptable and hazardous properties of mine drainage in relation to other water resources [1, 2, 3].

### **ACID MINE DRAINAGE CLASSIFICATION**

Mine drainage can be classified into several basic types:

TYPE 1 mine drainage is characterized by low pH (pH<4.5) and high concentration of Fe, Al, Mn and other metals, H<sup>+</sup> and oxygen. This type has been named AMD.





TYPE 2 mine drainage contains a lot of dissolved Fe and Mn, but very little or no O<sub>2</sub>, and has pH>6. Following oxidation the pH of this drainage is dramatically reduced and the drainage can become AMD (Type 1).

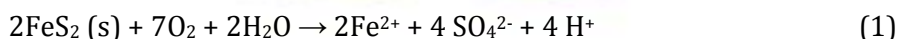
TYPE 3 mine drainage is characterized by a moderately increased content of dissolved elements (Fe, Mn) in the solution, they contain almost no oxygen, pH>6, and their alkalinity is higher than their acidity a (they start to be referred to as alkaline mine drainage). The acidity generated by the hydrolysis of metals and by the precipitation reactions is neutralized by the alkalinity contained directly in the water. TYPE 4 is represented by neutralized AMD with pH>6 and with a high content of dissolved elements. There is no precipitation of metal hydroxides. After some length of time, if kept at rest in a reception container, precipitation may occur and Type 5 is formed. TYPE 5 mine drainage is neutralized AMD with a high content of dissolved elements, but not metals. Following precipitation of metal hydroxides in the collection container the content of metal cations in the solution is much reduced and usually only Ca and Mg remain dissolved in the water. Soluble oxo-anions, as carbonates and sulfates remain in the solution. In case alkalinity and oxygen had been consumed in the neutralization processes, there will be no water.

## **EXPERIMENT**

### **WEATHERING OF SULFIDIC MINERALS IN MINES OF SMOLNIK**

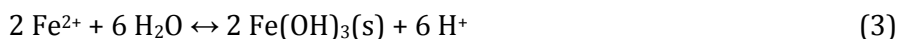
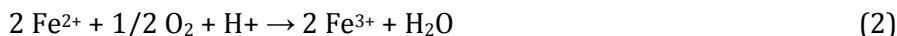
Sulfides usually present only a small part – a few percent of weight - of rocks and minerals. In spite of that they have a high potential of producing toxic substances and causing a degradation of the environment for long periods, often longer than several decades. In areas with ore deposits where pyrite represents a substantial ore component formation of mine water with extreme properties occurs over a period longer than one century (Jambor, Blowes 1994, Younger et al. 2002).

The chemical equations below demonstrate the process of dissolution, the increase of environment acidity, formation of ochres and mobilization of metals during oxidation of sulfides (Nordstrom 1982a, Nordstrom et al. 2000, Nordstrom, Alpers 1999, Jambor et al. 2000, Singer, Stumm 1970). The weathering reactions present an example of complex oxidation-reduction reactions or reactions with transfer of electrons between substances and intermediate products in several subsequent, or various alternative steps. For the sake of simplicity, summarizing equations are used that show the particular observable processes and manifestations (e.g. dissolution). The oxidation and dissolution of pyrite by oxygen in the presence of water can be expressed by equation (1):

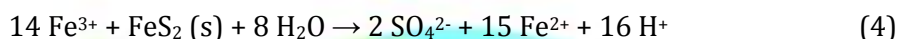


The above reaction which demonstrates the release of iron, sulfate and hydrogen ions (sulphuric acid) into the water is also relevant for weathering of marcasite which has the same composition but different crystallographic structure. Electrons are transferred from the mineral phase mainly from sulphur to oxygen. The electrons transferred from these reactions can also be taken away (bonded) by 13 bacteria which use them as a source of energy for maintaining the function of their cells. Microbial activity plays an important role in the kinetics of reactions and it can determine how fast the redox reactions – or the overall sulfide oxidation process will be (Nordstrom 1982a, Ritchie 1994). The stoichiometric record of the process shown below (1) is useful for evaluating the amount of contaminants; however it does not provide information

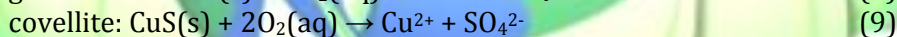
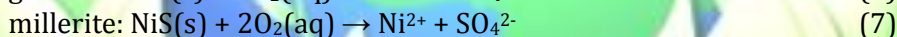
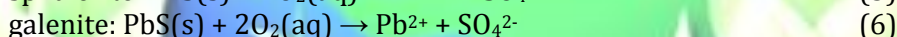
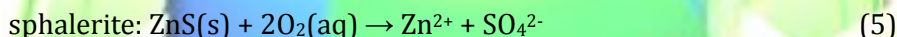
about the factors influencing the speed of weathering. If there is enough oxygen present in the water, or if the solution is in contact with the atmosphere, the dissolved Fe<sup>2+</sup> will oxidize further (2, 3):



More „acidity“ will be formed in the process than will be consumed, because Fe<sup>3+</sup> will react further and will precipitate as hydroxide – ochre (3), or will react with pyrite producing acid and dissolved Fe<sup>2+</sup> (4):



As the reactions in both directions in the Fe<sup>3+</sup> hydroxide precipitation and dissolution equation (3) are relatively fast compared to the observed speed of mine drainage in mining sites, mine water usually reaches a state of balanced dissolution with sulfides (FeS<sub>2</sub>). Fe<sup>2+</sup> ion can be repeatedly re-oxidized by the oxygen available; it becomes an oxidation agent, which in turn enables further dissolution of sulfide. In case oxygen is not available, iron in the form of Fe<sup>2+</sup> remains dissolved, which will be manifested by high concentration of Fe in the water. Sulfide metals such as Fe (other than pyrite) need not necessarily increase environment (water) acidity during oxidation, but will release metals into solutions:



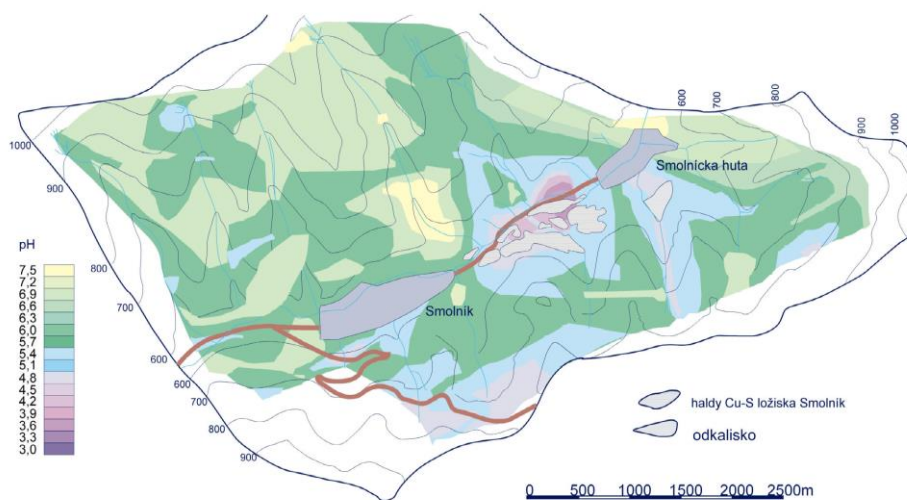
It follows from the above reactions that owing to the dissolution of minerals/sulfides, surface water that infiltrates mining sites can be enriched by soluble substances. The dissolution of pyrite releases acid which reduces the water's pH level. If there are other minerals present in the environment that can consume the generated acids by their own dissolution, the water pH is not reduced and the water-rock system may be characterized as buffered. Because the dissolubility and at the same time bioaccessibility of metal ions is pH dependant, the main indicator in water (mine, mineral) contamination forecasts is the rock and mineral composition. The natural consumption of produced acids and water pH buffering through mineral dissolution – these are the decisive processes or characteristics for (environmental) evaluation of metal ions behaviour, especially in terms of whether they will be dissolved and will be present in the mine drainage [4].

### THE SMOLNIK MINE DEPOSIT

The Smolnik Cu-Fe ores deposit is situated in the southern region of Slovak Ore Mountains, between Smolnicka Huta and Smolnik. The deposit was mined for approximately 700 years and has been thoroughly explored and documented. At the beginning, mining operations were mainly focused on Cu, Ag, Au and Fe ores from the rich oxidation zone close to the surface. The deposit belonged to the largest deposits with polymetallic sulfide type of mineralization in former Czechoslovakia. Besides standard Cu ore exploitation methods, copper recovery by



cementation was also used for many centuries. For centuries, up to the 80s of the 20<sup>th</sup> century, mining areas, refuse dumps and water flows had been adjusted to provide the highest possible concentration of copper in the mine waters. With the aim of stronger pyrite oxidation in mining spaces the area through which water flowed was enlarged, rocks were broken down; channels for distribution of water into mining areas were built, etc. The cementation water acquired in this way (in fact acid mine drainage) was brought into cementation tanks with metal scrap on which layers of pure copper precipitated. It was then metallurgically processed. This means that for several centuries open and underground mines were adapted in order to produce the highest possible amount of acid mine drainage. It resulted in what is today an ecologically unacceptable situation in the vicinity of Smolnik Stream. At the end of the 80s it was decided the mine would be closed. On 15th December 1990 flooding of the mining spaces began. During the flooding, the quality of water in the Smolnik Stream immediately improved. According to data available, in 1991 and 1992 the pH levels ranged from 5.85 to 6.95 and neither did the content of metals exceed the limits for surface waters. Flooding of the mine ended in May 1994 and on June 6, 1994 the first leakage of mine waters was observed in the stream close to shaft Péch. (Jaško et al., 1996). If the mine had been flooded and measures taken to ensure there would be no flow of mine waters and no oxygen would get into the mine, the ecologically undesirable situation in the mine would not have arisen. Without access to oxygen and fresh water there would be no oxidation of sulfide minerals. Unfortunately, fresh water from the surface keeps entering the mine, where it attacks sulfide minerals. Together with the impact of oxidation bacteria it turns the whole mine area into a bioreactor producing large amounts of AMD. AMD discharges near the former Pech shaft into the Smolnik Stream. The gradual neutralization of AMD causes precipitation of Fe and Al oxyhydroxides which are carried by the water as far as River Hnilec and further on to the Ruzin reservoir. A large amount of sludge settles in the reservoir (approx. 224,000 m<sup>3</sup> per year). Part of it is brought in by River Hnilec and this is an additional cause of significant problems. In the sediments brought in by rivers Hnilec and Hornad, and even in the live organisms living in these rivers there is an increased content of Cu, Zn, Co, Ni and Hg (Bobro et al., 1999). [5]



**Figure 1** Localisation of the Smolnik deposit in a geomorphological model and pH of surface waters in the affected area [6]



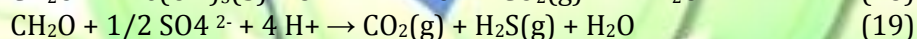
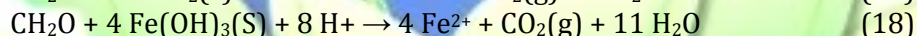
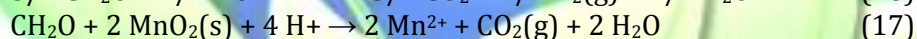
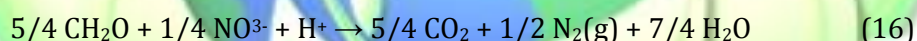


## MOBILITY OF DISSOLVED SUBSTANCES IN THE MINE DEPOSIT AND ITS SURROUNDINGS

During the process of dissolution of sulfides, metal ions are released into the solutions. These can either remain in the solution or they can precipitate mainly as hydroxides. For example,  $\text{Zn}(\text{OH})_2(\text{s})$ ,  $\text{Al}(\text{OH})_3(\text{s})$ , or  $\text{Fe}(\text{OH})_3(\text{s})$ , which can precipitate continuously from flowing water. The decisive parameter for the process of mobilisation of metals in water is the dissolubility of these phases. Dissolubility depends on the water pH; it usually grows as pH level falls. Water discharges with low pH are usually enriched by dissolved metals, whereas waters with pH close to neutral have a low content of dissolved metals. We can say that the critical parameter for metals mobility, and, therefore, for their bioaccessibility, is the pH level. The dissolution of carbonates and silicates is a significant type of reaction forming the water pH level in this area.

Metal ions released in the process of sulfide weathering will also precipitate as sulfates, carbonates and in some cases also as silicate minerals. The most frequent soluble sulfates that immobilize bivalent and trivalent iron and can be found in the weathering zone of sulfidic sediments include:

melanterite ( $\text{Fe}^{2+} \cdot \text{SO}_4 \cdot 7\text{H}_2\text{O}$ ), rosenite ( $\text{Fe}^{2+} \cdot \text{SO}_4 \cdot 4\text{H}_2\text{O}$ ) or szomolnokite ( $\text{Fe}^{2+} \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$ ). Besides oxidation and neutralization reactions, the „acidity“ and „alkalinity“ of natural water (and the mobility of elements) in the weathering process are influenced by many other factors, especially the reactions of live organisms and biomass reduction reactions. These reactions can release but also consume  $\text{H}^+$ . Due to the presence of organic matter, oxidation during which  $\text{O}_2$  is consumed creates anaerobic conditions on the water-sediment boundary (11-13). In an anaerobic river sediment or in a swamp microbial reduction of sulfates (by microorganisms from the organic matter) can take place, where the content of acids ( $\text{H}^+$ ) is reduced and sulfide ions are produced (14) that can react with the present metals ( $\text{FeS}$ ,  $\text{ZnS}$ , etc.). This process is the opposite of sulfide oxidation.



Processes that enable the growth and dying away of biomass have a great influence on soil chemistry. These processes are also important for mining areas reclamation and for exploitation of various physiological functions of plants and bacteria in recultivation techniques. The removal of bases as the main nutrients has a significant effect on the removal of alkaline elements from the soil and on the increase of soil acidity. The withering of organic matter returns these bases into the soil and they also change the soil pH. Therefore, the biological production of plants on the soil surface represents an implicit or returnable soil basicity. All processes that change soil pH can be exploited in territory assessment in terms of the risks of acidification and can be applied in area reclamation planning.

## CONCLUSION

Remediation of areas affected by AMD presents a very comprehensive and complex issue. A very important factor influencing the choice of methods is the type and location of the AMD source. It is especially waters discharged from mines that need to be taken into account. For the territory of Smolnik, taking into consideration economic issues and the size of the mining sites, passive



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methods seem to be more suitable. The main advantage of passive systems is that they do not demand continuous provision of chemical (e.g. neutralizing) substances for the cleaning plant and they run without operative intervention on basis of reactions with (preferably) natural materials that form a part of the system's structural design. The system is set up so that the chemical and biological reactions employed, leading to cleaning the contaminated mine waters, run on a long-term basis. A disadvantage of the process are greater demands for time and space, as well as for a correct understanding and set-up of the dynamic complex of chemical and biological processes taking place in the passive systems that lead to the remediation of acid mine drainage.

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## DETERMINATION OF THE DISSOLUTION VELOCITY CONSTANT OF ATMOSPHERIC POLLUTANTS IN THE WATERSTREAM AND INFLUENCES TO THE VERTICAL VELOCITY OF THE MOLECULS OF WATER

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### ABSTRACT

The working hypothesis of this study is that the cause of the decrease in the concentration of atmospheric pollutants in the air in May 2014 by establishing the equilibrium temperature of water and air and the equilibrium pressure of the saturated vapor pressure of the molar ideal gas, allowing equal velocity diffusion in a double film of water and water vapor in the boundary area of gas and liquid phases. The increase of the number of active centers of condensation can cause more precipitation and more intense dissolution of pollutants through the interface with the water stream, followed by the increment of the active transport of pollutants in the stream specific vertical velocity of the water molecule.

**Keywords:** water molecule, equilibrium, transport, gas phase

### INTRODUCTION

Based on the simulation results of the hourly mean values of the content of the observed pollutants NO<sub>x</sub> and PM10 for a day with precipitation and no precipitation, negative diffusion constants and negative changes of free energy, we identified the same dissolution period, after the maximum pollution was reached. In addition to the rate diffusion constant, which corresponds to the slowest stage in the process of dissolution in most cases, the adsorption constant and volumetric coefficient of pollutant transport (determined by the hydration velocity) were determined.

### THEORETICAL BACKGROUND

The dissolution of pollutants adsorbed at the boundary layer of the atmosphere and water stream can be displayed by the equation,  $dn/d\tau = kA(c_{sat}-c)/r$ . At the boundary layer, there is a saturated solution where the concentration of a substance is  $c_{sat}$  which is established after reaching the equilibrium chemical potential in the film, both on the gas and liquid phases. Toward inside of the liquid the concentration decreases to the value of  $c$ , which corresponds to the concentration of the solution after a certain period of time determined by the constant of diffusion velocity  $k_d=1/\tau_d$ . For a number of cases, the constant of diffusion velocity is smaller than the velocity of the reaction in the contact of water and pollutant on the boundary layer, so it determines overall velocity of dissolution. Due to the combination with the surface reaction of segregation of hydrogen and oxygen during cathodic and anodic reactions of water in some cases the overall dissolution velocity is determined by the slowest adsorption rate.





Based on the Fick's law the diffusion flux  $dn/dtA=D_{pol}c/r$ , depend on the coefficient of diffusion, than:

$$dc/d\tau = (Da/r) \cdot c$$

$$v_d = dc/d\tau = -k_d c \quad (1)$$

$$dc/c = -k_d d\tau \quad (2)$$

After the integration, the constant of diffusion velocity is:

$$\ln c = -k_d \tau + \ln c_0 \quad (3)$$

$$k_d = Da/r \quad (4)$$

The volumetric coefficient of active transport for hydrophilic pollutants depends on the hydration velocity at water flow,  $v_L$ , m/s and specific boundary area,  $a=A/V$ , m<sup>-1</sup>:

$$k_L = v_L a \quad (5)$$

Calculation of the change of potential energy at the double boundary film of border surface  $\Delta E_{pot}$  is possible by Van't Hoff's law (3),

$$\ln c_{atm} = \Delta E_{L/G}/RT + \ln c_L \quad (6)$$

In the period at which there is a linear correlation of  $k_{d,pol}$  and  $\Delta E_{pot}$  based on (Ševaljević, et. al. 2009):

$$3RTk_L = 3RTk_d + k_a \Delta E_{pot} \quad (7)$$

It is possible to determine the volumetric coefficient of transport of hydrated pollutant,  $k_L$  and its adsorption velocity constant,  $k_a$ .

## CALCULATION DATA

Input data shown in Table 4.2 and Table 4.3 represent results of previously analysis implemented using program ADMS5. The analysis was conducted for the contribution of the Heating and Power Plant "TeTo Zrenjanin".

*Table 1: Average values of pollutants per hour on 22<sup>nd</sup> and 24<sup>th</sup> June 2014 and relative air humidity above surface watercourse, Bega river, Zrenjanin*

Hours 22 <sup>th</sup> June	$\gamma(\text{NO}_x)$ $\mu\text{g}/\text{m}^3$	$\gamma(\text{PM}_{10})$ $\mu\text{g}/\text{m}^3$	$\gamma(\text{NO}_x)$ $\mu\text{g}/\text{m}^3$ , akci.	Hours 24.04	$\gamma(\text{NO}_x)$ $\mu\text{g}/\text{m}^3$	$\gamma(\text{PM}_{10})$ $\mu\text{g}/\text{m}^3$	Relative humidity %
1	0,02	0,000006	0,4	1	0	0	91
2	0,015	0,000006	0,2	2	0	0	91
3	0,01	0,000004	0,15	3	0,004	0,000002	90
4	0,01	0,000003	0,1	6	0,4	0,00012	89
5	0,006	0,0000015	0,04	7	1,8	0,00053	89
6	4	0,001	40	8	2	0,0006	85
7	4	0,001	50	9	1,5	0,0005	84
8	2	0,0015	40	10	1	0,0006	85
9	2	0,001	20	11	1	0,0004	84
10	2	0,0005	20	12	1,5	0,0005	80
11	2	0,0005	20	13	1	0,0004	72
12	2	0,0005	20	14	0,5	0	58
13	2	0,0005	20	15	0	0,0001	48
14	2	0,0005	20	17	0	0	41
15	2	0,0005	40	20	0	0	37
16	2	0,0005	20	21	0	0	34

17	2	0,0005	20	22	0	0	34
18	1	0,0004	20	23	0	0	41
19	0	0	0	24	0	0	59

*Table 2: Average values of temperature per hour above surface of Bega river 22<sup>nd</sup> and 24<sup>th</sup> June 2014 and meteorological data for 22<sup>nd</sup> June 2014 (Cloudiness and rainfall at 22<sup>nd</sup> June 2014 were "0")*

Hours 22 <sup>nd</sup> June	t, oC 22 <sup>nd</sup> June	t, oC 24 <sup>th</sup> June	Wind velocity 22 <sup>nd</sup> June m/s	Wind velocity 24 <sup>th</sup> June m/s	Relative humidity 22 <sup>nd</sup> June %	Relative humidity 24 <sup>th</sup> June %	Rainfall 24 <sup>th</sup> June mm.
1	14	22	1,7	0,8	68	91	0,89
2	13	21	1,5	0,8	70	91	1,03
3	13	21	1,4	0,9	73	90	0,83
4	12	21	1,3	1,3	76	89	0,88
5	14	21	1,1	1,6	79	89	0,94
6	16	22	0,8	2,3	67	85	1,01
7	19	22	0,8	3,2	57	84	1,01
8	22	21	1	3,5	51	85	1,03
9	23	21	1,5	3,4	42	84	0,64
10	24	22	1,6	3,6	38	80	0,18
11	25	24	1,6	3,7	36	72	0,06
12	26	26	1,6	3,6	35	58	0,06
13	27	27	1,8	3,7	34	48	0,13
14	27	28	1,7	3,7	33	41	0,11
15	27	28	1,4	3,8	33	37	0,1
16	27	28	1,4	4	33	34	0
17	27	28	1,4	4	34	34	0
18	26	26	1,7	3,5	39	41	0
19	23	23	2	2,9	58	59	0
20	22	21	2,4	2,7	55	58	0
21	20	20	2,5	2,6	58	61	0
22	19	19	2,6	2,5	62	63	0
23	18	19	2,7	2,5	65	65	0
24	18	18	2,6	2,5	68	65	0

## RESULTS AND DISCUSSION

*Table 3: The law of pollutants dissolution kinetics that fit (equation 3) simulation results with correlation coefficient  $R^2 > 0.8$*

Hours	NOx 22 <sup>nd</sup> June $L_{nc}=k_d\tau+lnc_0$	PM10, 22 <sup>nd</sup> June $L_{nc}=k_d\tau+lnc_0$	NOx 22 <sup>nd</sup> June $L_{nc}=k_d\tau+lnc_0$	Humidity 22 <sup>nd</sup> June $L_{nc}=k_d\tau+lnc_0$	NOx 24 <sup>th</sup> June $L_{nc}=k_d\tau+lnc_0$	PM10 24 <sup>th</sup> June $L_{nc}=k_d\tau+lnc_0$	Humidity 24 <sup>th</sup> June $L_{nc}=k_d\tau+lnc_0$
1	$y = -0,2813x - 21,8$	$y = -0,3466x - 11,5$ , $R^2$	$y = -0,5298x - 18,5$ , $R^2 = 0,9633$	$y = 0,0382x + 4,2$ , $R^2 = 0,9968$			$y = -0,0067x + 4,52$ , $R^2 = 0,9$



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	$R^2 = 0,946$	$= 0,9019$					
2	“	“	“	“			“
3	“	“	“	“	$y = 3,0546x - 32,3$ $R^2 = 0,9209$	$y = 2,7899x - 21,06$ $R^2 = 0,9321$	“
4	“	“	“	“	“	“	“
5	“	“	“	“	“	“	“
6	$y = -0,3466x - 14,56$ $R^2 = 0,75$	$y = 0,2027x - 8,2$ $R^2 = 0,75$	$y = 1,038x + 0,772$	$y = -0,129x + 4,9$ $R^2 = 0,9769$	$y = -0,2485x - 16,0$ $R^2 = 0,8998$	$y = 0,1241x - 8,1629$	$Y = 4,435$
7	“	“	(6)+(8)	“	“	$y = -0,1823x - 6,3$ $R^2 = 1$	“
8	“	(6)+(9)	$y = -0,4581x - 10,9$ $R^2 = 0,9194$	“	“	$y = -0,3256x - 4,65$ $R^2 = 0,7761$	“
9	$y = -8E-15x - 17,453$	$y = -0,5493x - 2,0599$ $R^2 = 0,9777$	“	“	“	“	$y = -0,1216x + 5,56$ $R^2 = 0,9118$
10	“	“	$y = -15,137$	“	$y = -0,5493x - 12,2$ $R^2 = 0,9777$	“	“
11	“	$y = -7E-16x - 7,6009$	“	“	“	“	“
12	“	“	“	$y = -0,0206x + 3,8$ $R^2 = 0,8922$	“	“	“
13	“	“	“	“	“	“	$y = -0,1137x + 5,33$ $R^2 = 0,9788$
14	“	“	“	“	“	“	“
15	“	“	$y = -0,3466x - 9,4$ $R^2 = 0,75$	“	“	“	“
16	$y = -0,3466x - 11,792$ $R^2 = 0,75$	$y = -0,1116x - 5,7786$ $R^2 = 0,75$	“	$y = 0,1829x + 0,5$ $R^2 = 0,8276$	“	“	“
17	“	“	“	“	“	“	$y = 0,2756x - 1,19$ $R^2 = 0,9669$
18	“	“	$y = 6E-14x - 15,137$	“	“	“	“
19	“	“	“	“	“	“	“
20	“	“	“	$y = 0,0538x + 2,93$ $R^2 = 0,9948$	“	“	$y = 0,0291x + 3,49$ $R^2 = 0,9148$



21							
22							
23							
24							

Table 4: Results of determination of diffusion rate constant,  $k_d$ , for  $\text{NO}_x$ ,  $\text{PM}_{10}$  and humidity according to data,  $y = a_x + y_0$  in Table 3 ( $k_d = a$ )

Hour s	$k_d$ ( $\text{NO}_x$ ) 22 <sup>nd</sup> June $\text{h}^{-1}$	$k_d$ ( $\text{PM}_{10}$ ) 22 <sup>nd</sup> June $\text{h}^{-1}$	$k_d$ (Humidity) 22 <sup>nd</sup> June $\text{h}^{-1}$	$k_d$ ( $\text{NO}_x$ ) 22 <sup>nd</sup> June $\text{h}^{-1}$	$k_d$ ( $\text{NO}_x$ ) 24 <sup>th</sup> June $\text{h}^{-1}$	$k_d$ ( $\text{PM}_{10}$ ) 24 <sup>th</sup> June $\text{h}^{-1}$	$k_d$ (Humidity) 24 <sup>th</sup> June $\text{h}^{-1}$
1	-0,2813	-0,3466	0,0382	-0,5298			-0,0067
2	-0,2813	-0,3466	0,0382	-0,5298			-0,0067
3	-0,2813	-0,3466	0,0382	-0,5298	3,0546	2,7899	-0,0067
4	-0,2813	-0,3466	0,0382	-0,5298	3,0546	2,7899	-0,0067
5	-0,2813	-0,3466	0,0382	-0,5298	3,0546	2,7899	-0,0067
6	-0,3466	0,2027	-0,129	1,038	-0,2485	0,1241	0
7	-0,3466	0,2027	-0,129	1,038	-0,2485	-0,1823	0
8	-0,3466	0,2027	-0,129	-0,4581	-0,2485	0,3256	0
9	-8E-15	-0,5493	-0,129	-0,4581	-0,2485	0,3256	-0,1216
10	-8E-15	-0,5493	-0,129	0	-0,5493	0,3256	-0,1216
11	-8E-15	-7E-16	-0,129	0	-0,5493	0,3256	-0,1216
12	-8E-15	-7E-16	-0,0206	0	-0,5493	0,3256	-0,1216
13	-8E-15	-7E-16	-0,0206	0		0,3256	-0,1137
14	-8E-15	-7E-16	-0,0206	0			-0,1137
15	-8E-15	-7E-16	-0,0206	-0,3466			-0,1137
16	-0,3466	-0,1116	0,1829	-0,3466			-0,1137
17	-0,3466	-0,1116	0,1829	-0,3466			0,2756
18	-0,3466	-0,1116	0,1829	6E-14			0,2756
19			0,1829				0,2756
20			0,0538				0,0291
21			0,0538				0,0291
22			0,0538				0,0291
23			0,0538				0,0291
24			0,0538				0,0291

Table 5:  $\text{Inc}_{(G)} = \Delta E_{\text{pot}}/RT - \text{Inc}_{(L)}$ , (Van't Hoff's law), in periods of reaching equilibrium chemical potential of atmospheric pollutants in boundary surface with the watercourse (equation 6)

Hour s	$\text{NO}_x$ 22 <sup>nd</sup> June	$\text{PM}_{10}$ 22 <sup>nd</sup> June	$\text{NO}_x$ 22 <sup>nd</sup> June accident	Humidity t 22 <sup>nd</sup> June	$\text{NO}_x$ 24 <sup>th</sup> June	$\text{PM}_{10}$ 24 <sup>th</sup> June	Falcity 24 <sup>th</sup> June
1		-28881x + 88,6R <sup>2</sup> = 0,7001	-57762x + 182,07 R <sup>2</sup> = 0,9393	3226,9x - 6,9779 R <sup>2</sup> = 0,7433			6975,7x - 19,221 R <sup>2</sup> = 0,889
2		"	"	"			"
3		"	"	"			"
4		"	"	"			"

5		-101412x + 341,3R <sup>2</sup> = 0,6628		“			“
6		“		“	-47685x + 144 R <sup>2</sup> = 0,8794		“
7	16145x - 72 R <sup>2</sup> = 0,9436	“	16633x - 71,087 R <sup>2</sup> = 0,6992	“	“		“
8	“	15840x - 60,495 R <sup>2</sup> = 0,679	“	y = 6063x - 16,7 R <sup>2</sup> = 0,8506	“		“
9	“	“	“	“	“	21643x - 81,1 R <sup>2</sup> = 0,7705	“
10		“		“	24235x - 99,8 R <sup>2</sup> = 0,9765	“	“
11		“		“	“	“	“
12		“		“	“	“	“
13		“		“	“	“	5183,1x - 13,569 R <sup>2</sup> = 0,8795
14		“		“			“
15		“		“			“
16		“		“			“
17		“		“			“
18		“		“			“
19				2822,4x - 5,5199 R <sup>2</sup> = 0,7407			“
20				“			“
21				“			“
22				“			“
23				“			“
24				“			“

*Table 6: Changes of potential energy of pollutants ( $\Delta E_{pot} = R \cdot T \cdot g$ , according to data from Table 5), after reaching equilibrium chemical potential at surface between two phases, identified as possible electrochemical reactions according data in table (Bard, et.al. 1983)*

H o u r s	$\Delta E_{L/G}(\text{NO}_x)$ 22 <sup>nd</sup> June kJ/mo	$\Delta E_{L/G}(\text{PM}_{10})$ 22 <sup>nd</sup> June	$\Delta E_{L/G}(\text{NO}_x)$ 22 <sup>nd</sup> June (acid)	$\Delta E_t = \Delta H_{(L/G)} - T \cdot \Sigma S_{eq}$ Humidity 22 <sup>nd</sup> June	$\Delta E_{L/G}(\text{NO}_x)$ 22 <sup>nd</sup> June	$\Delta E_{L/G}(\text{PM}_{10})$ 22 <sup>nd</sup> June	$\Delta E_t = \Delta H \cdot T \cdot \Sigma S_{eq}$ (vlažnost) 22 <sup>nd</sup> June
1		<b>240,116</b>	<b>480, 233</b>	<b>-18,501</b>			<b>49,407</b>
2		“	“	“			“
3		“	“	“			“
4		239 = - - $\Delta H^\theta(\text{H}_2\text{O})g$	472 + $T \cdot \Sigma \Delta S_{aq}$ = $\Delta H^\theta(\text{N})g$	“			“
5		<b>843,189</b>		“			

6		“		“	<b>396,453</b>		
7	<b>-134,229</b>	$2RT + E_{\text{eff}}(O^-/O^{2-}) - \Delta nH(H^+ + OH^-)$	<b>-138,286</b>	$-17 - RT/2 = \Delta H^\theta(N_2H_4 \cdot H_2^{2+}_{\text{aq}})$	“		
8	“	<b>-131,693</b>	“	<b>-41,848</b>	“		
9	$-135,1 = \Delta H^\theta(HNO_3)_g$	“	$138,3 + RT_0/2 = -\Delta H^\theta(NH_2OH_2^+)$	“	$330 + 66 = \Delta G^\theta(N)_g - \Delta G^\theta(NH_2OH_2^+)$	<b>-179,939</b>	
10		“		“	<b>-201,489</b>	“	
11		“		“	“	-“	
12		“		“	$-207,5 - 5 = \Delta H^\theta(NO_3^-)_{\text{aq}} - 2RT$	“	$50,63 = \Delta H^\theta(N_2H_4)_L$
13		“		“		$-178,2, \Delta H^\theta(FeS_2)_c$	<b>-34,388</b>
14		“		“			“
15		“		“			“
16		“		“			“
17		“		“			“
18		$= \Delta H^\theta(HNO_3)_g + 2RT$		$-43,1 - RT_0 = \Delta H^\theta(N_2O_5)_c$			“
19				<b>-14,877</b>			“
20				“			“
21				“			$-37 - RT \Delta G^\theta(NO_2^-)$
22				“			<b>-43,092</b>
23				“			“
24				$-15,5 + 2RT/2 = \Delta G^\theta(NH_3)_g$			$-46,1 + RT_b = \Delta H^\theta(NH_3)_g - RT_b$



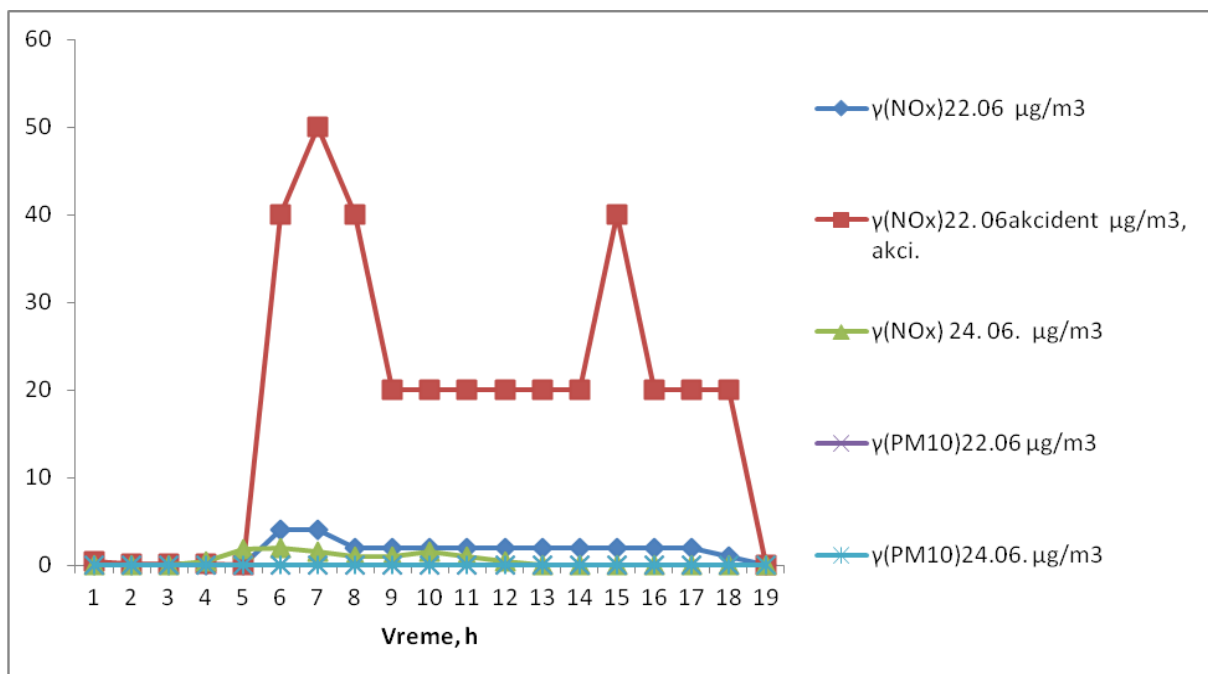


Figure 1: Average values of concentrations per hour for pollutants and velocity of diffuse transport during 22<sup>nd</sup> and 24<sup>th</sup> June 2014 above surface of Bega river

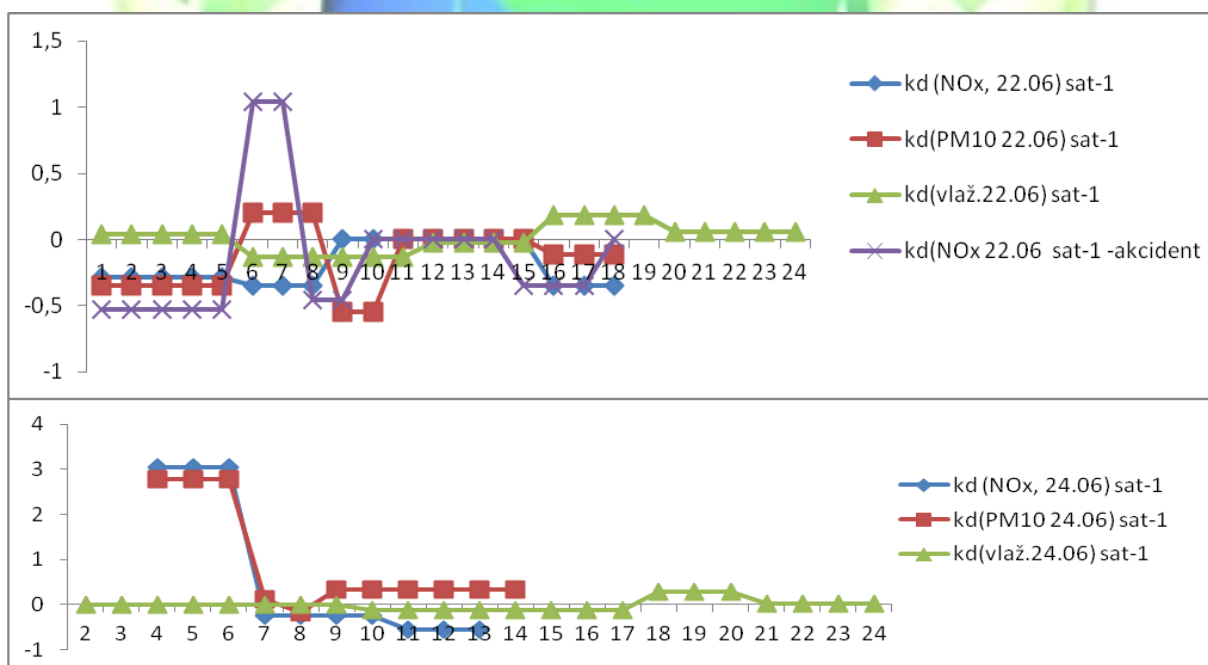


Figure 2: Velocity constants of diffuse transport of pollutants and humidity in first order reactions above the surface of Bega river,  $k=ln c/\tau=const$ , during 22<sup>nd</sup> and 24<sup>th</sup> June 2014

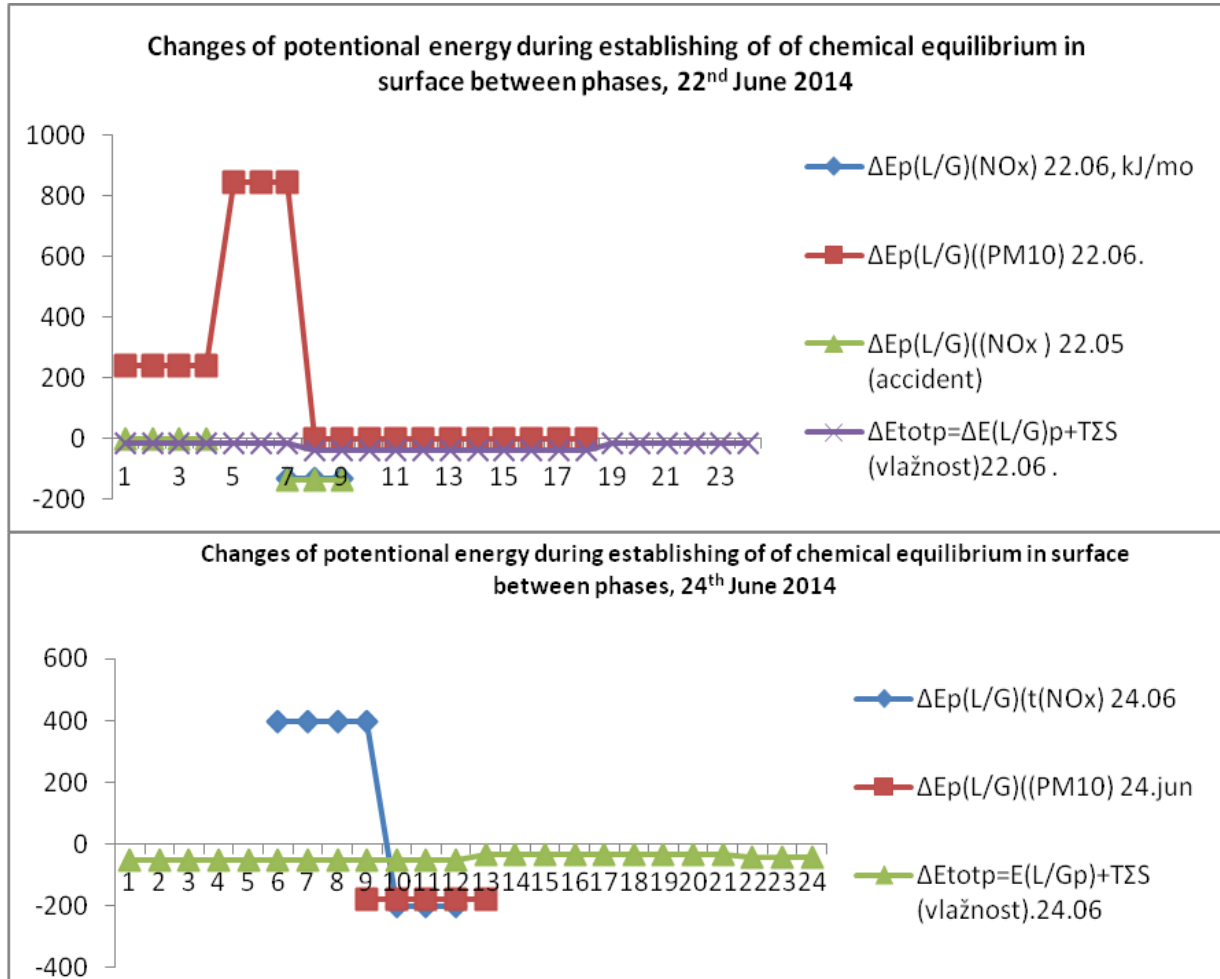


Figure 3: Changes of potential energy after reaching equilibrium chemical potential at surface between two phases, 22<sup>nd</sup> and 24<sup>th</sup> June 2014

Results on figures are showing that after maximum average concentration of pollutants per hour (huration) comes period of negative dissolution velocity constant and negative free energy ie, period of pollutants dissolving in water.

Table 7: Data for figures that provide determination of volumetric transport of hidration water coefficient and adsorption coefficient (Figure 4)

Hi	$k_d(\text{humidity}) \text{ h}^{-1}$ 22 <sup>nd</sup> June	$\Delta E_{\text{pot}}(\text{humidity})$ 22 <sup>nd</sup> June	$k_d(\text{humidity}) \text{ h}^{-1}$ 24 <sup>th</sup> June	$\Delta E_{\text{pot}}(\text{humidity})$ 24 <sup>th</sup> June
1	0,0382	-18,501	-0,0067	-49,407
2	0,0382	-18,53	-0,0067	-49,436
3	0,0382	-18,53	-0,0067	-49,436
4	0,0382	-18,559	-0,0067	-49,43
5	0,0382	-18,473	-0,0067	-49,436
6	-0,129		0	-49,407



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7	-0,129		0	-49,407
8	-0,129	-41,848	0	-49,43
9	-0,129	-41,819	-0,1216	-49,436
10	-0,129	-41,79	-0,1216	-49,407
11	-0,129	-41,761	-0,1216	-49,349
12	-0,0206	-41,732	-0,1216	-49,291
13	-0,0206	-41,703	-0,1137	
14	-0,0206	-41,703	-0,1137	
15	-0,0206	-41,703	-0,1137	
16	0,1829		-0,1137	
17	0,1829		0,2756	-34,359
18	0,1829		0,2756	-34,417
19	0,1829	-14,877	0,2756	
20	0,0538	-14,906	0,0291	
21	0,0538	-14,964	0,0291	
22	0,0538	-14,993	0,0291	-43,092
23	0,0538	-15,022	0,0291	-43,092
24	0,0538	-15,022	0,0291	-43,092

8am 22 <sup>nd</sup> June	$\Delta E_{pot}$ 22 <sup>nd</sup> June	$k_d, h^{-1}$ 22 <sup>nd</sup> June
NO <sub>x</sub>	-134,229	-0,3466
NO <sub>x</sub> acc.	-138,286	-0,4581
H <sub>2</sub> O	-41,848	-0,129
12 h 24 <sup>th</sup> June	$\Delta E_{pot}$ 24 <sup>th</sup> June	$K_d, h^{-1}$ 24 <sup>th</sup> June
NO <sub>x</sub>	-201,489	- 0,5493
PM10	-179,939	>0
H <sub>2</sub> O	-49,291	-0,1216



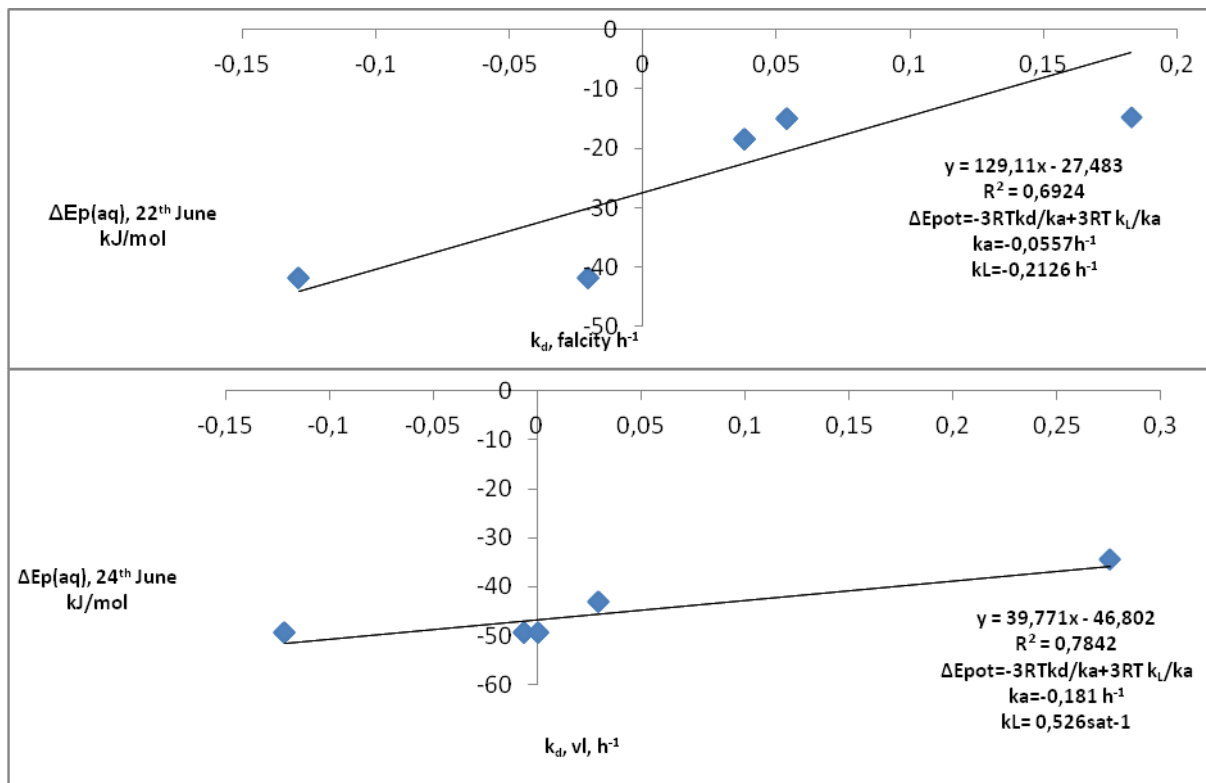


Figure 4: Functions between  $\Delta E_{pot}$  and  $k_d$  according to equation (7) that provide determination of volumetric transport of hidratation water coefficient ( $k_L$ ) and adsorption velocity coefficient  $k_a$

## CONCLUSION

According to the results there can be concluded:

1. The dissolution velocity constant of pollutants molecules after reaching of equilibrium chemical potential is determined by the slowest successive stage of complex process of dissolving (electrochemical reaction, diffusion, desorption and hidretation in solution);
2. During the day with or without precipitation dissolution velocity constant of  $NO_x$  is determined by the constant of the slowest successive stage of complex process of dissolving  $k_{dissolv.}(NO_x) = k_a = -0,02 h^{-1}$ ;
3. Proces of dissolving of PM10 are shown by negative velocity constants of diffusion,  $k_d(PM10)_{22.06.} = 0.3466 h^{-1}$  that is preceded by dissolving of  $NO_x$  during the day without rainfalls. During the day with rainfalls negative value is noticed only during the 7<sup>th</sup> hour,  $k_d(PM10)_{24.06.} = -0,1823 h^{-1}$ ;
4. Velocities constants of hidratation processes by air humidity during dissolving of  $NO_x$  and other pollutants are defined by adsorption velocity constant during the day without rainfalls during period from 9am to 6pm,  $k_a = -0,0557 h^{-1}$ ;
5. During day with rainfalls (24<sup>th</sup> June 2014) the slowest stage is diffusion trough specific border surface  $a = k_d r / D$ , so velocity of water transport,  $v_L$ , after depolarization ( $k_L = k_d$ ),  $v_L = D(HNO_3)/r$ . In that moment for stabile drops with diameter  $r < 0.08 \text{ nm}$ , velocity of hidratated pollutant transport is  $v_L < 3,7 \text{ m/s}$ .



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## **RISK ASSESSMENT IN THE ENVIRONMENT**

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### **ABSTRACT**

Issues related to environment have become an integral part of our everyday life and they represent a relentless tax for the comfort that most of the world can afford today. These issues affect all components of the environment, i.e. water, air, soil, and man is no exemption. Social development has resulted in an extreme increase of anthropogenic pressures on the individual components of the environment. The consequences of these pressures lead to the devastation of the environment, to the degradation of its components and to a significant reduction of their self-cleaning abilities. Considering these facts, the need to monitor and to address environmental risks appears to be more urgent than ever.

**Keywords:** *risk, environmental risk, risk assessment, methodology, analysis*

### **INTRODUCTION**

Risk analysis represents the process of hazard identification and of risk assessment for individuals or for a group of people, for the objects of the surrounding environment and for other examined objects. Risk analysis identifies the probability and extent of consequences of a negative event resulting from a specific work activity or from other activities of equipment or of a system. Based on the identification of hazards it reveals the magnitude of risk (Plura, J. 2001 - Sinay, J. 1997 - Ladomerský, J. et al., 2011). There are many definitions of risk, but in the most common case risk is defined as the possibility that a certain fact may happen, which can subsequently cause undesirable consequences and also potential political, financial, moral and environmental damages or losses. A risk in terms of its structure can also be defined as a combination of a probability of occurrence of an event and of its consequences. According to the Act N<sup>o</sup> 261/2002 Coll., a risk is the probability of occurrence of a risk event and the extent (severity) of its possible consequences that may occur during a certain period of time or under certain circumstances (Act N<sup>o</sup> 277/2005 Coll - Act N<sup>o</sup> 261/2002 Coll).

### **ENVIRONMENTAL RISK**

A risk can be considered to be an environmental risk if it is associated with a potential negative impact on the environment. The risk represents a conditional probability of occurrence of specific environmental events associated with some of the consequences of these events.

The process of environmental risk management is based on several steps (Hrubec, J. ete al., 2009):

- risk identification,
- risk analysis and risk assessment,



- solution of risks, decision making of their solution and adopting measures,
- residual risks,
- monitoring and assessment of the risk management process.

The process of assessment and management of an environmental risk comprises the application of procedures, methods and practices, with the aim of managing and reducing the risk event, or of their reporting (Figs. 1, 2) (Hrubec, J. ete al., 2009).

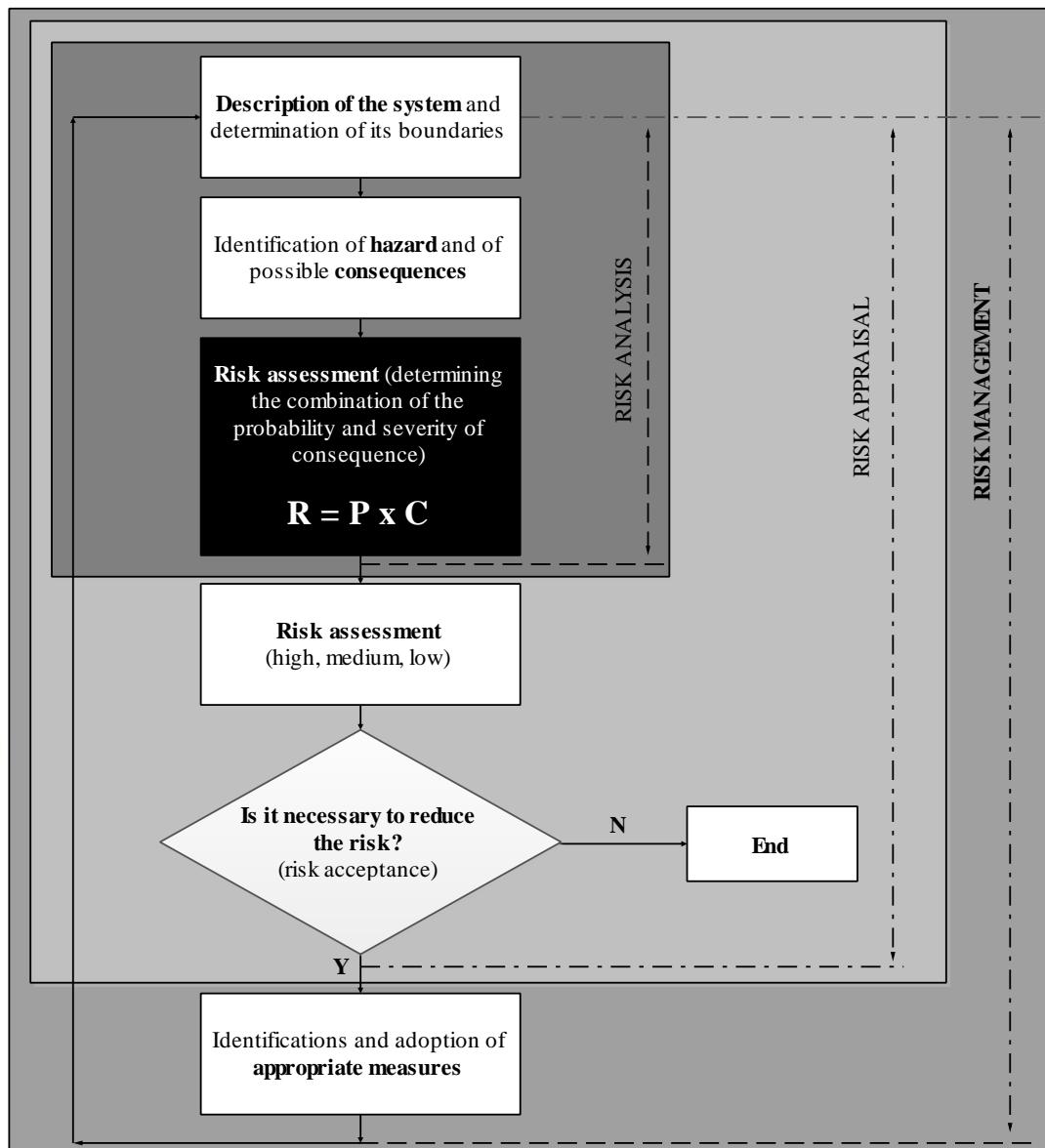


Figure 1 Algorithm of risk assessment and of risk management

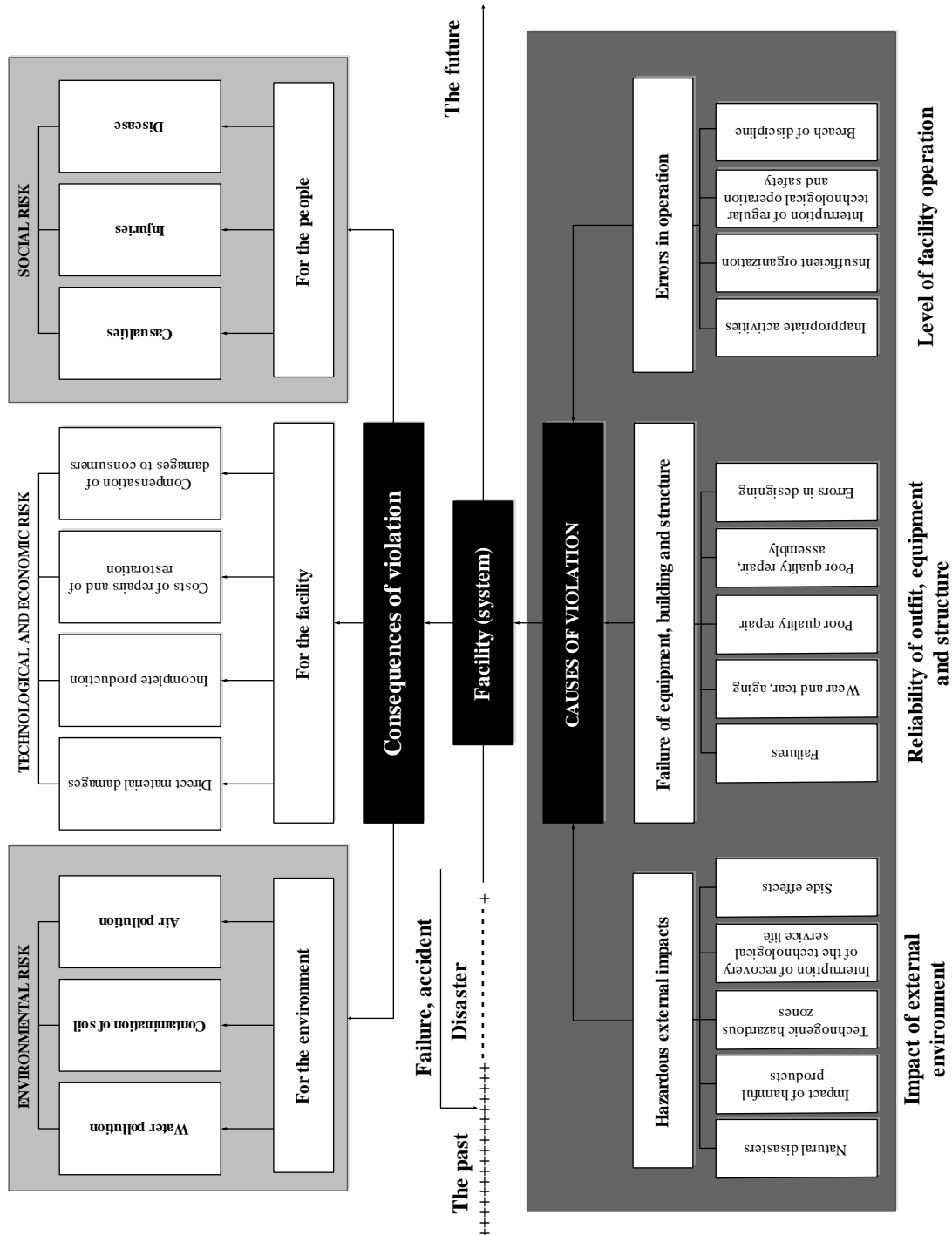




Figure 2 Model of risk development

**ENVIRONMENTAL RISK ASSESSMENT**

The assessment of the impacts on individual components of the environment is very exacting due to the magnitude and diversity of anthropogenic impacts on the environment and

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due to the complexity of natural systems. There are a number of suitable methods, which are used in risk assessment (Table 1).

Table 1 Some additional methods of risk assessment (Hrubec, J. et al., 2009 - № 489/2002)

Method	Description
<b>FTA Method (Fault Tree Analysis)</b>	A deductive method based on a considered risk event, the outputs of which are a number of critical paths leading to it.
<b>Delphi Method</b>	The basis of the method is forecasting, in the course of which ideas are generated. It uses an explicit estimate of experts for assessing the probability of each risk event.
<b>MOSAR Method</b>	The method comprises a systematic risk analysis. The system is divided into subsystems, which are gradually identifying hazards, the adequacy of measures and their interdependence. Safety measures are arranged into a logical tree and residual risks are analysed on the basis of an agreement.

Other instruments for assessment of risk significance can also include Pareto analysis and the so-called UMRA (Universal Matrix of Risk Analysis) Method. In our paper we will address the semi-quantitative method for environmental risk assessment, namely by creating the so-called risk matrix. The probability (frequency) of occurrence and severity of the impact of a risk event on the environment (or its components: soil, water, air) is most often expressed by using a three-degree or a five-degree scale. A five-degree system for risk assessment is shown in Tables 2 and 3 (Šebo, D. et al., 2006).



Table 2 Probability / frequency of occurrence of an environmental risk event

Probability	Denotation	Value	Probability of risk occurrence
<b>Rare</b>	<b>A</b>	1	It is almost inconceivable that a risk event could occur.
<b>Possible</b>	<b>B</b>	2	Very unlikely (its occurrence is not known).
<b>Probable</b>	<b>C</b>	3	Unlikely, but possible occurrence (it occurs rarely).
<b>Highly probable</b>	<b>D</b>	4	Probability of occasional occurrence (it occurs irregularly).
<b>Almost certain, frequent</b>	<b>E</b>	5	Probability of a very frequent occurrence (it occurs regularly).

Table 3 Severity / consequence of the impact of an environmental risk event on the environment

Severity level	Denotation	Value	Severity of risk occurrence
<b>Negligible, insignificant</b>	<b>I</b>	1	Minimum, almost no impact of the risk event on the environment, or on its components.
<b>Minor</b>	<b>II</b>	2	Small extent of the impact of the risk event on the environment, or on its components.
<b>Major, moderate</b>	<b>III</b>	3	Medium extent of the impact of the risk event, less severe impact on the environment, or on its components.



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<b>Significant</b>	<b>IV</b>	4	Extensive, serious impact of the risk event on the environment, or on its components.
<b>Severe, disastrous</b>	<b>V</b>	5	Disastrous impact of the risk event on the environment (environmental disaster), or on its components.

The assessment of environmental risks is used for making decisions on the severity of risks and for deciding whether a given risk is acceptable or whether actions should be taken to address it. It makes use of methods and procedures used by ecology, chemistry, toxicology, ecotoxicology, hydrology, and other sciences for determining the probability of occurrence of adverse events and of the severity of their impact on the environment (Hrubec, J. et al., 2009 - Říha, J. 1995).

Table 4 Risk matrix

Probability	Severity of the impact of a risk event (Consequence, Impact)				
	Negligible (I)	Minor (II)	Major (III)	Significant (IV)	Severe (V)
Almost certain (E)	I-E	II-E	III-E	IV-E	V-E
Highly probable (D)	I-D	II-D	III-D	IV-D	V-D
Probable (C)	I-C	II-C	III-C	IV-C	V-C
Possible (B)	I-B	II-B	III-B	IV-B	V-B
Rare (A)	I-A	II-A	III-A	IV-A	V-A

An important step in the environmental risk assessment is to determine the degree of significance of the risk and at the same time to determine the level of its acceptability. The degree of significance of the risk is in the simplest case the product of the point rating of the probability of occurrence and of the severity of impact of the risk, i.e.  $R=P \times D$ .

According to, when using a five-degree risk assessment, the numerical value of 15 expresses an unacceptable risk. Table 5 shows a proposed scale for numerical assessment of the significance of the environmental risk.

Table 5 The level of environmental risk assessment

Probability	Severity of the impact of a risk event (Consequence, Impact)				
	Negligible	Minor	Major	Significant	Severe
Almost certain	5	10	15	20	25
	Medium	Medium	High	Extreme	Extreme
Highly probable	4	8	12	16	20
	Medium	Medium	High	High	Extreme
Probable	3	6	9	12	15
	Low	Medium	Medium	High	Extreme
Possible	2	4	6	8	10
	Low	Medium	Medium	Medium	High
Rare	1	2	3	4	5
	Low	Low	Medium	Medium	High
Low	<b>Very low, negligible level of environmental risk</b>				

<b>Medium</b>	<b>Low level of environmental risk</b>
<b>High</b>	<b>High level of environmental risk</b>
<b>Extreme</b>	<b>Very high level of environmental risk</b>

## DECISION ON ADDRESSING ENVIRONMENTAL RISKS

The decision is the final result of the risk management stage. The decision on the acceptability or non-acceptability of an environmental risk is based on two levels of risk:

- A negligible level of risk represents a socially acceptable level of risk, at which the probability of occurrence of an undesirable consequence is so small, the effects of the risk impact are so mild and the benefit of the situation is so substantial that persons, groups, an organization or the society as a whole are willing to undergo this risk. This level does not require any control measures for reducing the environmental risk.
- An unacceptable level of risk requires immediate adoption of control measures for reducing the risk.

According to the Health and Safety Executive (HSE), there are three basic levels of risk acceptability (Fig. 3).

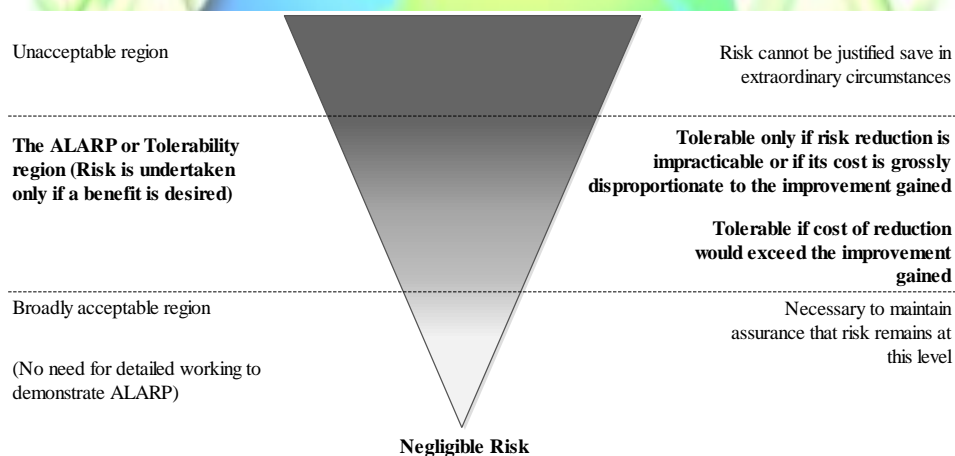


Figure 3 Levels of risk acceptability according to HSE

**The intermediate level** is defined as the level, where the so-called ALARP (As Low as Reasonably Practicable) philosophy is applied, i.e. this is an area where the reduction of risk value is managed by the approach “to invest so far as to keep the risk value so low as it may be reasonable and practical”. At **an unacceptable level**, it is necessary to take immediate measures, which ensure the reduction of its value to an acceptable level. In the case of **a negligible level of risk** this is a condition, when risk is monitored (or regularly checked), but it does not require any measures for its reduction (Demo, M. et al., 2007 - Hrubec, J. et al., 2009).

The occurrence and the degree of severity of an environmental risk can be influenced by reducing the probability of the occurrence of a risk event or by reducing the severity of the consequence of the risk. Many environmental risks can be eliminated or their level can be reduced by appropriate regulatory measures. When reducing the level of risk by introducing corrective measures these should be based on the basic parameters of the risk. Environmental

risk can be reduced by reducing the probability of the occurrence of a risk event or by reducing the consequences of this event.

## COMPREHENSIVE ASSESSMENT OF THE IMPACT OF RISK ON THE ENVIRONMENT AND HUMAN HEALTH

In addition to the impact on the environment, also severity of the impact on human health is often monitored.

Table 6 Severity / consequence of the impact of an environmental risk event on human health

Severity level	Level	Value	Severity of the risk event
Negligible	$\alpha$	1	Without impact on human health
Minor	$\beta$	2	Minor influence on health
Major	$\gamma$	3	Significant damage to health
Significant	$\delta$	4	Serious damage to the environment
Severe, catastrophic	$\varepsilon$	5	Catastrophic consequences (death)

For a comprehensive assessment of mutual relations between probabilities of risk, consequences for the environment and impacts on human health, a cubic diagram can be used (Fig. 4). This type of diagram allows building of an interrelationship between all three parameters at the same time (Šebo, D. et al., 2006).

The degree of significance of risk  $R$  is in this case determined by the product of the point rating of the probability (frequency) of occurrence of risk  $P$  of the consequence of impact on environment  $C_E$  (environmental risk), and of the consequence of impact on human health  $H$  (risk to human health). It is expressed by the formula:  $R = P \times C_E \times H$ .

The value of the degree of significance of risk  $R$  can range from 1 to 125. It should be noted, however, that this value can take only certain discrete values. Also in this case the resulting numerical assessment of risk and determination of its degrees is influenced by subjective opinions, where values in the range from 70 to 125 can be regarded as an unacceptable risk.

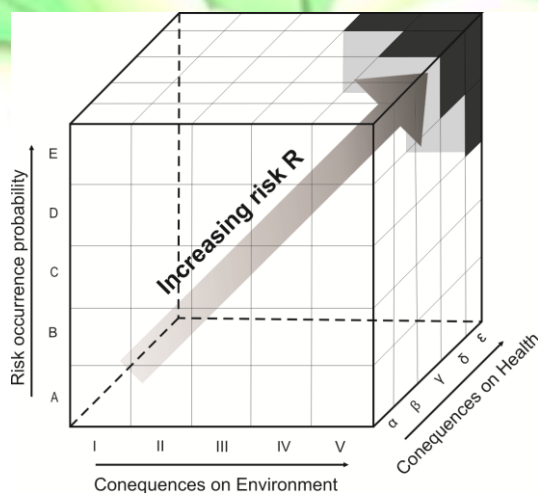


Figure 4 Cubic risk matrix diagram





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Table 7 Determination of the range of the resulting risk

<b>Risk</b>	<b>Range of point rating</b>	<b>Impact on environment and human health</b>	<b>Remedial measures</b>
<b>Insignificant, negligible risk</b>	<b>1 – 4</b>	The system is safe, negligible impact on human health and environment.	Routine procedures, it is not necessary to take any measures.
<b>Acceptable, minor risk</b>	<b>5 – 10</b>	Acceptable risk with increased attention, first aid needed.	Opportunity to achieve improvement, corrective plans.
<b>Undesirable risk</b>	<b>11 – 50</b>	The risk cannot be accepted without protective measures, medical treatment inevitable.	It is necessary to take safety precautions.
<b>Significant risk</b>	<b>51 – 100</b>	The system is dangerous, high possibility of a major emergency event, and/or extensive injury, loss of ability to work.	It is necessary to take immediate corrective actions with a short deadline.
<b>Unacceptable risk</b>	<b>101 – 125</b>	The system is unacceptable, permanent threat of a risk event, death.	Immediate application of safety measures, system shutdown.

## CONCLUSION

Environment influences the life of all of us. It consists of the space around us. Just as the environment affects us, people also affect it in various ways. For decades, warning messages have been appearing in the media reminding us of the gradually degrading state of the environment. Soil, water and air are polluted, endemic species, but also other certainly not less important species of plants and animals are threatened with extinction, mineral resources and drinking water supplies are irretrievably consumed.

Risk assessment is a process, which is in most cases going on individually, but it cannot be understood in isolation. Risk assessment is a part of risk management and it represents a process, currently requiring heavy demands for its implementation and use.

Risk analysis and environmental risk management are focused on elimination of risks, even if we have to realize that their complete removal is not possible. It is important to reduce risk to an acceptable level. This level reflects the residual risk, which is acceptable for an individual, for an organization and for the society. The results of the analysis of environmental risk are of great importance for the adoption of reasonable and preventive solutions, which are very important for protection of health and safety of humans and for protection of the environment.

## ACKNOWLEDGMENTS

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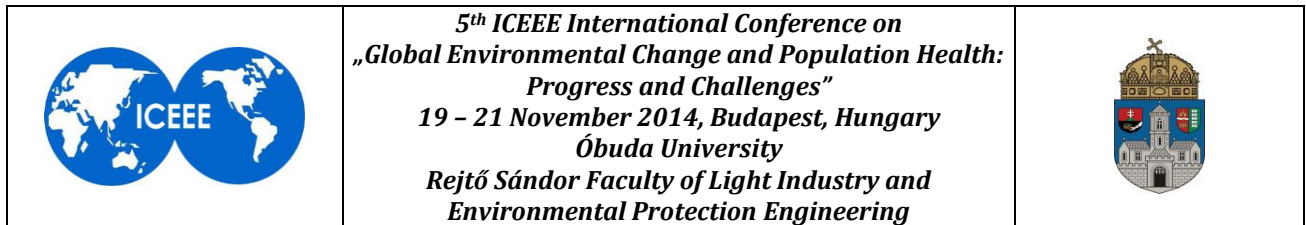


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## **LAND ZONING: CONCEPT AND ITS URGENCY IN BANGLADESH**

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Bangladesh is a least developed South Asian country and its economy is based on agriculture. Among the natural resources, land and soil are the key resource for agriculture. We have to ensure its proper utilization for ensuring food security without decreasing its extent and quality. In Bangladesh the natural resources especially the land resources of an area is used for multiple purposes, which have strong influences on the socio-economic development of the area. Due to huge population pressure land resources are under continuous human and natural interventions so its land use is naturally diverse and complex. The land resources of an area is intensively used for agriculture, settlements, forests, water bodies and fisheries, salt production, industries and infrastructural development, tourism, preservation and management of environmentally important and special areas.

Land and soil resources are vital and limiting resource for agriculture. The encroachment on agricultural land is a pressing problem in the rapidly growing areas of our country. Cultivable land has reduced from 9.72 million hectare (1991) to 8.52 hectares (2011). This is alarming for an over populated country like Bangladesh. Food security of the country would be threatened if land and soil resources are degraded and cultivated area is reduced at present rate. To arrest negative balance land zoning is a must for sustainable agricultural development of the country. Secondary data were obtained from publications of Soil Resource Development Institute (SRDI) and Department of Land Records (DLR). They provided spatial information pertinent to land zoning in Kaliganj. All maps were constructed in ARC/Info and exported into shape file formats compatible with ArcView 3.2. All themes were projected in the LCC having a scale of 1:50,000. Current land use data were collected by field survey which provided an opportunity to develop a working relationship with land use, topography and landscape characteristics.

The ultimate output of this study was a map showing the distributions of the various land zones. The Kaliganj Upazila comprises of about 21,316 ha land surface. Agriculture zone, Forest zone and Aquaculture zone accounts for 5,247ha, 8,760 ha and 5,871 ha respectively. About 858 ha area accounts for Commercial and Residential Zone and about 583 ha for Water bodies including rivers. The proposed urban zone accounts for 715 ha.

**Keywords:** Bangladesh; soil and land resource; land zoning

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## **GEOCHEMICAL SIGNALS FOR GLOBAL ATMOSPHERIC WARMING; NUBIAN AQUIFER, AL KUFRA BASIN, SE LIBYA**

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Global warming is a serious threatens to our universe. North Africa region, including Libya had been recharged by numerous paleo-rivers from the southern areas (Chad and Victoria Lakes), as well as the local rains. Al Kufra Basin, the study area, is located at the southeast of Libya. The study area consists of two giant well fields, Al Kufra and Tazerbo, with total of 408 production wells. Geochemical analyses of the selected water samples have been performed. The noble gases (<sup>3</sup>He and <sup>4</sup>He) shows that the temperature of the water during infiltration in the late Pleistocene (40,000 years ago) was several degrees (5-6°C) cooler than today. The reason of this variation in temperature between today and the past could be due to volcanic eruptions. Moreover, analyses of the stable isotopes of groundwater (<sup>2</sup>H (Deuterium), <sup>18</sup>O), and the Radioactive Carbon isotope (<sup>14</sup>C) were used to determine the age of the water in the aquifers in order to estimate the paleo-climate at the time of recharge. Finally, this study concluded that the groundwater forming was during the late Pleistocene and early Holocene, which means in cooler climate than today.

**Keywords:** *Al Kufra; climate; isotope; groundwater; Libya*

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## REMEDIATION OF PAH CONTAMINATED SOILS BY SURFACTANTS

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The contamination of soils and groundwater by polycyclic aromatic hydrocarbons (PAH) is a widespread environmental problem and the removal of such hydrophobic compounds from contaminated area is becoming a major concern. PAH possess low water solubility and are strongly adsorbed to soils and sediments. Therefore, the natural attenuation of PAH by biodegradation or volatilization is very slow, resulting in their persistence in environment for long periods of time. However, surfactants can increase hydrophobic organic compounds solubility in the aqueous phase through micellar solubilization and can improve their mobilization due to interfacial tension reduction. Up to now, various remediation techniques have been developed; among them, the soil washing process with surfactants and biosurfactants solutions, biological methods using surfactants to enhance biodegradability or bioavailability of hydrocarbons, electrokinetic technique apply for surfactant as a flocculation or flotation agent. The use of surfactants for the remediation of contaminated soils has been studied by many authors. However, due to the complexity of phenomena observed in a soil/HAP/surfactant system (micellization, adsorption, solubilization, and mobilization), the dependence of surfactant efficiency on system properties and the continuous increase of hydrocarbon consumption, this field is still a matter of interest and merits investigation.

In this work, we tried to pass in view the most important studies realized on the application of surfactants in the soil remediation processes. The main results obtained from these studies were classified into two parts. The first part dealing with synthetic surfactants application and their benefits and inconvenients reported some remediation projects. In the second part are summarized the advantages of biosurfactants compared to chemical surfactants. The effect of surfactant on PAH removal from contaminated soil and its dependence on some parameters (soil texture, soil composition, surfactant concentration, contamination ratio, age of contamination, pollutant type, pH, ionic strength,...) was treated by many authors. The obtained results for each factor were presented in detail.

**Keywords:** Contaminated soil; remediation process; surfactant; hydrocarbons; PAH; Removal

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## **THE KINETICS STUDY OF THE SILVER NANOPARTICLES GREEN SYNTHESIS**

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### **Abstract**

The green synthesis of metal nanoparticles of different shapes, sizes, chemical composition and controlled monodispersity is an important field of research in nanotechnology because of their interesting physical properties and technological applications. Biological systems such as fungi, microbes and plant extracts have been investigated because of their ability to form silver nanoparticles. In recent years, the plant materials are in the centre of intensive investigations due to their eco-friendliness and suitability for scaling up to large scale synthesis.

In the present study, we report the results of the kinetic studies of the green synthesis of silver nanoparticles in water at ambient conditions using the extracts of balm, peppermint and marigold.

All chemicals were used as received from commercial sources (Sigma-Aldrich, Fluka). Dry plant materials, leaves of balm (*Melissa officinalis* L.) and peppermint (*Mentha piperita*) and flowers of marigold (*Calendula officinalis* L.), were purchased from “Liktravy” company (Zhytomyr, Ukraine). The properties of final and intermediate substances were examined IR spectroscopy (Shimadzu IRAffinity-1 with ATR 8200HA) and UV-Vis spectroscopy (Shimadzu UV1800).

Silver nanoparticle synthesis was evaluated at different reaction conditions (concentration, time) using UV-vis spectroscopy. The reaction velocity was studied by observation of the characteristic surface plasmon resonance band for silver nanoparticles, centred at 446 nm. Formation of silver nanoparticles started within 5 min and increased up to several days. After that only slight variation can be observed. The intensity of the surface plasmon resonance peak increased as the reaction time increased, which indicated the increased concentration of the silver nanoparticles. This result implies that the silver nanoparticle prepared by this green synthesis method is stable but aggregation takes place at certain concentrations.

**Keywords:** *surface plasmon resonance, Melissa officinalis L., Mentha piperita, Calendula officinalis L.*

### **INTRODUCTION**

Most of nanoparticle applications depends on the fact that the material has in nanoscale other more advantageous properties, as in the original condition (cluster). Therefore, many research groups around the world trying to make a new method of synthesis of various materials [1]. Over the last few decades are the noble metal nanoparticles produced at high speed. It concerns the integration of the new nanocomposites in a range of products and technologies [2].

In our work we deal with kinetics of silver nanoparticles that possess excellent antibacterial properties and have many applications ranging from medicine to the industry and



their preparation is feasible in our conditions. We chose medicinal, normally accessible plants as intermediaries for biosynthesis. Using the leaves peppermint (*Mentha piperita*) we already know from several experiments. Leaves and haulms of *Melissa officinalis* and flowers of *Calendula officinalis* are new elements in this area. Experimental part deals the progress of the nanoparticle synthesis of in terms of time and concentration. Akhtar, Panwar & Yun (2013) [3] described the dependence of the shape of the end-products of synthesis depending on time (Table 1).

Table 1– Time factor affecting the synthesis of metal nanoparticles (adapted [3])

Time of synthesis	Shape
<i>Gold nanoparticles</i>	
2 min.	smaller spherical
10 min.	triangular
2.5 h.	spherical
5 h.	spherical
12 h.	spherically-triangular
25 h.	triangular
<i>Silver nanoparticles</i>	
10 min.	spherical
15 min.	spherical
1 h.	spherical
4 h.	cubic, hexagonal
5 h.	spherical
8 h.	spherical
9 h.	crystalline
11 h.	polycrystalline
11-15 h.	spherical and crystalline
24 h.	spherical, triangular, rod-shaped

## EXPERIMENTAL

For the experiments were used peppermint (*Mentha piperita*), lemon balm (*Melissa officinalis*) and marigold (*Calendula officinalis*) plant extracts in interaction with silver nitrate AgNO<sub>3</sub> as a reducing and stabilizing agents simultaneously.

The synthesis of silver nanoparticles and nanoparticles themselves was analyzed by UV-Vis and FTIR. For the data processing and graphical results representation was used program Origin 6.0.

FTIR spectroscopy is a chemical analysis technique that measures the intensity of infrared light in the wavelength dependence. It is used for characterize the merge molecules of plants or their extracts and nanoparticles. Samples were studied by FTIR (IR-Prestige-21 Fourier Transform Infrared Spectrometer, Shimadzu) using the optional accessory MIRacle / Miracle (Single Reflection HATR for Shimadzu IRPrestige-21/ IRAfinity-1/ FTIR-8000 series).

FTIR spectrometer obtains and digitizes the interferogram, performs the FT function and the output is spectrum. This technique was used in the characterization of silver and gold nanoparticles and their associated molecules from plant extracts in various studies [4]. ATR spectrum was processed by the correction program available on the device.



## RESULTS & DISCUSSION

Colloidal solution of silver nanoparticles (AgNPs) reduced by extract of *Mentha piperita* has in various concentrations different colours, according to their size and shape. The colour change is related to the high absorption of visible light depending of nanoparticles excitation by surface plasma [1]. Also in our case, as in [5], reduction of silver nitrate to AgNPs during the extract exposure followed by a gradual increase in the colour development from clear to yellow-brown colour, due to the phenomenon of surface plasmon resonance.



Figure 1: Colour change of peppermint extract with different amounts of  $\text{AgNO}_3$

IR spectra were collected from dried extracts (Fig. 1). The peaks at  $1093$  and  $1022\text{ cm}^{-1}$  corresponding to the CO stretch of carboxylic acids, ethers and alcohols [6], and peaks observed at  $1076\text{ cm}^{-1}$  belong to the ether bonds, and thus indicates the presence of flavonoids and terpenoids [7]. Bands which were found at  $1605$ ,  $1420$  and  $1383\text{ cm}^{-1}$  could be assigned to the characteristic asymmetric and symmetric stretch of the carboxyl group [6]. The bands present at  $1651$  and  $1520\text{ cm}^{-1}$  can be identified as the amide I and II (Kora, Sashidhar & Arunachalam, 2013). Siddiqui et al. (2004) [8] refers to the fact that the C = C groups are located around  $1600\text{ cm}^{-1}$  and Shankar et al. (2004) [7] identically assigned a peak at  $1608\text{ cm}^{-1}$  to the C = C groups.

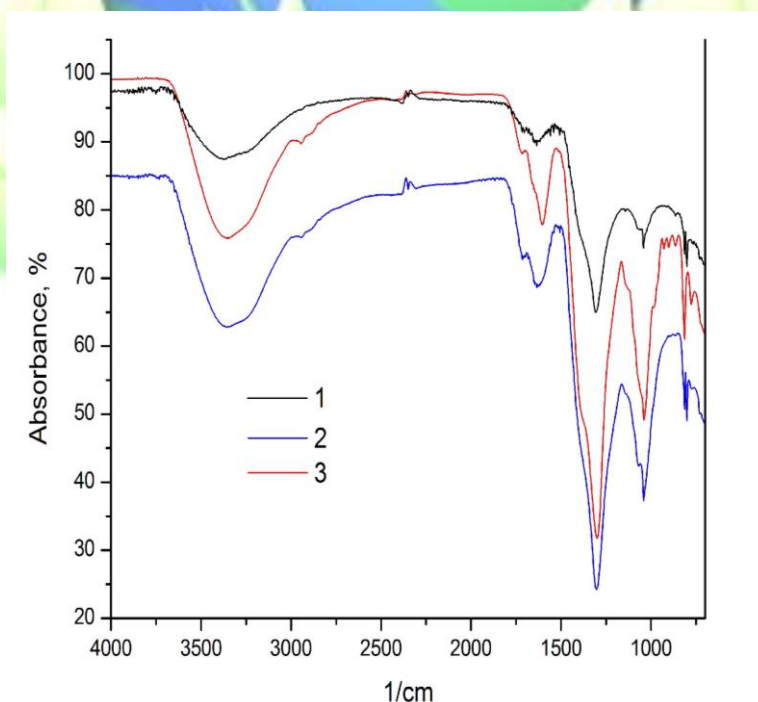


Figure 1: IR spectra of silver nanoparticles containing extracts (1 – Peppermint; 2 - Lemon balm; 3 - Marigold)

Amide I bonds correspond to the wavelength of 1651-1630  $\text{cm}^{-1}$  and amide II correspond to the wavelength of 1520-1537  $\text{cm}^{-1}$ , which suggests that the proteins are responsible for stabilizing the nanoparticles [9, 10, 11]. Zayed, Eisa & Shabaka (2013) [8] also identified a wavelength of 1671 and 1621  $\text{cm}^{-1}$  as characteristic of amides I, while the band at 1575  $\text{cm}^{-1}$  as characteristic of amides II. It is well known that proteins can bind to AgNPs either through the free amino groups or cysteine residues in proteins [12], and therefore the stabilization of AgNPs in the green synthesis is possible.

Siddiqui et al. [8] reports about the existence of the aldehyde C-H bonds (around 2910  $\text{cm}^{-1}$ ). These bonds indicate terpenoid group compound present in the aqueous extract [8]. Bonds to 2963, 2926 and 2858  $\text{cm}^{-1}$  correspond to the asymmetric and symmetric methylene groups vibrations [6].

Kora, Sashidhar & Arunachalam (2013) [6] argue that the shift in absorbance peak with reduced group intensity of the observed 3395-3436  $\text{cm}^{-1}$  represents the binding of silver ions with hydroxyl groups [13]. He et al. (2013) [2] correlates intense broad band at 3384  $\text{cm}^{-1}$  with the O-H bond. Approximate results summary is available in the Table 2.

Table 2: Results of IR spectra

	<i>Mentha</i> (1/cm)	<i>Melissa</i> (1/cm)	<i>Calendula</i> (1/cm)	Examples of chemical functional groups in the sample
Wavelength FTIR spectra	1400-1300	1360	1400	carboxyl group
	1600-1630	1640-1590	1600	amides I, II
	2920-2940	2880	2940-2950	methylene group
	3260-3360	3250-3380	3290-3360	hydroxide group

The first dependence, we have investigated was the dependence of absorbance on the concentration (Fig. 3). Jagtap & Bapat (2013) [14] report that the particles synthesized with 2% extract reach the peak at 410 nm. When concentration is increased to 10% is increased  $\lambda_{\text{max}}$  to 420 nm. Slight variations in the  $\lambda_{\text{max}}$  values means changes in particle size depending on the changing of extract concentration.

We have also seen a slight shift of the peak. With a higher concentration the peak is moving towards 450 nm. This shift to the higher wavelength in the plasmon bond is related to the larger size of the nanoparticles obtained by slow diffusion of the reducing agent [7]. Zayed, Eisa and Shabaka (2013) [16] recorded absorption of colloidal silver nanoparticles in the visible range 380-450 nm as a result of excitation of surface plasmon vibration.

Clearly visible growth of the absorption peak at these wavelengths in our reaction solutions indicating a successful synthesis and hence, the presence of silver nanoparticles. The absorption peak around 420 nm shows a small particle size and a homogeneous spherical shape [17, 18].



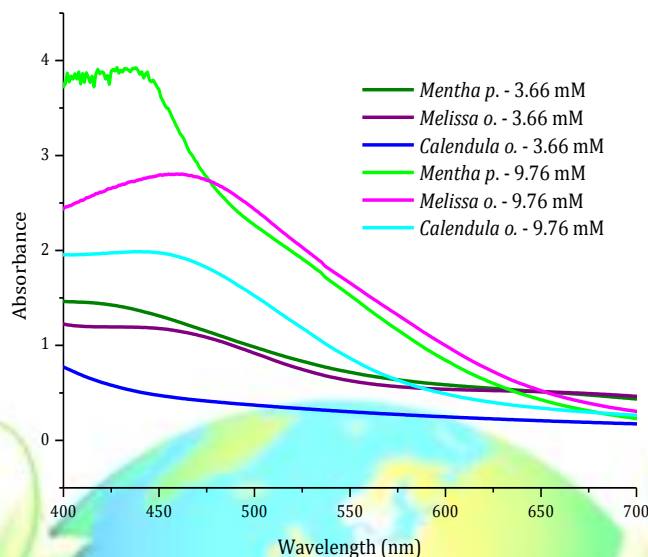


Figure 3: Silver nanoparticles containing extracts with different concentrations of  $\text{AgNO}_3$

Comparing the size of the reduction in our reaction solution, it is clear that peppermint is a fast reductants. In the publications available on this plant are given three absorption peaks, namely 420 nm [17], 439 nm [15] and 450 nm [19]. Thus, from our results we can confirm that the wavelength increases with increasing concentration.

The reduction of  $\text{Ag}^+$  ions to metallic silver was monitored by measuring the UV-Vis spectra for the first two hours (Fig. 3) and in the following 20 hours. From Khan et al. (2013) [20], we know that the absorbance is higher, if the solution is prepared at a higher temperature. Similarly, the intensity of the absorbance increases with the time which indicating a continuous reduction of silver ions, and this leads to an increase in the number of nanoparticles [17].

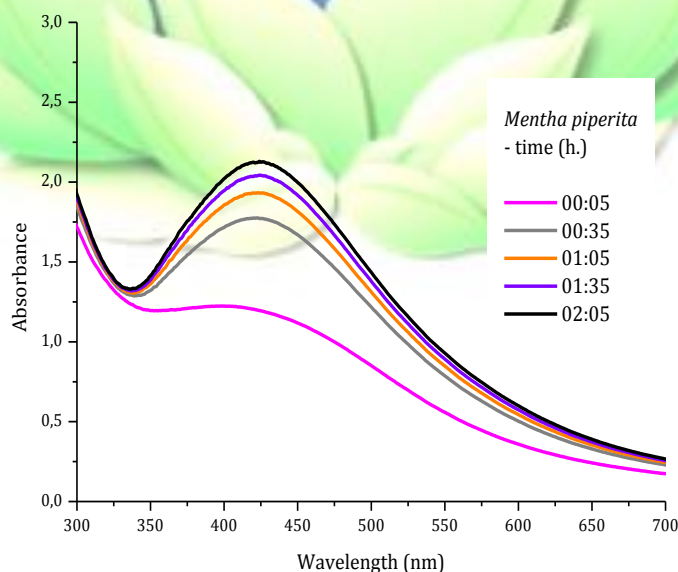


Figure 3: UV spectrum of silver nanoparticles containing extracts of peppermint after different interaction time (first 2 hours)

In each reaction solution the reduction of silver ions is in progress at different speeds. In [21] Saxena et al. (2013), the surface plasmon resonance of silver was visible after five minutes at 410 nm and regularly increased. In our case, we have also seen changes in the spectrum immediately after the first measurement.

Lemon balm and marigold are plants which have not been found published information. However, we can say that in the case of lemon balm it is a very good perspective on the green synthesis. Spectrogram showed values that were close to the values peppermint and a way for further research is open here. The marigold is weaker reductants in comparison with other plants.

We conclude that in the case of silver nanoparticles photosynthesis the final product depends not only on the conditions of the reaction, the temperature, pH, pressure, time, concentration of the reaction solutions, but also on the qualitative aspect of the herbal extract. The individual extract component acts as reducing and stabilizing agent and also from them depends the quality of nanoparticles, because their properties are derived by the size and shape.

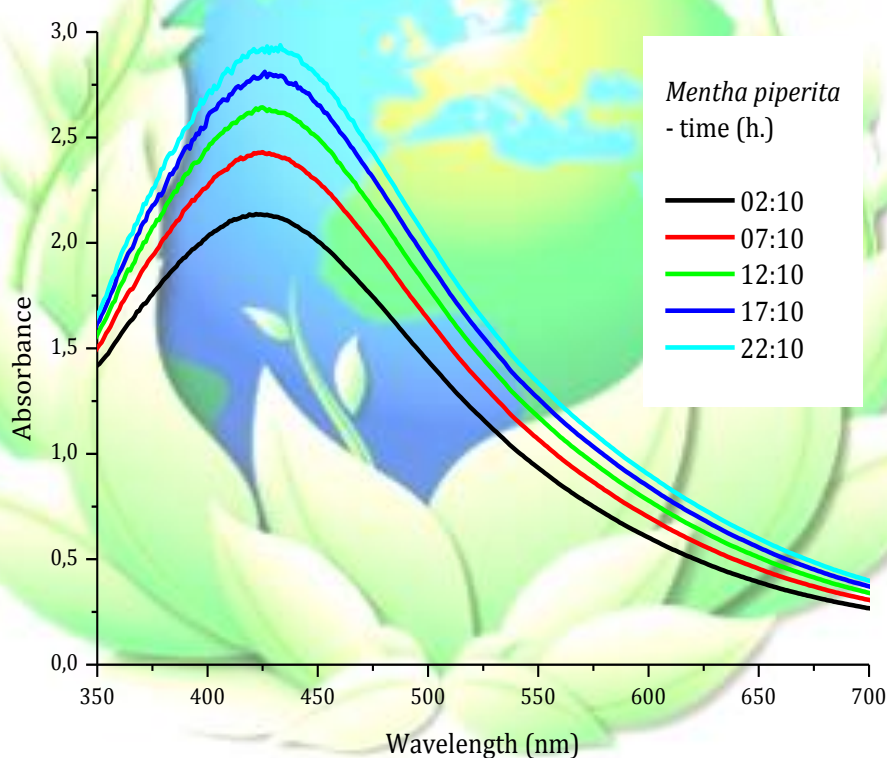




Figure 4: UV spectrum of silver nanoparticles containing extracts of peppermint after different interaction time

## CONCLUSION

We report that we have managed successful repeat the synthesis of *Mentha piperita*, which also confirmed the correctness of our biosynthesis procedure. Comparison of our results we have found the benefits of the new advantageous reductants, *Melissa officinalis* plant extract, which showed for our purpose interesting properties. Obviously, it is necessary to carry out further

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research to obtain new and more accurate information in terms of the course of the synthesis and the resulting nanoparticles. We assume that the nanoparticles of each extract have different characteristics and therefore different properties. Accordingly, we do not want exclude from the center of our interest the *Calendula officinalis*.

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## **SYNTHESIS OF 5-AMINO-4-BENZOYL-1,2,4-TRIAZOLE-3-THIONES AS LIGANDS FOR THE DETERMINATION OF HEAVY METALS IN ENVIRONMENT**

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The main motivation for controlling of heavy metals concentrations in environment (air, water, soil, plants) is its high toxicity. Atomic absorption spectroscopy is one of the most used methods for heavy metals determination. However, the protocols for sample preparation, extraction of heavy metals from probes still need to be improved. The reactions of ionic associations may also be used as organic carriers of heavy metals from samples to laboratory probes. We consider the combination of the dithiocarbamates with aminopolycarboxylic acids as prospective extractants for transferring heavy metal ions into an organic phase.

The presented research work is decided to synthesis of 5-amino-4-benzoyl-1,2,4-triazole-3-thiones as prospective extractants for improvement of atomic absorption spectroscopy method for determination of heavy metals in environment.

All chemicals were used as received from commercial sources (Sigma-Aldrich, Acros, and Fluka). The properties of final and intermediate substances were examined by methods of elemental chemical analysis (Perkin-Elmer 240), thin layer chromatography, IR spectroscopy (Shimadzu IRAffinity-1 with ATR 8200HA), UV spectroscopy (Shimadzu UV1800), and <sup>1</sup>H NMR.

We have synthesized an 5-amino-4-benzoyl-1,2,4-triazole-3-thiones and its derivatives which contains mercapto-group as dithiocarbamates for the formation of strong sulphur-metal covalent bond, carbonyl and amino group for the additional bonds and formation of stable complexes.

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**Keywords:** *atomic absorption spectroscopy; ionic associate; triazole*

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## **THERMAL COMFORT IN THE WORKING ENVIRONMENT - ASSESSMENT THROUGH OBJECTIVE AND SUBJECTIVE APPROACHES**

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### **ABSTRACT**

The indoor environmental quality affects not only health and comfort, but also the productivity, so it strongly influences working and learning efficiency, with repercussion on production and social costs. This paper describes two methods realised to assessment of thermal parameters in the working environment. Thermal environment parameters were measured: indoor air temperature, mean radiant temperature, air relative humidity, air velocity and outdoor air temperature. Through these data were analyzed these microclimatic conditions. The subjective survey investigated the thermal sensation, the thermal acceptability and the thermal preference, using subjective scales. The subjective judgments about the thermal environment were compared with the results of the field measurements. The responses and measurement results from these two different methods were analyzed and compared. This hypothesis needs to be verified by further studies and researches.

**Keywords:** *microclimate, environment, thermal, humidity, working conditions.*

### **INTRODUCTION**

Thermal and humidity microclimate is an environment significantly influencing working conditions in workplaces. Thermal and humid conditions are given by a temperature, relative humidity and air velocity. These physical quantities define a subjective feeling of a comfort or discomfort. In extreme cases, it is possible to consider them as harmful substances, which have or may have a negative influence on human health.

A workplace microclimate has the direct influence on employees' performance, their working comfort and on total occupational safety as well. Thermo-humidity microclimate defines a thermal comfort of a workplace, sufficient supply of liquids, regular air circulation, air humidity level and acceptable physical load at a job performance. A thermal balance is important for human being thermal condition, i.e. the relation between heat volume produced by a human being and heat volume delivered from the organism to surroundings. [3]

It is in the employers' interest to establish such working conditions so that optimum microclimatic conditions could be provided during a job performance, taking the energy demand of the job into account for acclimatized as well as un-acclimatized groups of employees and to determine an optimum regime of their work and rest. It is suitable to utilize air conditioning or fans inside the buildings, which at least ensure air circulation.

A draught - cold air flow is usually felt as very unpleasant. If it is not possible to eliminate a non-uniform flow, it is needed to ensure a rest option outside such space [6]. Introduction should provide a clear statement of the problem, the relevant literature on the subject, and the



proposed approach or solution. It should be comprehensible to academicians around the globe of scientific disciplines.

## MATERIALS AND METHODS

The aim of our research was to monitor and evaluate parameters of thermal and humid microclimate under real conditions of an engineering company and to determine satisfaction or dissatisfaction of employees relating to microclimatic conditions on their workplaces through a questionnaire survey. We used the objective method and the subjective questionnaire survey method.

## OBJECTIVE METHODS

These methods consist in a measurement of determining physical quantities. They are based on the measurement results of basic parameters that are decisive for determination of the environment condition. Optimum and permissible values of these indicators (parameters) of thermal and humid microclimate that include operative temperature, air velocity and relative humidity for warm and cold seasons of the year in a confined workplace and for particular job classes are given in the Annex of Act No. 544/2007 Coll. [2]

## RESULTS OF MEASUREMENT

The real measurement was carried out during a warm day. Daily temperatures ranged from +30° C up to +35° C, with relative humidity ranged from 45% to 56% and air velocity  $v_a$  from 2,27 to 6,25 (m/s). Determine the places, which are most significant from the point of view of discomfort and other factors, where people are to stay. There were eight samples taken at each 4 measuring places (M1 – M4). The measurements of values of ambient dry air temperature  $t_a$ , relative humidity  $r_h$ , air velocity  $v_a$  and temperatures of globe thermometer  $t_g$  at four various working places.

From measured values, the values of parameters of thermal - humidity microclimate for all points of measurements were subsequently calculated resulting average and compare with hygienic limits - optimum and permissible values according Act of National Board of the Slovak Republic No. 355/2007 Coll. [1]:

- air temperature  $t_a$ ,
- operative temperature  $t_o$ ,
- relative humidity  $r_h$  and
- air velocity  $v_a$ .

The evaluation objectivized by measurement ascertained the values that were in the interval of optimal values, see Table1.

Table 1. Comparison of resulting values of measured with optimum and permissible values

	MEASURED AND CALCULATED VALUES			OPTIMUM AND PERMISSIBLE VALUES (JOB CLASS 1B)			
	$t_o$ [°C]	$v_a$ [ms <sup>-1</sup> ]	$r_h$ [%]	optimum $t_o$ [°C]	permissible $t_o$ [°C]	$v_a$ [ms <sup>-1</sup> ]	$r_h$ [%]
M 1	22 ± 0.2	0.15 ± (0.05 + 0.05 $v_a$ )	43.85 ± 3	20 - 24	17 - 26	< 0,3	30 - 70
M 2	21.6 ± 0.2	0.14 ± (0.05 + 0.05 $v_a$ )	44.11 ± 3				

M 3	22.46 ± 0.2	0.14 ± (0.05 + 0.05v <sub>a</sub> )	41.88 ± 3			
M 4	22.6 ± 0.2	0.16 ± (0.05 + 0.05v <sub>a</sub> )	41.10 ± 3			

Next we found out, by basic statistical methods and analysis of variance, that there are statistically significant differences between values of parameters of microclimate depending on measuring point in manufacturing premises.

## SUBJECTIVE METHODS

Subjective methods are based on a user’s subjective opinion survey on a condition of the environment in which he/she occurs. Subjective methods of microclimatic conditions allow deciding necessity to perform additional objective examination.

### Questionnaire Survey

The evaluation by subjective method is most often performs by a questionnaire survey. The questionnaire survey is a method of data collection, at which information, obtained by set of questions in a special form – a questionnaire – are needed. A questionnaire presents a structured set of questions which help to obtain needed information from respondents. The questionnaire is usually anonymous, in order the respondents could answer to questions subjectively, without a pressure and fear of, e.g. loss of employment. The questionnaire must not have too many questions, since a willingness of respondents to complete the questionnaire decreases with increasing number of questions. The questionnaire must only include the questions that will be analyzed. It is necessary to focus on readability, simplicity of completion, language correctness, typographical and graphic layout. The questionnaire must have a logical structure and dynamics, the function of which is to maintain a respondent’s interest at the questionnaire completion.

Questionnaire Survey on Difficulties at Job, Persisting after Its Completion and depending on microclimatic conditions at workplace was performed in the given organization during warm season of the year. Contingence tables and basic statistic methods were used in questionnaire processing. [4]

There were 40 employees participated in the survey, including 24 men (60%) and 16 women (40%). The age category of the respondents is from 25 to 46 years, while the average age is 38 years. All employees have stated in the questionnaire that they are of good health condition and do not suffer from any serious disease. We were interested in following spheres of information:

- A. Microclimatic conditions at a workplace
- B. Health troubles in connection with microclimate parameters
- C. Additional information (relation of employer, drinking regime and thermal sensation).

For questions of A. and B. group we used 4-grade rating scale: “never = 1”, occasionally/rarely = 2”, “often = 3”, very often/almost always = 4”.

## RESULTS

A thermal sensation corresponding to a comfort evaluated 25 employees (62.5%) as “slight warm”. Only nine employees (22.5%) assessed their thermal sensation as “neutral



sensation” (including 7 ones with age under 40) and six employees (15%) feel “warm”. The graphic presentation of thermal sensation of all respondents is on following diagram, see Fig. 1.

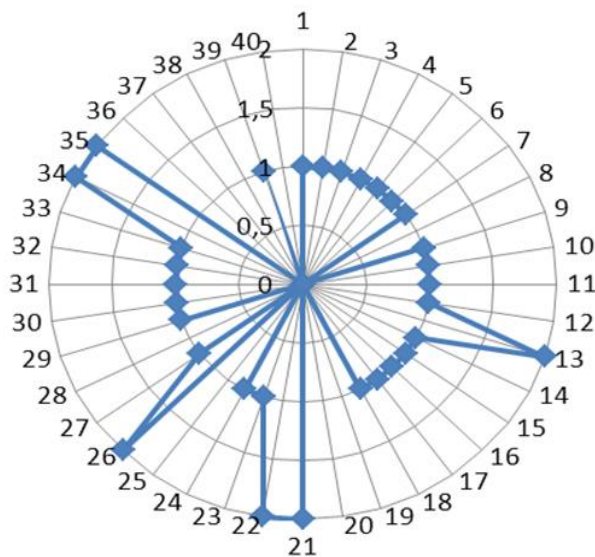


Fig. 1 Employees’ thermal sensation (2-warm, 3-slight warm, 4-neutral)

## DISCUSSION

The aim of our paper was to monitor and evaluate parameters of thermal and humid microclimate under real conditions of an engineering company. In order to evaluate microclimatic conditions, both methods objective and subjective, were used.

From the evaluation objectivized by measurement were ascertained the values of microclimate parameters that were in the interval of optimal values.

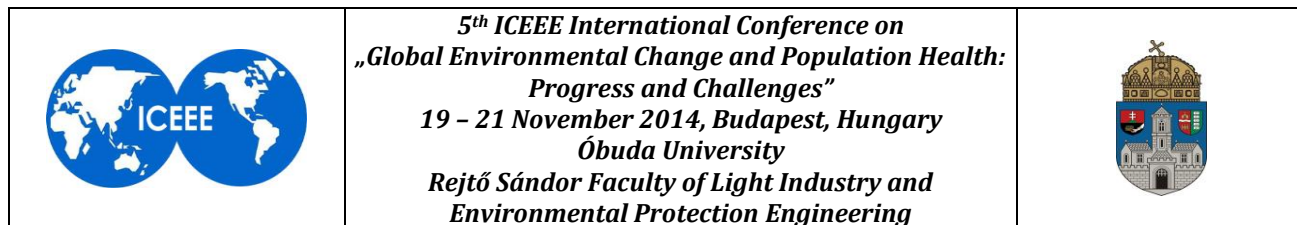
But the results from questionnaire survey showed that less than 23% of employees felt absolute comfort and are satisfied with microclimatic conditions at their workplace. That low value may considerably indicate to employer that is it necessary to create more hospitable working conditions for its employees. The aim of our paper was to monitor and evaluate parameters of thermal and humid microclimate under real conditions of an engineering company.

## CONCLUSION

Employer is to create a hospitable working environment on a long-term basis through taking care about its employees so as to motivate them to high working performance. A suitable or comfortable working environment is of its relevant significance and brings not only positive results in the form of high working performances, but also in the form of satisfied employees.

Increasing labour productivity as well as quality of services provided reflects positive working climate. Similarly, a quality of working environment motivates and encourages activity, expecting creative improvement of performance. Thus, the expectations of an organization could be fulfilled only provided that the expectations of its employees are fulfilled. The results of the



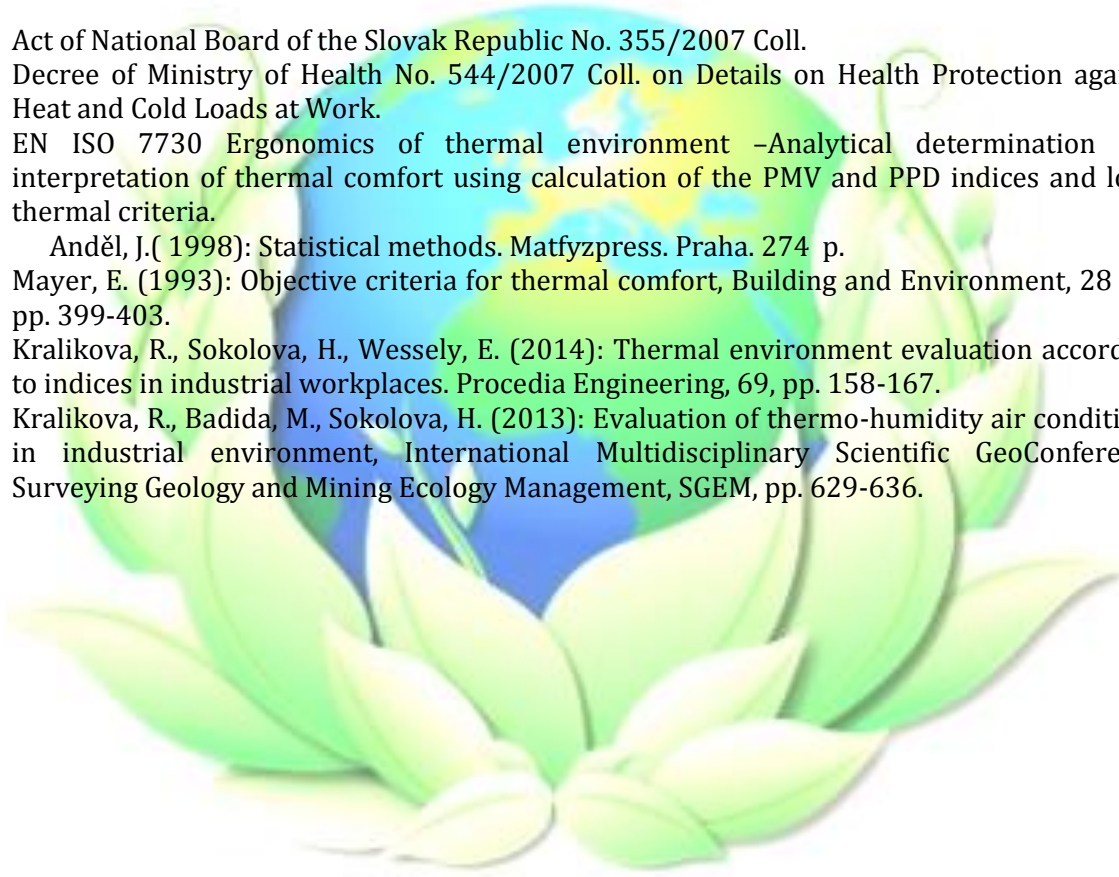


survey can be instrumental for the company management in elimination of potential drawbacks in the sense of a principle of continuous improvement also in the sphere of microclimatic conditions with the aim to ensure high level of hygiene, quality and safety of working environment.

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## PCR IDENTIFICATION OF LACTOBACILLI STRAINS FOR POTENTIAL PROBIOTIC IN POULTRY

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### ABSTRACT

Antibiotics use had its limitations due to the emergence of new strains caused by multi-resistant misuse of these compounds in the poultry sector. The use of probiotics is necessary to promote healthy microflora antagonistic to pathogens and screws can register as an alter-native strategy proposed to protect poultry pathogens and to replace antibiotics as growth factor. The digestive microflora of two Algerian farmer's cocks were studied to isolate and identify lactic acid bacteria for use as potential probiotic in food animal production in order to protect against animal diseases as alternative to antibiotics. A total of 22 strains were isolated from different compartments as crop, caecum, ileum, jejunum, gizzard and colon to evaluate their probiotic proprieties. A use of specific primers targeting partial regions of 16S rDNA gene and sequencing of the amplified fragments preconized to 480 pb were used to identify isolates belonging to the *Lactobacillus* genus. The most diagnostic strains by analysis BLAST were *Lactobacillus acidophilus*, *Lactobacillus gallinarum*, *Lactobacillus crispatus* and *Lactobacillus johonossi*, about 99% of homology for all strains. The study on antagonism cultures of *Lactobacillus* strains using the disc diffusion method showed inhibitory activity during interactions opposite pathogens including *Staphylococcus aureus*, *Escherichia coli* and *Salmonella typhi* by appearance of clear halos in vitro and twelve of them were selected due to their strong inhibitory action. Furthermore, the inhibitory effect of neutralized cell free supernatants of these isolates was studied and confirmed that the selected strains secreted substances which are responsible for the antagonistic action observed on the pathogens. In long term, these strains, once best characterized, could be proposed as probiotics in poultry feed.

**Keywords:** poultry sector, probiotics, pathogens, BLAST

### INTRODUCTION

In 2006, the European Union has permanently banned the use of antibiotics as growth promoters in poultry production. Recently new prevention strategies have been proposed as alternatives to antibiotics to reduce the incidence of enteric pathogens in poultry. These strategies include the use of probiotic lactobacilli [1-3] seem to offer the most promising results. Microorganisms authorized in Europe today feed belonging to bacteria of the genus *Lactobacillus*, *Enterococcus*, *Streptococcus*, *Bifidobacterium*, *Pediococcus*, *Bacillus* and yeasts, probiotics additives are mainly used in mono- or multi- strains [4]. Probiotics has been defined by WHO as “a live microbial feed supplement which beneficially affects the host animal by improving its intestinal balance” [5]. However, lactic acid bacteria (LAB) have attained major attention for probiotic activity and have generally been considered as good probiotic organisms [6,7]. Among of them, lactobacilli are the most important [8]. The crop and ileum flora are mainly composed of lactobacilli in poultry [9]. LAB constitutes important members of the



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microbial population in chick-en intestine, crop, and feces and plays an essential role in maintaining the ecological equilibrium between the different species of microorganisms inhabiting these environments. Recently, Nazef, et al [10] showed that most LAB found in poultry feces were *Streptococcus* and *Lactobacillus* species, while Souza, et al [11] reported the presence of different lactobacilli species in chicken cecum. Attempts to use LAB as a probiotic for poultry have been described. Some probiotics as *Lb. johnsonii* reduced salmonella [12], *Bifidobacterium*, *Enterococcus* and *pediococcus* increase animal performance parameters and modulate the composition of the microflora of the cecum [13]. Other of them, such as *Pediococcus acidilactici* or *Saccharomyces boulardii* improves resistance to coccidiosis [14].

Moreover, the authors reported that the benefits due to lactobacilli as probiotics are multiples such inhibition of *Campylobacter* [15], *Eimeria tenella* inhibition in vitro [16] and the action of *Lactobacillus johnsonii* FI9785 in endemic control necrotic enteritis caused by *Clostridium perfringens* reducing economic losses and the use of antibiotics [17]. Under the use of probiotics, a legal framework has been established in 2002 by the EFSA (European Food Safety Agency) where three principal chapters main spring; identity, safety and efficacy of strain. The identification of microorganisms by DNA methods has become an essential method [18,19]; it is more discriminating compared to traditional methods of identification and classification. However, recent molecular techniques indicate that only 20 to 50% of the bacterial species present in the intestinal tract have been cultured [20]. The aim of this work was to isolate lactobacilli strains from avian microbiota and to identify those with DNA methods using genus-specific primers to an internal region of the 16S rDNA gene. In addition, probiotic properties of these isolated *Lactobacillus sp.* strains were studied to evaluate the antagonistic activity of the isolates against enteric pathogens and partially characterize substances of the cell-free supernatant responsible for antibacterial activity.

## **MATERIALS AND METHODS**

### **Sampling**

Two native's cocks (24 weeks, weight 1.5 -1.8 kg, fed without antibiotics) were collected; they had been raised under natural farming and feeding conditions in different arid areas. Once sacrificed cocks, their gut recovered and transported to the laboratory in sterile conditions at 4°C.

### **Bacterial Isolation and Culture Media**

Fresh intestinal contents weighing 1g, obtained after dissection of each digestive tract compartment from crop, cecum, gizzard, duodenum, jejunum and ileum was collected and homogenized with 0.9% NaCl in sterilized dionized water. Suitable dilutions of 100ul were spread in MRS Agar adjusted to pH 6.5 (De Man Rogosa and Sharp) [21] and incubated at 30°C and 45°C in anaerobic conditions for 48h to 72h for isolation of mesophilic and thermophilic lactobacilli. In order to obtain pure isolation, re-streaking on agar of the same media and conditions was done. Two references strains were used as negative and positive control successively *Streptococcus thermophilus* CNRZ1066 and *Lactobacillus delbrueckii* ATCC11842. Indicator strains were collected from hospital (UHU Oran), namely *Escherichia coli* ATCC 25922, *Staphylococcus aureus* ATCC 25923 and *Salmonella typhi*.

### **Bacterial Morphology and Catalase Assay**

Gram staining of each isolate was done in order to separate Gram positive, Gram negative, rod and cocci forms. Catalase reaction by 3% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and also cells



morphology using phase contrast microscopy were used for primary investigation of the isolates [22, 23]. Selected strains were stored at -80°C in MRS broth supplemented with 20% glycerol until further study.

### **Genomic DNA Extraction of Selected Bacterial Strains**

The genomic DNA of selected bacteria was extracted using the modified method of Gevers, et al [18]; cells from one plate were harvested into 1 ml of sterile distilled water, centrifuged and frozen for at least 1 hr. at -20°C. The thawed pellet was washed in 1 ml TES buffer (6.7% sucrose, 50 mM Tris-HCl, pH 8.0, 1 mM EDTA) and re-suspended in 300 µl STET buffer (8% sucrose, 5% Triton X-100, 50 mM Tris-HCl, pH 8.0, 50 mM EDTA). Lysis buffer 75 µl (TES containing 1330 U/ml mutanolysin and 40 mg/ml lysozyme) was added and the suspension was incubated at 37°C. After addition of 40 µl preheated (37°C) 20% SDS in TE buffer (10 mM Tris-HCl, 1 mM EDTA, pH 8.0) and glass beads, cells were vortexed for 60 s and incubated at 37°C for 10 min, followed by 10 min incubation at 65°C. TE buffer 100 µl was added and the lysate was extracted with 1v phenol/chloroform/isoamylalcohol. The phases were separated by centrifugation (12,000x g, 10 min). The aqueous phase was carefully mixed with 70 µl 5 M NaCl and 1 ml isopropanol, and DNA was precipitated on ice for at least 15 min. DNA was collected by centrifugation (12,000x g, 10 min) and the pellet washed in cold 70% ethanol. The pellet was re-suspended in 250 µl of distilled water. The DNA was verified by a 1% agarose gel electrophoresis in Tris-acetate-EDTA buffer (TAE). A DNA Smart Ladder 200 pb (Bio-Rad, Hercules, CA) was used as a size marker.

### **Amplification PCR**

*Lactobacillus* genus-specific primers V3-357f (5'-CTCCTACGGG AGGCAGCAG-3'), V4-R806 (3'-GGACTACCAGGGTATCTAAT-5'), targeting 16S rRNA gene was used for the confirmation of *Lactobacillus* genus as previously described [24].

The PCR mixture (50 µl) contained 100ng template DNA polymerase, 0.2 mM of dNTP, 1.0 µM of each primer and 2.0 mM MgCl<sub>2</sub>. Amplification was performed on a PCR TECHNE TC-312 (Barloworld Scientific Ltd, stone ST 15 OSA, UK) programmed as follows: 5 min at 95°C for initial heat activation and 35 cycles of 30 sec at 94°C for denaturation, 30 s at 60°C for annealing and 1 min at 72°C for extension and 7 min at 72°C for a final extension. Amplification was verified by electrophoresis on 1.5% (w/v) agarose gel in 1 X TAE buffer using a 200 pb Smart Ladder (Bio-Rad, Hercules, CA) as a molecular weight marker. Gels were stained with ethidium bromide (1 mg·mL<sup>-1</sup>) and visualized under UV light.

### **Sequencing of the PCR Product**

Sequences were performed from PCR product in PCR TECHNE TC-312 (Barloworld Scientific Ltd, stone ST 15 OSA, UK). Sequencing reaction of 16S rDNA (V3/V4) was done using the big dye terminator sequencing Kit on the 370A DNA analyzer (Applied Biosystem).

### **Inhibition Spectra of *Lactobacillus* Strains against Indicator Microorganisms**

Inhibitory activity was carried out according to the standard Disc diffusion method by Tadesse, et al [25] to assess the ability of strains to produce antimicrobial substances. An indicator bacteria culture (which has been adjusted to 0.5 McFarland standard), was used to lawn agar MRS plates evenly using a sterile swab. The plates were dried for 15 minutes and then used for the sensitivity test. 30 µl of lactobacilli cultures from 24-72 h were added to paper

sterile discs (diameter 6mm) and placed on the MRS agar surface. The plate was then incubated at 37°C for 18 to 24 hours depending on the species of bacteria used in the test. After incubation the plates were examined for inhibition zone formation around the discs.

#### **Preparation of cell-free filtrate**

*Lactobacilli* strains were cultured at appropriate temperature incubated anaerobically for 48-72h in MRS broth. The cultures were then centrifuged at 3000 rpm for 15 min and supernatants were collected in conical flasks and the pH was adjusted to 6.8. The cell-free supernatant was sterilized by membrane filtration (0,22µm pore size) [26] and used for the antagonistic activity assay by means of disc diffusion method described above.

#### **RESULTS**

##### **Morphological Characteristics of the Selected Strains**

A total of 48 strains were isolated from 2 avian digestive tract compartments. Microscopic identification could determine the rod shaped cells. The gram's staining and catalase test could support the characterization of lactobacilli. After taking these criteria into account, 22 strains were found to be gram positive rod shaped, non-spore forming, and catalase negative which indicated the typical basic characteristics of lactobacilli [Fig-1].

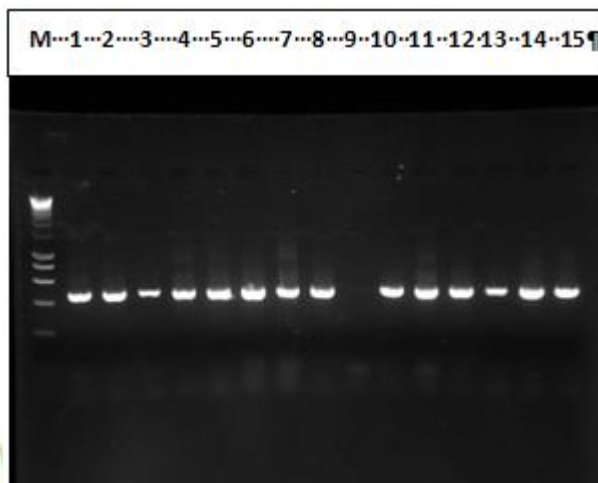


**Figure 1:** Microscopic observations of isolates identified to the genus *Lactobacillus sp.*

##### **Molecular identification of lactobacilli strains**

A DNA band of 480 bp was amplified for 22 lactobacilli strains and for the reference strain *Lactobacillus delbruekii* ATCC 11842 used as positive control, the presence of any significant band was observed for the strain *Streptococcus thermophilus* CNRZ 1066 reference used as negative control [Fig-2].





**Figure 2:** 16S rDNA PCR product of 480 pb fragment on 1.5 % agarose gel  
*Lane M:* Smart Ladder 200 bp DNA; *Lane 1:* LGM A14; *Lane 2:* LGM A15; *Lane 3:* LGM A73, *Lane 4:* LGM A74, *Lane 5:* LGM A63 strain; *Lane 6:* LGM A71 strain, *Lane 7:* LGM A72 strain; *Lane 8:* *Lactobacillus delbruekii* ATCC 11842 (positive control), *Lane 9:* *Streptococcus thermophilus* CNRZ 1066 (negative control); *Lane 10,11,12,13,14,15:*LGM's: lactobacilli strains.

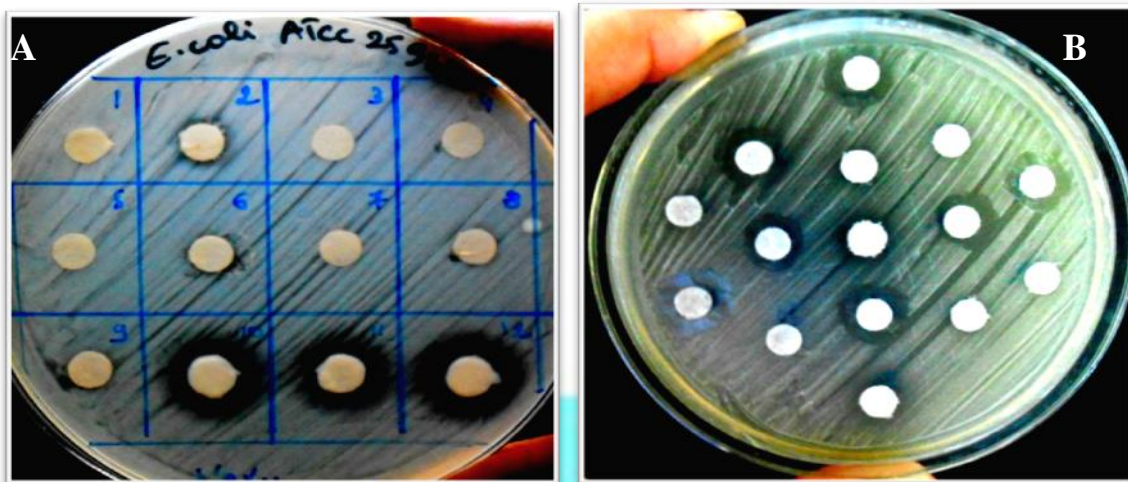
#### Analysis of the 16S rDNA Gene Sequence

Sequencing of different amplification product obtained was done and the scores displayed when processing sequences by BLAST via internet showed high homology with sequences deposited in the database. This high homology around 99% similarity between sequences notified the presence of *Lb. acidophilus*, *Lb. gallinarum*, *Lb. crispatus*, *Lb. johnnossi*, *Lb. fermentum* and *Lb. helveticus* for the majority of isolates examined. At this level of investigation, the selected strains cannot be assigned to the species level and are grouped only in the genus *Lactobacillus sp.*

#### Inhibitory Activity and Spectrum of *Lactobacillus sp.* Strains

The isolated *Lactobacillus sp.* strains were found to possess anti-bacterial activity. From 22 isolates, 11 strains showed an inhibitory activity against several pathogenic bacteria including *Escherichia coli* ATCC25922 [Fig-2A], *Staphylococcus aureus* ATCC25923 and *Salmonella typhi* (data not shown). The inhibition zones were estimated and the results indicated that the inhibition intensity and range varied depending on the *Lactobacillus species* assayed. The average diameters of *Lactobacillus sp.* strains LGM A62, LGM A63 and LGM A14 isolated respectively from cecum, jejunum and ileum against *E. coli* ATCC25922 revealed various diameters but highest than the other LGM strains [Fig-3A]. In other hand, activity of neutralized cell-free supernatant was evaluated against enteric pathogens. The strains tested showed remarkable inhibition spectra against the latter [Fig-3B].





**Figure 3:** Inhibition effect of *Lactobacillus sp.* strain on enteric pathogenic *Escherichia coli* ATCC25922; **(A)** effect of lactobacilli cultures; **(B)** effect of neutralized cell free supernatant.

Furthermore, to investigate whether the cause of the inhibition was due to the protein substance, buffered supernatants adjusted to pH 6.8 were used, the results obtained did not show the complete loss of antibacterial activity of the extracts which indicated that the causative inhibitory agent of some *Lactobacillus sp.* strain was the acid lactic produced. The remarkable inhibition spectra of the other strains obtained against the pathogens may be caused by bacteriocin activity. These results agree with previously reported results [28,29]. The inhibitory capacity of LAB in vitro against pathogens seems to be a good probiotic property.

## DISCUSSION

Understanding the microbial ecology of chicken gut is an important issue in the development of exclusive culture of probiotic and lactobacilli microflora present in the gut microbiota of Algerian arid area farmer's coq shows an enriching diversity of microorganisms whose phenotypic profile can be exploited in the field of fight against pathogens. They represent 49,9% from the total flora, a review dedicated to the bacterial population in the digestive tract of chicken [31] reported a predominance of *Lactobacillus* strains (68.7%) in the ileum and jejunum. The strains isolated in this work were identified to *Lactobacillus sp.* by amplifying a 480 bp fragment from partial region of ADNr16S gene, these results are consistent with those of [32], this by amplifying a partial region of 250 bp between ADNr16S regions and the 23S rDNA showed their strains belonging to the genus *Lactobacillus sp.* In the other hand, the work done in this study demonstrated that inhibition of the digestive tract lactobacilli are characterized by a wide spectrum of antagonistic action against pathogens used in this instance *Staphylococcus aureus*, *Escherichia coli* and *Salmonella typhi*. While Zang, et al [33] isolated 41 strains of *Lb. salivarius* with strong antagonism against *Salmonella* and *Campylobacter*; they did not demonstrate the nature of this antagonism. Makras, et al [34] studies have confirmed the antagonistic activity of LAB against pathogenic bacteria. The antibacterial properties of lactic acid bacteria depend on several criteria: the pH, the growth medium and the production of antibacterial substances as bacteriocins, organic acids, fatty acids and hydrogen peroxide [35]. Lactic acid plays an important role in the inhibitory capacity of LAB against several pathogenic bacteria acidification of the medium by the acid. Our findings on the production of acidity is



consistent with those of Goepfert and Hicks [36] which have confirmed that although lactic acid and acetic acid produced by lactic acid bacteria are involved in the inhibition of *Staphylococcus aureus*. Sakaridis, et al [37] work showed that the LAB are characterized by a strong inhibitor against *Salmonella sp.* and *Listeria monocytogenes*. As a result, supernatant of lactobacilli were used and anaerobic condition were imposed to decrease H<sub>2</sub>O<sub>2</sub> inhibitory activity, and the pH was adjusted to 6.8. So, the inhibition zone that was seen around the discs may be dependent on bacteriocin activity. According to several researchers, probiotics are well placed to take over antibiotics because of their nutritional and antimicrobial compounds very interesting abilities.

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## **ENVIRONMENTALLY FRIENDLY LASER CLEANING OF MATERIALS**

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### **ABSTRACT**

The contribution deals with environmentally friendly laser cleaning of various types of materials. The aim of this contribution is to present the new abilities of cleaning of materials in the future. There are mentioned and compared various material cleaning methods from classic ones to progressive ones and their influence on the environment. Laser cleaning is one of the newest progressive methods of the material cleaning. The results of this technology were recently tested and shown in the Department of Process and Environmental Engineering, Faculty of Mechanical Engineering, Technical University of Kosice together with the firm Trumpf Slovakia s.r.o.

The laser cleaning technology can be used in the various fields of industry, in the production sphere, in the renovation of products and materials and also minimised the influence of harmful impact on the environment.

**Keywords:** *material, laser cleaning, environmentally friendly technology*

### **INTRODUCTION**

In various branches of industries we must lubricate metal materials, their surfaces, components. Equally, the important role as lubrication is also degreasing and scouring of these metal surfaces. Degreasing of metal materials in the mechanical industry is an important technology for cleaning materials to further processing or as a finishing treatment of surfaces, or is used in the maintenance of machinery parts, tools and the like. By degreasing of metal surfaces not only removes lubricant from surfaces, but also cleans mechanical particles of dust, abrasion and others. With the continuously deteriorating of environment, it is necessary to use such degreasing technologies of materials that have no negative impacts on the environment. Also the environment protection is encompassed by standards and decrees of REACH.[1]

### **CLEANING TECHNOLOGY OF MATERIALS**

Cleaning technology of materials should be clear and shortly we can divide the decreasing of materials according to various methods of degreasing as [3]:

- Mechanical cleaning technologies - by W) technologies, [2],
- Chemical technologies [4]:
  - degreasing in organic or inorganic solvents,
  - degreasing in alkali solution,
  - degreasing by detergents,
  - emulsion degreasing,
  - degreasing by steam/ vapour,

- Progressive cleaning technologies – ultrasonic cleaning technology (together with degreasing in solvents or water)
  - dry ice cleaning technology, [5], [6], [7]
  - laser cleaning.

### CHEMICAL CLEANING DEGREASING TECHNOLOGY

The degreasing of metal materials by chemical method belongs to the oldest method of the degreasing. This technology requires the using of various degreasers, chemicals, which are very dangerous for the environment both in terms of storage of new and pure chemicals, their utilisation and at the storage of the chemicals. Chemical degreasing is performed most often by using of degreasing machines. Their classification and examples are as follows [3], [4]:

- Tub and wettable immersion degreasing machine (degreasing washing machine,
- Continuous Spray degreaser machine (grate),
- The chamber Degreaser Spray Machine (grate),
- Transition tunnel device,
- Carousel spray degreasing machines and others.

### CLEANING BY DRY ICE CLEANING TECHNOLOGY

Dry ice blast cleaning utilizes a unique combination of forces to powerfully lift surface contaminants without causing of damage or creating harmful secondary waste. Similar to sand, bead and soda blasting, dry ice blast cleaning prepares and cleans material surfaces by using a medium accelerated in a pressurized air stream. In the Figure 1 is shown the principle of dry ice blast cleaning [5], [6]:

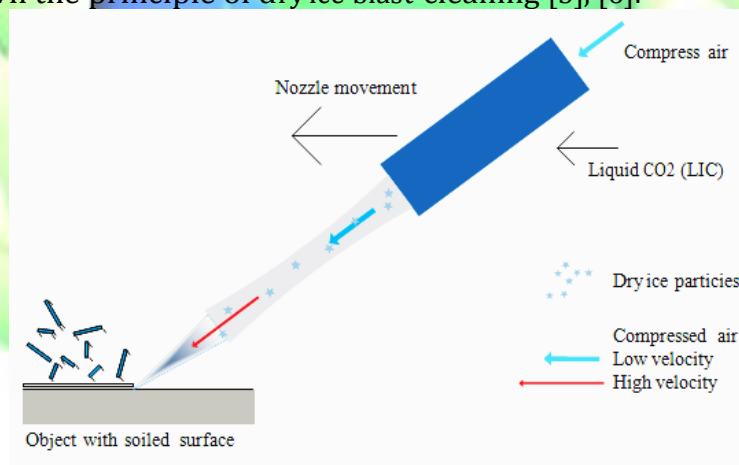


Figure 1 The principle of dry ice blast cleaning [6]

Dry ice blast cleaning offers comprehensive cleaning benefits over traditional methods, and can save up to 80% over current cleaning costs. Technical arguments against classic blasting technologies are [6]:

- A method is significantly faster and more efficient compared to any other cleaning system,
- Non-abrasive cleaning: absolutely no wear to cleaned surfaces, increasing the life of moulds, machinery and production equipment,
- Guarantee of the high quality finish to manufactured products,
- Ecological and economical dry ice leaves no trace and does not any additional

- waste to be processed,
- significant increase in productivity due to reduced production stops resulting from cleaning without disassembly or reassembly or cooling down.

In the Figure 2 and Figure 3 is the result of dry ice cleaning of the extrusion screws at the plastic production.



Figure 2 The extrusion screws before [7]      Figure 3 The extrusion screws after [7]

In the Table 1 is shown the comparison of blasting technologies according to environmental requirements.

Table 1 Blasting technologies according to environmental requirements [7]

CLEANING METHOD	NO SECONDARY	NON-CONDUCTIVE	NON-TOXIC	NON-ABRASIVE
Dry Ice Blasting	•	•	•	•
Sand Blasting*		•	•	
Soda Blasting*		•	•	
Water Blasting*			•	•
Hand Tools	•		•	
Solvents/Chemicals				•

\* Upon contact, traditional blasting materials become contaminated when used to clean hazardous substances and objects. These blasting materials are also then classified as toxic waste and require appropriate safe disposal.

## LASER CLEANING

Laser cleaning is a valuable addition toolbox as it offers a highly selective, reliable and precise method of removing layers of corrosion, pollution, unwanted paint and other surface coatings.

Developed over the last 10 years, the innovative laser cleaning systems combine power and versatility, with the lowest operating cost of all industrial cleaning methods. They offer a safe cleaning method and are environmentally friendly, using no water or chemicals and producing





no effluent. Primarily used for industrial cleaning and surface treatment, renovation and paint removal applications they also remove contaminants, production residue and coatings without damaging the substrate. Metallic and reflective surfaces are ideal although other substrates can be addressed. Laser cleaning systems offer an extremely high level of control and precision. Laser cleaning systems are currently in use in the automobile, aerospace, bakery, food, electronics, restoration and other industries.

### **THERMAL BEHAVIOUR OF THE LASER CLEANING PROCESS**

The cleaning surface reflects laser energy and is minimally affected, however, any contaminants on the surface absorb the laser energy and are quickly vaporized, with any fumes or particulates removed by an in-built filter.

When a laser beam irradiates on the material surface, it may be considered that energy flows in only one direction in a semi- infinite body.

The depth the laser energy penetrated into the material surface is constrained by the duration of the laser irradiation. Increasing ir- radiation time will allow the laser energy to penetrate deeper so as to raise the material substrate temperature. In the Figure 4 is shown the dependence of increase of surface temperature under different laser irradiation conditions.

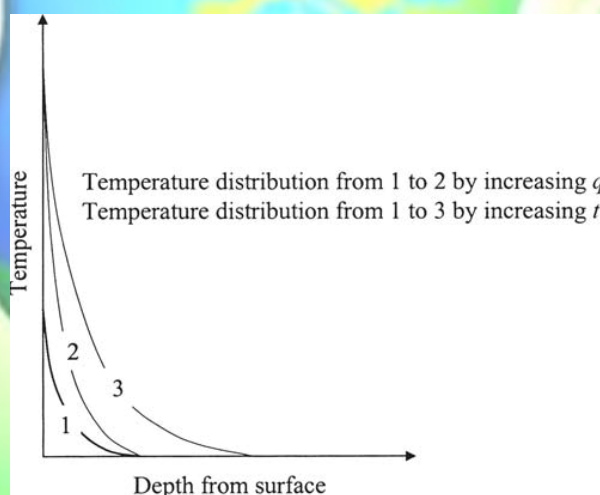


Figure 4 Increase of surface temperature under different laser irradiation conditions, where:  $q$  - laser power flux absorbed by the tested material,  $t$  - the time after laser irradiation begins [8]

Figure 4 illustrates the different effects of laser power flux and irradiation duration on the temperature elevation in the material. For the purpose of laser cleaning, higher surface temperatures are desirable for the removal of machining debris. However, the elevation of temperature under the wheel surface may damage the wheel structure, which should be prevented. Therefore, high power flux and short irradiation laser pulses are likely to be optimum for laser cleaning purposes. [8]

The cleaning of material surface stops when the contaminant is consumed, and consequently there is a minimal heat build-up, avoiding the microscopic roughening and cracking of metal surfaces that can be present when using traditional cleaning methods. [9]

In the Figure 6 is shown the principle of the laser cleaning technology.

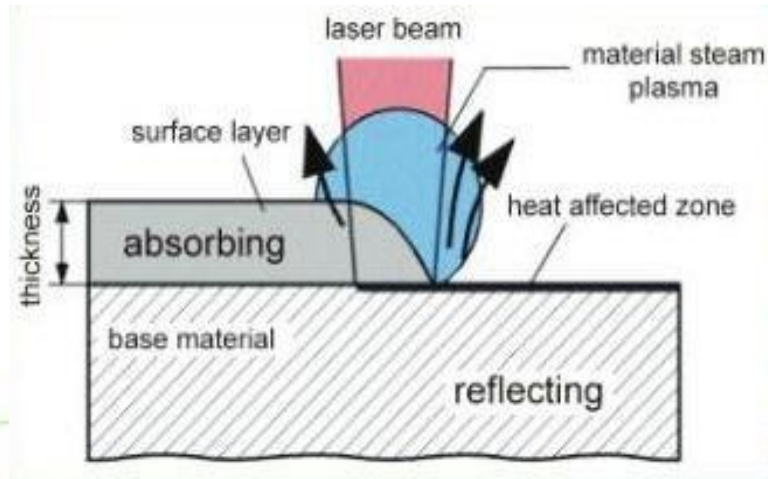


Figure 5 The principle of the laser cleaning technology [9]

The technology steps can be summarized in the following points: [8]

- Powerful, very short, rapid and moving laser pulses produce micro-plasma bursts, shockwaves and thermal pressure resulting in sublimation and ejection of the target material.
- A focused laser beam precisely vaporizes the target coating or contaminant.
- Process optimization of the laser beam produces maximum reaction with the target material for speed while, at the same time, does so safely and without harm to the base material.
- Metal surfaces are well-suited for many laser cleaning applications. Optimized beam settings will not metallurgically change or damage the laser treated surface. That depends on the focus position I the work piece, Figure 6

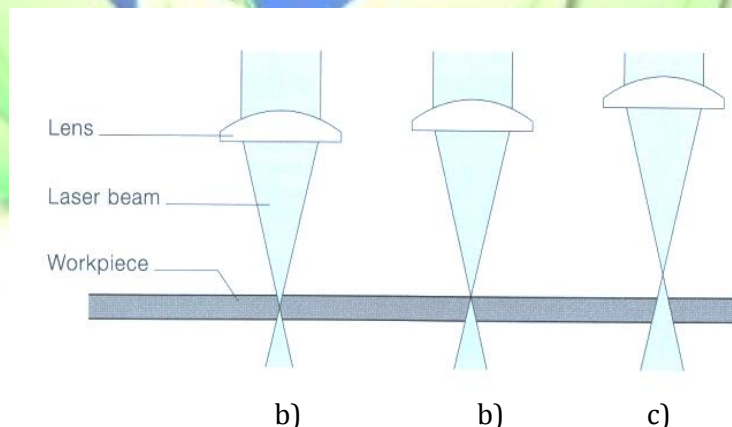


Figure 6 The focus position of laser beam: a) in the workpiece, b) on the surface, c) above the part [11]

- Only the coating, residue or oxide targeted for removal is affected as the laser beam is precisely adjusted not to react with the underlying metal surface.
- Laser beam power density is accurately and easily adjusted to achieve cleaning results

**Technology and environmental benefits** of laser cleaning technology are [8], [9], [10]:



- Fast set-up
- Easy to operate
- Quiet
- No clean-up
- Leaves no residue
- Highly reliable
- Easy to automate
- Low operating costs
- Virtually maintenance-free
- No consumable media - no abrasives, chemicals, solvents
- Green process - no pollution
- Laser beam settings are precisely adjustable to optimize process speed and gentleness

**Laser ablation applications are following [8], [9], [10]:**

- Mould cleaning,
- Surface Preparation,
- Removal of coatings and release agents,
- Weld and joining pre-treatment,
- Removal of oil and grease,
- Oxide removal,
- Paint removal,
- Surface cleaning,
- Gluing pre-treatment,
- Tool cleaning,
- Baking tray cleaning,
- Use of mirror attachment to work on complex shapes
- Historic Restoration.

In the Figure 7 to Figure 10 are shown the examples results of laser cleaning.



Figure 7 Tooth before and after  
Laser cleaning [8]



Figure 8 Brake pads before and  
after laser [cleaning](#) [9]



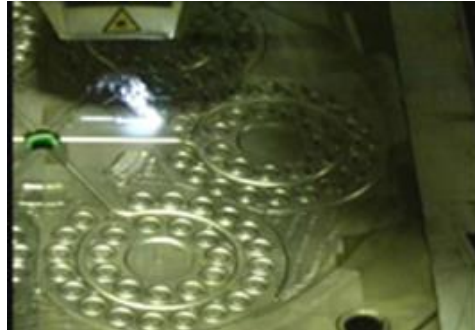


Figure 9 Cleaning of an injection mould [10]

Lasers have been successfully used to clean prehistoric artefacts, sculptures and monuments, while preserving patina, fine surface detail and important surface coatings, [12]

### EXPERIMENTAL TESTING AND VERIFICATION OF LASER CLEANING TECHNOLOGY

The realisation of the first experimental testing was made in the cooperation with the firm Trumpf, Slovakia s.r.o. Materials used for the experiments were:

- c) Steel sheet (deep-drawn steel sheet KOSMALT 190), table: 100x50 mm, thickness: 2 mm, according to standard STN 038737
- d) Synthetic lubrications with various properties (various viscosity):
  1. **Berutox M21 EPK 420**, temperature range: -5°C to + 200 ~ + 220°C, viscosity of the basic oil: 490 mm<sup>2</sup>.s<sup>-1</sup>, at the temperature t = 40°C [13]
  2. **Berutox M 21 KN**, temperature range: -5°C to + 200 ~ + 220°C, viscosity of the basic oil: 490 mm<sup>2</sup>.s<sup>-1</sup>, at the temperature 40 °C [ 14]
  4. **Beruplex LI-EP 2**, temperature range: -30°C to + 150°C [15]

There were used 5 tested pieces for each experiment. Figure 10 shows the dimensions and tested pieces.

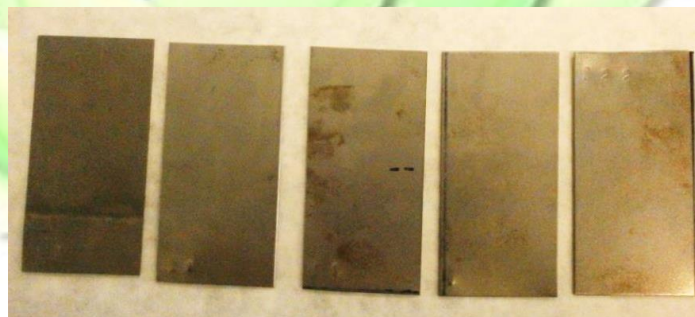
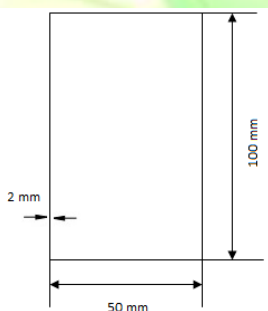


Figure 10 Rectangular profile of deep-drawn sheet KOSMALT 190

After degreasing with technical white gasoline, the tested samples were weighed on laboratory scales MS, METTLER TOLEDO. The lubricants were applied by a paintbrush and were weighed again. The decreasing of tested samples by laser cleaning were experimentally provided on the laser compact machine TruMarkStation 5000, with the least power, to not do an effect on the surface layer of the metal by hardening. There was used the “c” type of focus position of laser beam as it is shown in the Figure 6. The condition of the laser parameters are shown in the Table. The example of testing and workplace is shown in the Figure 11.

Table 2 Testing parameters of laser beam at the degreasing of testing sample

beam source	TruMark 6130
Optics	F 163
wavelength $\lambda$	1604 $\mu\text{m}$
The speed of the laser beam v	1000 mm/s
frequency	50 kHz
defocus	1,5 mm



Figure 11 The example of laser cleaning – position of the sample

After laser cleaning, the tested samples were weighted again and were found the weight loss of tested samples. The weighted values of the tested samples are shown in the Table 3.

Table 32 Examples of the values of the tested samples cleaned by laser beam – sample U1-U5

Sample	weight			
	Degreased sample by white gasoline	Sample + lubrication	Degreased sample by laser	Used lubricant
1	53,189	53,607	53,505	Berutox M 21 EPK 420
2	52,029	53,074	52,77	Berutox M 21 KN
3	53,972	55,518	54,593	Beruplex LI-EP2
4	52,577	53,661	52,598	Berutox M 21 KN

The results after first planned experiment, where the laser beam passed only once through the surface sample during the laser cleaning,, are shown in the Figure 12 to Figure 21.





Figure 12 The sample after laser cleaning  
Lubricant Berutox M 21 EPK 420

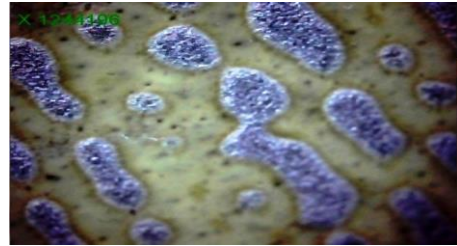


Figure 13 Detail of degreasing of  
lubricant by USB microscope



Figure 14 Tested sample before (light field) and after laser decreasing (dark field), lubricant  
Berutox M 21 KN



Figure 15 The sample after laser cleaning  
lubricant Berutox M 21 KN

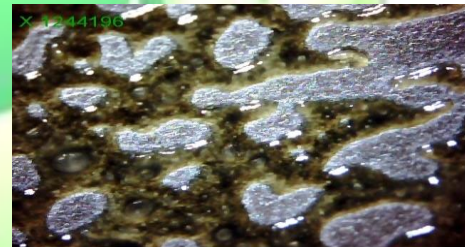


Figure 16 Detail of degreasing of  
lubricant by USB microscope



Figure 17 The sample after laser cleaning,  
lubricant Beruplex LI-EP2

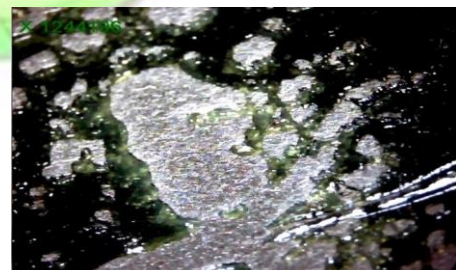


Figure 18 Detail of degreasing of  
lubricant by USB microscope

The results of the comparison of the chosen tested samples weighted on the laboratory scales and cleaned by laser beam are shown in the Figure 19.



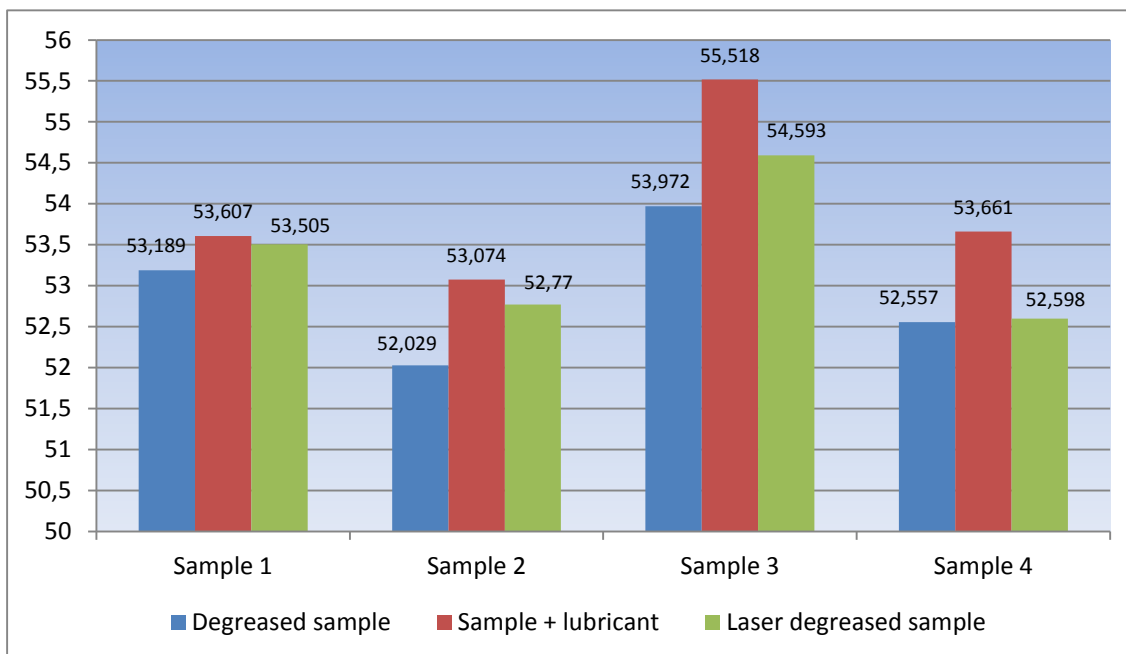


Figure 19 Degreasing of tested sample by laser beam, sample 1 – Berutox M 21 EPK 420, sample 2 – Berutox M 21 KN, sample 3 – Beruplex LI-EP 2, sample 4 – Berutox M 21 KN

## CONCLUSION

Due to the ongoing problem of environmental degradation, we try to find ways to minimize these negative factors. The engineering industry as a whole is greatly contributes to environmental degradation. That is why we try and look for the ways how to minimize the impact on the environment. One of these ways was to try decrease of the material without the using of chemicals.

In cooperation with TRUMF Slovakia s.r.o., we tested and verified the possibility of cleaning of the samples with a laser beam (with the compact machine TruMark 5000) for the first time. From the experiments, we can make a conclusion after visual control that during the laser cleaning tests of the samples No. 4, they reached the best results .The samples were greased by the lubricant BERUTOX M 21 KN, and on the other hand the worst results were reached with the samples No.1, which were greased by the lubricant Berutox M 21 EPK 420.

## Acknowledgement

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Óbuda University  
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Environmental Protection Engineering*



## **CARBON SEQUESTRATION ENABLES TO TREAT WASTE WATERS BY CULTIVATING ALGAE A RESOURCE FOR VALUE ADDED BIO-PRODUCTS AND BIO FUELS IN ORDER TO MITIGATE GLOBAL WARMING**

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### **Abstract**

*Chlorella* is a natural whole food supplement derived from surface water bodies with single celled species micro green algae. The Morphological studies were examined by utilizing Fourier Transform Infrared Spectroscopy, Microscope studies, Scanning Electron Microscopic studies and isolated and identified with PCR studies and based on these studies that the collected specimen is *Chlorella* sp. The phytochemistry of this *Chlorella vulgaris* has been studied which reveals that the *Chlorella vulgaris* has rich with the antioxidants and some bioactive substances which are good resource for vitamins, minerals and some bio-active substances. The confirmation of the presence of alkaloids, saponins, steroids, flavonoids and phenol compounds has been identified a new avenue for drug design and discovery with this species. This study supports the medicinal use of *Chlorella vulgaris* by positive results on antimicrobial tests. Phytochemicals present in these algae are non-nutritive plant chemicals that have protective or disease preventive properties. They are nonessential nutrients, meaning that they are not required by the human body for sustaining life.

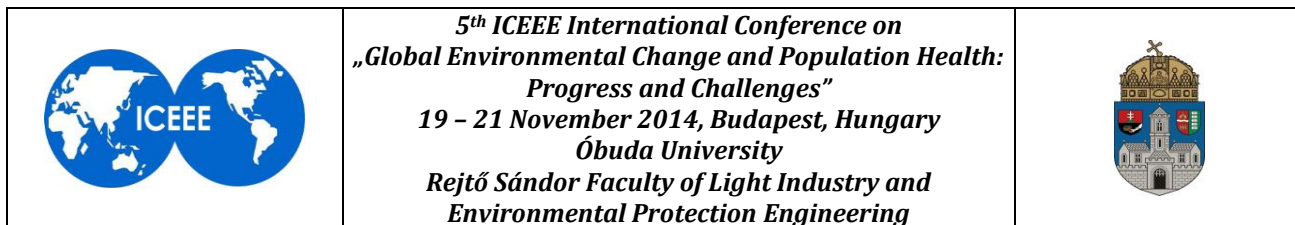
**Keywords:** *Chlorella vulgaris*, PCR study, FTIR, Spectrophotometer, Phytochemical compounds.

### **Introduction**

The economical development depends upon uninterrupted energy and it increase the demand of energy in developing nations and increase the consumption of fissile fuels and gives crucial place to vehement competition for the world's decreasing energy resources [12]. The increase in the usage of fossil fuels results in larger greenhouse gas (GHG) emissions and becomes the main reason for global warming and influenced in climate change. As per the reports of EIA, 2006 states that the fossil fuels are the main contributor of GHGs. The goal of a 5.2 % reduction in GHG emissions worldwide from 1990 values are proposed in the Kyoto Protocol during 1997 [19] becomes a Hercules task as per the status of this protocol as on 2011, about 193 countries which are currently part of this protocol and USA being the remaining signatory nation that has not ratified it. Greater the use of bio-fuels in competition to petroleum in transportation sector could help to meet that cut in emissions are the primary objective [9].

The large area requirement to cultivate the first generation bio-fuel, bio-diesel from rapeseed oil, ethanol from sugarcane, sugar beet, and corn and animal fats makes them dearer to utilize on economical basis. In this affair, a new attempt is made with Algae in order to reduce the GHGs and to cultivate this mass by photosynthesis and the cultivated algae species was tested with its efficiency to extract fuel oil. During these studies, some bio-techniques have been adopted to extract bio-diesel by trans-esterification process.





In the course of identification of mass extractive mechanism, a first attempt was made with the polymerase chain reaction (PCR). This is a powerful and sensitive technique which amplifies specific DNA sequences exponentially through a three-step process done in multiple cycles. First, the double-stranded DNA template is denatured at a high temperature. Then, sequence-specific primers are annealed to the target sequence followed by the addition of a thermo stable DNA polymerase, such as Taq DNA polymerase [4] in order to know the presence of Oligonucleotide, which are the major constituent of Bio-oils, further it is subjected for few tests and from that qualitative analysis it shows some good medicinal character apart from bio-fuel applications. Several disagreements between traditional morphological classification and phylogenetic analysis still remain. But the utilization of chemotaxonomic markers, such as lipids and their fatty acids have been considered as complementary approaches and they provide some data for taxonomic position assignments. This shows some correlations with morphological properties of cyanobacteria [6] with *Chlorella Sp* which is tested in determine its efficiency.

The knowledge about the Traditional medicinal plants has always guided the search for new cures. In spite of the advent of modern high therapeutic drug discovery and screening techniques, traditional knowledge systems have given clues to the discovery of valuable drugs. These Traditional medicinal plants are often cheaper, locally available and easily consumable, raw or as simple medicinal preparations [1]. This traditional medicinal practice now turns an integral part of complementary or alternative medicine. Although their efficacy and mechanism of action have not yet tested on scientific manner in most cases, but the simple medicinal preparations of these materials often mediate beneficial responses due to their chemical constituents [12].

Some modern methodologies give more emphasis is given to functional foods which are being consumed as part of usual diet but are demonstrated to have physiological benefits and reduce the risk of chronic disease beyond basic nutritional functions. The studies with respect to functional foods revealed that they contain some primary and secondary biologically active metabolite components which produced a numerous chemical defense systems and acts against predation, herbivores and competes for a space. These Primary and secondary biologically active metabolite compounds were identified from microorganisms, Algae.

It enables to function as a rich resource for pharmaceutical industries and secondary metabolites presents in the Algae is in favour of producing a numerous chemical defense systems and act against predation, herbivores and competes for a space.

## Materials and methods

The sample microalgae species *Chlorella vulgaris* sp was cleaned and necrotic parts were removed. Then the sample was rinsed with sterile water to remove any associated debris. The pure culture of the sample was incubated in water medium. Pure cultures prior to the stationary phase of growth (10 days) were harvested and collected by centrifuging at 10,000 rpm for 3 min. The Collected micro algal pellets were dried under shade and made into a coarse powder with mechanical grinder for further studies.

### Serial Dilution, Streak Plate Method

The sample was taken and serial dilution was done. To this serially diluted culture, streak plates were done in MRS agar plates to obtain pure colonies (Figure-1).



### **DNA Purification**

Ten  $\mu\text{l}$  of 3M sodium acetate solution (pH 5.2) and 275  $\mu\text{l}$  of 95 % v/v ethanol were added to each sample's DNA, mixed by flipping and placed in dry ice for 15 min. The samples were then centrifuged for 15 min at 15,700 x g at 4°C (Hermle Z233 MK-2 High Speed Refrigerated Centrifuge) to remove the supernatant. The pellets were each washed once with 1 ml of 95% v/v cold ethanol and centrifuged for 5-6 mins. After supernatants were discarded, DNA pellets were placed in an oven (Isotemp Vacuum Oven Model 280A, Fisher Scientific, Pittsburgh, PA) at 37°C for 10 min to dry under a vacuum of -25 inches of Hg.

After drying, 80  $\mu\text{l}$  of TE buffer was added and DNA concentration was determined with a ND-1000 Spectrophotometer (Nano drop, Wilmington, DE). Two readings were taken per sample (2  $\mu\text{l}$ ).

### **PCR Amplification for 16s rRNA**

The DNA was amplified using universal 16S rRNA primers A 8F and A 1492R (Ocimum Biosolutions Ltd) (PCR reaction was performed in a 50  $\mu\text{L}$  containing 0.1 ng of template DNA, PCR Master Mixer, 10 pmol concentration of each primer and 0.025U of Taq DNA polymerase enzymes. The final volume was adjusted with sterilized Mili-Q water. A PCR thermo cycler (Bio-rad) was used to amplify the reactions through an initial denaturation step at 94°C for 2 min and followed by 25 cycles at 94°C for 1 min, 52.3°C for 1 min and with an extension of 72°C for 1 min followed by an final extension temperature at 72°C for 2 min. Amplified PCR products were stored at -20°C for further purification and downstream application.

### **PCR primers for 16S r RNA amplification**

<b>Primers</b>	<b>Target for amplification</b>	<b>Oligonucleotide 5'-3'</b>
A 8F	16S rRNA	AGAGTTTGATCCTGGCTCAG
A 1492R	16S rRNA	TACGGCTACCTTGTTACGACTT

### **Agarose gel electrophoresis for PCR product**

About 5  $\mu\text{l}$  aliquot of PCR amplified product was loaded on 1.4% agarose in 1X TAE buffer at 50 V for 45 min and the PCR products were visualized in an UV transilluminator. Lambda DNA double digested with EcoR I and Hind III was used as a marker.

### **Fourier transforms infrared spectroscopy**

The IR spectrum of dried algal biomass was recorded on Nicolet IR spectrometer at room temperature. The dried algal powder was blended with potassium bromide (KBr) powder, and pressed into tablets before measurement. A region of 4000–400  $\text{cm}^{-1}$  was used for scanning [13].

### **Preliminary Phytochemical Screening**

The sample of 1 gm was transferred into clean screw cap bottle of 10 ml capacity. Solvent of 10ml is added separately. The extracts are separated and collected for storing at 4°C and utilised for the remaining analysis is to be carried out.

A systematic and complete study of crude drugs includes with complete investigation of both primary and secondary metabolites obtained from derived algae metabolisms. Various qualitative tests as prescribed by standard procedure are carried out and various profiles are established for various extracts according to their chemical composition in nature.





The extracts obtained are subjected to chemical tests as normal routine procedure in identification of various phyto constituents which are followed as protocol as per the methods adopted by Harborne.

### Quantitative phytochemical analysis

The phytochemicals which are present in the ethanol extract of *Chlorella vulgaris* was determined and quantified by standard procedures.

### Determination of total phenolic compounds

100 mg of the extract of the sample was weighed accurately and dissolved in 100 ml of triple distilled water (TDW). 1 ml of this solution was transferred to a test tube, then 0.5 ml 2N of the Folin-Ciocalteu reagent and 1.5 ml 20% of Na<sub>2</sub>CO<sub>3</sub> solution was added and ultimately the volume was made up to 8 ml with TDW followed by vigorous shaking and finally allowed to stand for 2 hours after which the absorbance was taken at 765 nm. These data were used to estimate the total phenolic content using a standard calibration curve obtained from various diluted concentrations of gallic acid. [2]

### Determination of total flavonoids

The method is based on the formation of the flavonoids-aluminium complex which has an absorptivity maximum at 415nm. A 100µl of the plant extracts in methanol (10 mg/ml) was mixed with 100 µl of 20 % aluminum trichloride in methanol and a drop of acetic acid, and then diluted with methanol to 5ml.

The absorption at 415 nm was read after 40 minutes. Blank samples were prepared from 100 ml of plant extracts and a drop of acetic acid, and then diluted to 5ml with methanol. The absorption of standard rutin solution (0.5 mg/ml) in methanol was measured under the same conditions. All determinations were carried out in triplicates. [8]

### Determination of total alkaloids

5 g of the sample was weighed into a 250 ml beaker and 200 ml of 10% acetic acid in ethanol was added and covered and allowed to stand for 4 h. This was filtered and the extract was concentrated on a water bath to one-quarter of the original volume. Concentrated ammonium hydroxide was added drop wise to the extract until the precipitation was complete. The whole solution was allowed to settle and the precipitated was collected and washed with dilute ammonium hydroxide and then filtered. The residue is the alkaloid, which was dried and weighed [9].

### Determination of total tannins

500 mg of the sample was weighed into a 50 ml plastic bottle. 50 ml of distilled water was added and shaken for 1 h in a mechanical shaker. This was filtered into a 50 ml volumetric flask and made up to the mark. Then 5 ml of the filtered was pipette out into a test tube and mixed with 2 ml of 0.1 M FeCl<sub>3</sub> in 0.1 N HCl and 0.008 M potassium ferrocyanide. The absorbance was measured at 120 nm within 10 min [14].

### Determination of saponins

Twenty grams of plant sample was weighed into a 250ml conical flask. 100 ml of 20% C<sub>2</sub>H<sub>5</sub>OH was added. The mixture was heated over a hot water bath for 4 hours with continuous stirring at about 55°C. It was then filtered with a Whatman No.42 paper. The residue was re-extracted with another 200ml of 20% C<sub>2</sub>H<sub>5</sub>OH. The combined extract was reduced to 40ml over



a water bath at about 90°C. The concentrated extract was then transferred into a 250ml separator funnel and 20ml of (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O was added to the extract and shaken vigorously. The aqueous layer was recovered while the (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O layer was discarded. This purification process was repeated. 60ml of n-butanol was added and the combined n-butanol extract was washed twice with 10ml of 5% NaCl. The remaining solution was then heated on a water-bath in a pre-weighed 250ml beaker. After evaporation the residue was dried in a Gallenkamp moisture extraction oven (Size 1) to a constant weight.

$$\text{Percentage of total saponin} = \frac{\text{Weight of residue} \times 100}{\text{Weight of sample taken}}$$

### Determination of Cardiac glycosides

Cardiac glycoside content in the sample was evaluated using Buljet's reagent as described by El Oley et al [11]. 1g of the fine powder of *C. populnea* was soaked in 10ml of 70% alcohol for 2hrs and then filtered. The extract obtained was then purified using lead acetate and Na<sub>2</sub>HPO<sub>4</sub> solution before the addition of freshly prepared Buljet's reagent (containing 95 ml aqueous picric acid and 5ml 10% aqueous NaOH). The difference between the intensity of colours of the experimental and blank (distilled water and Buljet's reagent) samples gives the absorbance and is proportional to the concentration of the glycosides.

### Carbohydrate estimation

Phenol sulphuric acid method [7] was used for estimate of total carbohydrate content, which is based on principle that in hot acidic medium glucose is dehydrated to hydroxymethyl furfural. This forms a green coloured product with phenol and has absorption maximum at 490 nm. Different aliquots of sample were prepared and final volume was made to 1ml by water. 5ml of 96% of concentrated H<sub>2</sub>SO<sub>4</sub> was added followed by shaking and incubation for 40 minutes at room temperature. Then 1ml of 5% phenol was added to each tube and absorbance was read at 490 nm. Standard curve was plotted using different concentrations of 25mg % glucose.

### Results and discussion

In this study, using the designed primer pair, the 16S rDNA sequence of cultivated *Chlorella* was successfully amplified. Then, this PCR product was cloned and sequenced, and the algal strain was determined to be *Chlorella vulgaris* when blasted on the NCBI database.

According to the electrophoretic profiles, nine viral dsRNA bands were present in *Chlorella* cells. The sizes of these nine ds RNA segments ranged from 250 to 2500 bp, and the 150 segment 5 was much brighter than the others. Therefore, the segment 5 was selected to further analysis in our study.

This information was then put into practice to positively identify an environmental strain of the *Chlorella* genus of freshwater unicellular green algae. When compared with both an internal standard and GenBank submissions, we gained a 97% match with the type strain for *C. vulgaris* and have identified this solvent-degrading and solvent-tolerant strain as such. The genetic sequence gained using these primers, although only 600 bp in length, can be used successfully not only to positively identify the organism in question, but also to infer phylogenetic associations with similar accuracy to phylogenetic reconstructions involving the use of complete 16S rRNA gene sequences. It has been tabled here and by using various

bioinformatics tools on phototrophic eucaryote, primers are originally designed by Nubel et al. in cyanobacterial studies can be adapted for greater use and benefits. They are ideal for not only biodiversity studies of cyanobacterial communities, but can also be used as a tool in identifying a phototrophic eucaryotes either for the positive identification of new species or for phylogenetic related studies.

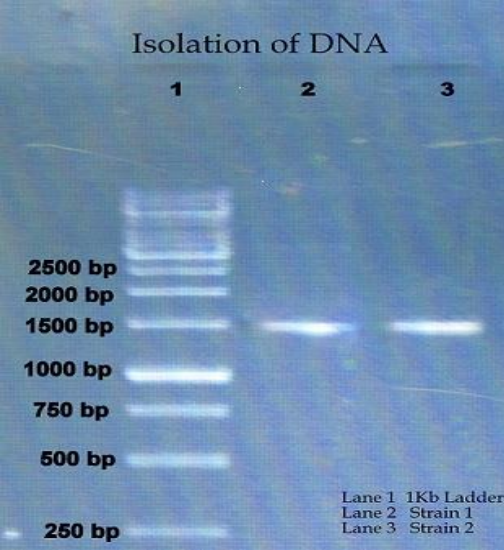


Figure-1

The Figure-2 is FTIR spectra of this *Chlorella vulgaris* in relation to specific groups in these spectra, each peak is assigned for a functional group. The molecular assignments of these bands are based on published data of phytoplankton, bacteria and other biological materials. In this FTIR spectral studies of chlorella vulgaris, the protein spectra characterized by strong peaks 1656 cm<sup>-1</sup> (amide I) and 1536 cm<sup>-1</sup> (amide II).

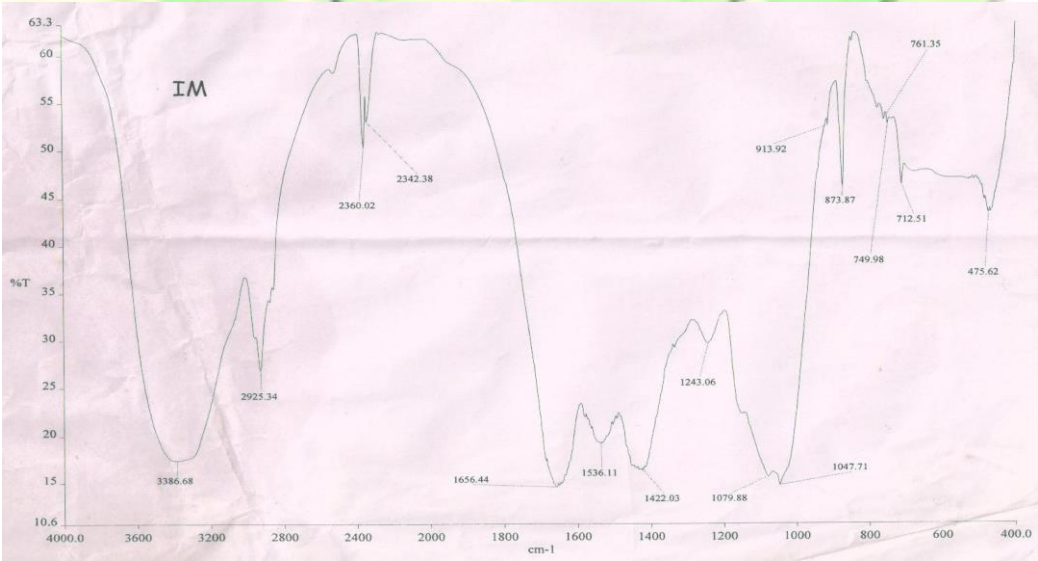


Fig-2: FTIR spectra of *Chlorella vulgaris*

These bands were due primarily to C=O stretching vibration and a combination of N-H and C-H stretching vibrations in amide complexes. The Lipids and carbohydrates have been characterized by strong vibrations for C-H at 2925 cm<sup>-1</sup>, C-O-C of polysaccharides at 1079 cm<sup>-1</sup>, 1047 cm<sup>-1</sup> respectively, while carbohydrates are the strongest absorbers between 1200 and 1000 cm<sup>-1</sup>. Several other classes of compounds, such as nucleic acids have functional groups with absorption bands in the same region of the spectrum. The strongest peaks 1536 and 1422 shows that bending modes of methyl groups of protein. The peak 1243 shows carboxylic acid present in the algae. In this study, the close correlation between the peaks and the existence of with band 2 suggested that lipid content very high and also carbohydrate, nucleic acid also present in *Chlorella vulgaris*.

A very sensitive and an important phytochemical screening of the *Chlorella vulgaris* fraction have been performed which reveals the presence of bio-active compounds namely Flavonoids, Tannin, Phenolic compounds, Terpenoids, Cardiac glycosides, Saponins and Carbohydrates with positive results with the help of ethanol extract. (Table.1)

Table 1: Phytochemical screening for extracts

S.No	Phyto chemical compounds-test name	Result
1	<b>Flavonoids:</b> Ferric chloride test	Positive
2	<b>Tannin :</b> Ferric chloride test	Positive
3	<b>Phenolic compounds:</b> Ferric cyanide test	Positive
4	<b>Terpenoids:</b> Salkowski test:	Positive
5	<b>Cardiac glycosides:</b> Keller Killiani test	Positive
6	<b>Saponins:</b> Foam test (or) Haemolysis test	Positive
7	<b>Carbohydrates:</b> Fehling's Test: Molisch's Test:	Positive

The presence of Flavonoids possess vitamin like properties and a research finding proposed a short lived vitamin P in this compound. The flavonoids containing plants are used by the folks to treat the disorders with respect to thyroid and other hormones. The recent investigation identify that they possess antioxidant and antimicrobial, anti mutagenic, anti carcinogenic properties. The tannins attributed to the wound-healing and anti-inflammatory properties. The Phenolic compounds are considered to be an essential part of the human dietary methods since it contains antioxidant properties. The Terpenes are used as an anti-spasmodic, carminative and stimulant, with an effective antiseptic property. Hence they are used in foods, candies, teas, oil extracts. It is useful in treating cold and fever, headache and body aches due to its ability to decrease inflammation. The anti-spasmodic (sedative) nature helps inhaling the pains in the bowel and its muscles. The therapeutic application of Cardiac glycosides finds its therapeutic application due to positive isotropic effects which enables it to treat heart-related pathologies. More recently, considerable *in vitro*, *in vivo* and epidemiological data support the roles for such drugs for the treatment of several diseases. Saponins are having some strong antitumor effects and found beneficial in targeting and inhibiting the tumor angiogenesis by



suppressing its inducer in the endothelial cells in blood vessels and preventing and adhering, invasion of metastasis of tumor cells. Carbohydrate is used in the field of skin tissue engineering, wound healing modulation and a food material. All these bio active compounds are present in the *Chlorella vulgaris* sample and it is to be refined and could be utilised as food supplement as well as medicine in order to treat the above said ailments or could prevent the same if properly administered by oral method by preparing it as capsules.

## Conclusion

The microalgae species *Chlorella vulgaris* proves its ability to reduce the carbon level in our environment, considerable amount of lipids and nucleic acids presence proves its ability to prepare bio-diesel.

The detailed studies reveal its ability to act as anti microbial and the primary and secondary biologically active metabolic components produce a numerous chemical defense systems and it could functioned against predation, herbivores and competes for space. These studies enable us to understand that this algae species not only able to abate carbon dioxide loads in the atmosphere, and a able nutrient load in remove in water bodies and also a good potential supplier of Oxygen.

The detailed bio technological studies enable us to conclude that it is a rich resource of pharmaceutically and therapeutically useful bio-active molecules which will help to us to discover the drugs.

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## **UNMANNED AERIAL VEHICLES IN ENVIRONMENTAL MONITORING – AN EFFICIENT WAY FOR REMOTE SENSING**

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### **ABSTRACT**

Airborne photographs can be expediently used in environmental monitoring; e.g. in the surveillance of the state of natural reserve areas such as wetlands, or in the measurement and mapping of pollutants such as an oil spills on a lake or sea. A new, cost-effective platform of airborne remote sensing is the unmanned aerial vehicle (UAV or drone). In our experimental work, aerial photos were made in Bakony Mountains from normal perspective and from vertical perspective with using three UAVs equipped with small HD cameras. Within the framework of this work a small lake was photographed, where the beginning of eutrophication was detected. This hardly can be observed from ground, however, it is visible on the aerial photos. The airborne surveillance of areas of ragweed (*Ambrosia sp.*) populations was also investigated.

It was found that both UAVs are feasible for these tasks. We concluded, that using these platforms for environmental monitoring is advantageous, especially in case of natural reserve areas since those are very silent and – contrary to big aircrafts and helicopters – do not disturb the ecology even in natural reserve areas and the people living there, moreover those could be operated in a very flexible and economic way, and the aerial photos taken are highly informative.

**Keywords:** *UAV, remote sensing, aerial photographing, orthophoto, GIS*

### **INTRODUCTION**

Airborne monitoring - or airborne remote sensing - is a very useful tool in environmental monitoring if information is needed on a large territory within a short period of time. The only limiting factor is the cost, which could be high. For conventional monitoring it is needed to hire an airplane. A manned aircraft or helicopter needs fuel, well-trained pilot and an airbase, which could be far away from the working area. This makes the fuel costs even higher, thus the overall operational costs of the conventional airborne monitoring is high, in Hungary it is typically around 5-6,000 USD/hr for a helicopter and 1,000 USD/hr for a small aircraft (Cessna) (Méhes et al., 2011). However, the size (and weight) of the high-resolution cameras and other sensors have shown a significant decreasing trend during the last decades, giving an opportunity to use them onboard of small, unmanned aerial vehicles (UAV) (Eisenbeiss, 2009; Sauerbier et al., 2011). The use of UAVs is increasing, not only in the military applications, but in civilian sector as well (Eisenbeiss, 2011; Grenzdörffer and Niemeyer, 2011). The costs are significantly lower (by about a magnitude), and the flexibility of the application is much higher than that of the big aircrafts, due to the lack of airbase need (Méhes et al., 2011; Sauerbier et al., 2011, Watts et al., 2012).



Several types of airborne monitoring are known, which can be divided into three main types: photogrammetry (Eisenbeiss, 2009; Sauerbier et al., 2011; Eisenbeiss, 2011; Grenzörffer and Niemeyer, 2011; Haala et al., 2011; Kelcey and Lucieer, 2011; Laliberte et al., 2011; Suárez et al., 2010; Turner et al., 2012), sensor mapping (Daniel et al., 2009; Rojas et al., 2012; Towler et al., 2012; Watts et al., 2012) and sampling (Pöllänen et al., 2009; Aylor et al., 2011). In this paper, only the photogrammetry is dealt with.

In photogrammetry the information is image-type. These images could be high-resolution conventional photos (Eisenbeiss, 2009; Eisenbeiss, 2011; Grenzörffer and Niemeyer, 2011; Haala et al., 2011; Sauerbier et al., 2011; Turner et al., 2012) or lower-resolution photos but from a special, well-defined spectral range (multi/hyperspectral imaging, IR/UV imaging) (Suárez et al., 2010; Kelcey and Lucieer, 2011; Laliberte et al., 2011). In both cases, two perspectives are possible: perspective from bird’s-eye view or from vertical angle. The first one is simple, it provides rapid information and it is very easy to use if the information obtained is to be immediately evaluated e.g. in case of emergency operations. The latter one is often used in multispectral imaging, the photos can be used in geo-information (GIS) systems by converting the photos into orthographic projection and using them as “map layers”, e.g. if a pollutant identification and its distribution should be determined.

The airborne monitoring can be used in different types of environmental monitoring from disaster emergency actions to the monitoring of pollutants or natural reserve areas. In case of emergency/disaster situations a significant advantage of the airborne monitoring is that no human presence/involvement is required. Only the device/robot is subjected to the impacts of the disaster, e.g. radiation or toxic gases. Another advantage is that from a bird’s eye view more details are visible on one picture, which is very useful in the organization of the rescue measures (Fig. 1) (Daniel et al., 2009; Towler et al., 2012).



Fig. 1: Application of UAVs in disaster management



This perspective is utilizable in conventional environmental monitoring as well; e.g. in case of checking a dam, a mining spill, tail gases, etc. In these cases, some critical points are not detectable from ground view, however, from the air, everything is visible and can be checked (Fig. 2).



Fig. 2: Application of UAVs in facility monitoring

The protection of natural reserve areas is our primary task to keep the planet for the next generations. Aerial photographs can be used as well for monitoring of wildlife or vegetation (Gademer et al., 2010; Kelcey and Lucieer, 2011), in the latter case multispectral imaging is very informative (Fig. 3).

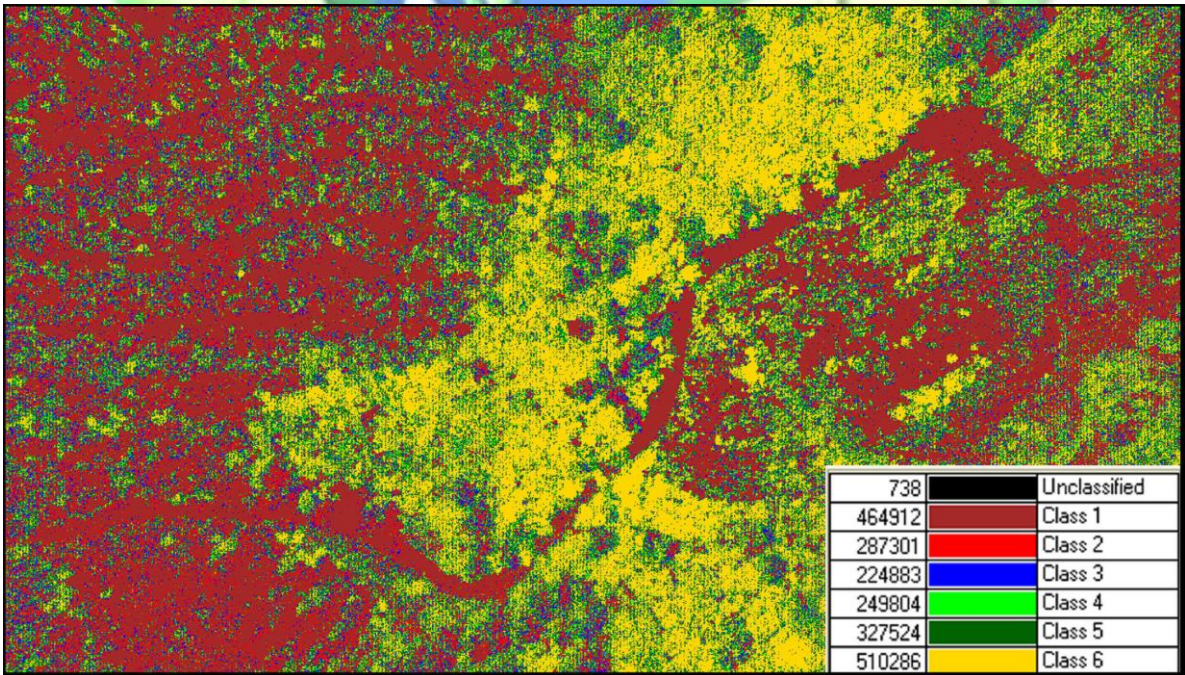


Fig. 3: Application of UAVs in population monitoring of plant species  
(Source: <http://www.resourcemappinggis.com>)



In pollution monitoring both conventional and hyperspectral types of imaging are usable. In case of conventional photographs only the visible pollutants (colours) or the impacts of the pollution (foaming, algae growth, etc.) are detectable (Fig. 4), while using hyperspectral, especially UV/IR remote sensing other pollutants are transformed into “visible” range (e.g. oil spills) and the concentration of the pollutants can be evaluated (Long, 2012). The previously mentioned sensor remote sensing or sampling methods are also widely utilizable technologies in pollution monitoring (Daniel et al., 2009; Pöllänen et al., 2009; Aylor et al., 2011; Rojas et al., 2012; Towler et al. 2012; Watts et al., 2012).



Fig. 4: Application of UAVs in pollution monitoring

## MATERIALS AND METHODS

For our own experimental work three UAVs were purchased: a MULTIPLEX Easy, a STYROMAN Smile and a Tarot 690 S hexacopter (Fig. 5). The most important properties of these UAVs are indicated in Table 1. The UAVs were equipped with electric motors (Turnigy and Blue Ray types) and were controlled by a novel 2.4 GHz RC remote control system (Futaba Inc.).



Fig. 5: The UAVs used in the experiments: MULTIPLEX Easy Star (left), STYROMAN Smile (centre) and TAROT 690S (right)



Table 1: Most important properties of the three UAVs

	<b>MULTIPLEX Easy Star II.</b>	<b>STYROMAN Smile 2800</b>	<b>TAROT 690S Hexacopter</b>
Wingspan (m)	1,4	2,7	1,3
Payload (g)	300	2000	3500
Flying weight (g)	1000	4500 - 5000	>5000
Material	Plastic foam (Elapor)	Plastic foam (EPP)	Carbon composite
Price (only aircraft, EUR, 2012)	300	650	2 000

In case of the fixed wing aircrafts (MULTIPLEX and STYROMAN types), a lightweight HD resolution (720x1280 pixels) camera (FLIP) was used for imaging. The camera was normally positioned in the nose section of the UAV as seen on photos. The angle of down looking was altered between 2 and 10. Alternatively, the camera mount could be fixed on the belly of the plane: using this set up vertical angle photographs were taken.

In case of the hexacopter, a high-resolution (5 megapixel) camera (GOPRO HD Hero 3+) was used for imaging. The angle was alterable without any barriers.

## RESULTS

The flights were carried out in the area of Bakony Mountains, in Hungary. Several aerial photographs were taken on forests, agricultural fields and on ecological important territories, nature conservation areas like wetlands. Some examples are shown in Fig. 6.



Fig. 6: Vertical axis photos of different land uses in Bakony Mountains; a farm landscape (left) and village (right)



One of the investigated wetlands (Csehbánya Lakes) was found rather interesting, since a significant part of the lake (only the northern part) exhibited the signs of eutrophication. The growth of algae is hardly detectable from the shore of the lake (ground view), however, it is clearly visible from the air (Fig. 7). The detected phenomena were photographed again in late summer (August) when the algae population shows seasonal maximum (Fig. 8).



Fig. 7: Eutrophication in Csehbánya Lakes detected from the air



Fig. 8: Eutrophication and siltation in the northern lake of Csehbánya Lakes in late summer

A further, control investigation was carried out in early autumn (middle September) using the high-resolution GoPro camera and the more maneuverable hexacopter (Fig. 9).





Fig. 9: Eutrophication and siltation in the northern lake of Csehbánya Lakes in early autumn

As it can be seen in Figs. 8 and 9, the eutrophication is strong in the northern lake; however, in the southern one it is not significant yet. Since this algae growth has only been detected very recently, further, more sophisticated investigations are necessary to be carried out in different seasons to study the ecology of the lakes and to devise a solution for this problem. It is planned to run these experiments for the next two years.

Another project was the investigation of the usability of UAVs for the surveillance of ragweed (*Ambrosia sp.*). The pollen of ragweed is strongly allergic for human, its reduction is important for our health. Recently, the government has been using helicopters for the surveillance of the larger ragweed populations in order to organize the protection more efficiently. UAVs provide a more cost-effective alternative for this aim since they do not need any airfield, they could be operated for lower costs (which is advantageous, even for small villages possessing smaller budgets), and, due to the electric motors, they are very silent, so the noise level to the inhabitants of the town/village is negligible (contrary conventional helicopters). In this part of our investigations, the detectability of the ragweed was studied. Fig. 10 shows an example of our vertical axis photos.





Fig. 10: Ragweed monitoring using aerial photographing from MULTIPLEX Easy Star.

It was concluded; that the detection of ragweed is possible using these photos, however, the margins of the populations are not clear enough (the contrast is not strong enough). So further orthophotos are needed, even using more sophisticated methods (e.g. hyperspectral imaging), and after the comparison of the conventional and the hyperspectral photos (and, naturally, ground analysis using reference points), it could be investigated that the identification accuracy of the target population is adequate or not (what is the accuracy of the identification of different plant species). Since these preliminary experiments showed promising results, the experiments will be continued in the next two years, as well.

## DISCUSSIONS

By studying the photos our UAVs are found to be very useful for this work; it is one of our future objectives to carry out an air monitoring project for the lakes in Bakony Mountains in collaboration with specialists. It was concluded that all UAVs are suitable for taking orthophotos as well. Especially the hexacopter shown good flexibility in application, since this could be operated from a ca. 20x20 m open square. The noise level was found to be very low in all cases due to the electric motors, making those applicable over nature conservation areas as well.

## CONCLUSIONS

Based on the successful results with this technique using single HD camera the photogrammetric survey will be continued in Csehbánya Lakes and it is planned to extend this work to other wetlands and natural reserve areas as well. In addition to the HD photographing the project is planned to be continued with other high performance cameras and sensors to build up a complete “environmental sensing package” for our unmanned aerial vehicles.

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## **VALIDATION OF METHODS FOR FAAS DETERMINATION OF CU, PB, ZN, CD EXTRACTANT WITH HNO<sub>3</sub> AND EDTA EXTRACTS ULTRASONIC EXTRACTION**

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### **ABSTRACT**

The aim of our paper was to optimize and validate FAAS methods in the determination of heavy metals with extraction reagents for the field of ultrasonic extraction. In the validation of analytical methods enabling the determination of analytes content in extraction reagents of fractionating analysis extracts it is often necessary to specially consider the absence of referential material for some types of samples, which include gravitation dust sediments. The research results have shown the range of application of the selected and evaluated validation characteristics in the described samples for the proof of the relationship between the extraction and the method of element content determination in the extracts.

**Keywords:** *ultrasonic extraction, validation, extraction reagent, EDTA*

### **INTRODUCTION**

The need for communication and understanding in conditions of globalization of chemical measurements and test procedures as well as in the presentation of results is especially significant in the field of analytical chemistry. Several important internationally accepted and valid documents have come in effect recently that either update already existing or introduce new metrological concepts and terms in the field of analytical chemical measurements and in the field of sampling for purpose of chemical analysis. On the one hand of this issue there is the international consensus in the formulation of the terms, on the other there is their proper understanding, translation and application.

Validation may be defined as the procedure the goal of which is to demonstrate and document the quality of an analytical method by determining defined criteria and by measurement of these criteria. Simply said, validation is the verification of the validity of a selected analytical procedure (method). The property that is the object of validation is called the validated property (concentration level of the principal substance, concentration levels of the impurities, physical and chemical parameter). Validation is always applied in the validation of a new method, in the transfer of a validated method (e.g. from the developing to the receiving laboratory, transfer of a published validated method), in the checking of system suitability and in method revalidation, when revalidation conditions have been strictly specified.

### **EXPERIMENT**

Validation of the flame atomic absorption spectroscopy method for the determination of selected hazardous elements in extracts obtained by fractionating analysis with ultrasonic

extraction as the method for fraction isolation was focused on the evaluation of those parameters (limit of detection and quantification, precision/repeatability and robustness) that have a connection between extraction (fractionation) and the method for determining the content of elements in extracts (by quantification).

The following parameters were used for the statistical evaluation of measurement data sets:

$\bar{x}$  : average value of results of 10 repeated measurements,

se: standard deviation of analyses in 10 extracts,

sm: standard deviation of 10 repeated measurements of analyte concentration level in one extract (repeatability),

ss: standard deviation of 10 repeated measurements of analyte concentration level in one blind experiment.

Precision is usually expressed by the standard deviation ( $\sigma$ ,  $s$ ) or relative standard deviation (RSD).

Standard deviation : 
$$\sigma = \sqrt{\frac{\sum_{i=1}^n (x - \mu)^2}{n}} \quad \text{resp.} \quad s = \sqrt{\frac{\sum_{i=1}^n (x - \bar{x})^2}{n - 1}} \quad (1)$$

Relative standard deviation: 
$$RSD / \% = \frac{s}{x} 100 \quad (2)$$

Standard deviation between two measurements: 
$$s = \sqrt{\frac{(a_i - b_i)^2}{2d}} \quad (3)$$

in which:  $x$  denotes the analyte content

$\mu$  denotes the real analyte content

$\bar{x}$  denotes the average analyte content

$n$  denotes the number of repeated measurements

$a, b$  denote analyte content values obtained by two measurements.

For testing outlying results the Grubbs' test was used (T-test), which is applicable for the number of repeated measurements lower than 30. For computing the relevant testing statistics T1 and T2 the following relations were used:

$$T_1 = (\bar{x} - x_1) / S_n \quad (4)$$

$$T_n = (x_n - \bar{x}) / S_n \quad (5)$$

in which

$x_1$ : denotes the smallest value in the measurements set,

$x_n$ : denotes the largest value in the measurements set,

$S_n$ : denotes the standard deviation calculated from the relation:

$$S_n = \sqrt{\frac{\sum_{i=1}^n (x - \bar{x})^2}{n}} \quad (6)$$

Values  $x_1$  and  $x_n$  are considered to be outliers if  $T_1 \geq TTAB$ , and  $T_n \geq TTAB$ , respectively (Grubbs' test evaluation criterion) [1].

### LIMIT OF DETECTION (LOD), LIMIT OF QUANTIFICATION (LOQ)

On basis of relations 1 to 4 we calculated the values of limits of detection and quantification based on the statistical evaluation of 10 repeated blind experiment measurements. The results of 10 repeated measurements of element concentration levels ( $\mu\text{g cm}^{-3}$ ) in one blind experiment together with statistical data required for the calculation are shown in Table 1. Grubbs' test did not confirm outlying results.

**Table 1** Statistical evaluation of blind experiments analyses

Element Extraction reagent Measurement	Cu		Pb		Zn		Cd	
	HNO <sub>3</sub>	EDTA	HNO <sub>3</sub>	EDTA	HNO <sub>3</sub>	EDTA	HNO <sub>3</sub>	EDTA
1	0.012	0.018	0.019	0.00	0.142	0.082	-0.002	-0.009
2	0.020	0.015	0.042	0.06	0.139	0.083	0.009	0.009
3	0.022	0.012	0.101	0.10	0.140	0.081	0.000	0.004
4	0.018	0.015	0.029	0.00	0.134	0.079	0.002	-0.004
5	0.024	0.012	0.058	0.05	0.133	0.082	0.002	0.010
6	0.013	0.007	0.047	0.03	0.136	0.085	0.008	0.003
7	0.025	0.007	0.015	0.00	0.133	0.080	0.004	0.012
8	0.023	0.005	0.040	0.11	0.141	0.081	0.001	0.011
9	0.021	0.009	0.034	0.03	0.138	0.082	0.006	0.005
10	0.019	0.010	0.053	0.05	0.132	0.081	-0.003	0.011
$\bar{x}$ / $\mu\text{g cm}^{-3}$	0.0197	0.011	0.0438	0.043	0.1368	0.0816	0.0027	0.0024
ss	0.0044	0.0042	0.0244	0.0395	0.0037	0.0016	0.0028	0.0041

**Note:** The negative values of Cd concentration levels in the blind experiment corresponded to the negative values of the measured absorbance.

Table 2 presents the calculated values of limits of detection and quantification valid for 2 M HNO<sub>3</sub> extracts analysis, and Table 10 values for 0.05 M EDTA extracts analysis. The said tables also include the slope of the linear part of the calibration dependence which is needed for the calculation of analyte concentration levels at both limits.

**Table 2** Detection and quantification limits of determined elements in 2 M HNO<sub>3</sub> extracts

Element	Limit of Detection LoD		Limit of Quantification LoQ		S
	$x_{LoD}/\mu\text{g cm}^{-3}$	$c_{LoD}/\mu\text{g cm}^{-3}$	$x_{LoD}/\mu\text{g cm}^{-3}$	$c_{LoD}/\mu\text{g cm}^{-3}$	
C	0.0329	0.0132	0.0637	0.0440	0.9998
Pb	0.1192	0.0762	0.2970	0.2540	0.9999
Zn	0.1479	0.0111	0.1738	0.0370	0.9995
Cd	0.0111	0.0085	0.0307	0.0284	0.9865



**Table 3** Detection and quantification limits of determined elements in 0.05 M EDTA extracts

Element	Limit of Detection $LoD$		Limit of Quantification $LoQ$		$S$
	$x_{LoD}/\mu\text{g cm}^{-3}$	$c_{LoD}/\mu\text{g cm}^{-3}$	$x_{LoD}/\mu\text{g cm}^{-3}$	$c_{LoD}/\mu\text{g cm}^{-3}$	
<b>C</b>	0.0236	0.0126	0.0530	0.0420	0.9998
<b>Pb</b>	0.0608	0.0429	0.1609	0.1430	0.9999
<b>Zn</b>	0.0864	0.0048	0.0976	0.0160	0.9995
<b>Cd</b>	0.0147	0.0125	0.0434	0.0416	0.9865

**Note:**  $S$  denotes the slope of the calibration line in units  $\text{A cm}^3 \mu\text{g}^{-1}$ .

The data presented in Tables 2 & 3 enable us to state that the limits of detection for determining Cu, Pb and Zn in EDTA ultrasonic extracts are more suitable than the limits of detection valid for determination in  $\text{HNO}_3$  extracts. On the other hand,  $LoD$  for cadmium is lower for determination in  $\text{HNO}_3$  extracts than in EDTA extracts.

## PRECISION

In the validation of the method itself only one kind of precision was examined, and that is repeatability. Repeatability in the FAAS method was examined by statistical evaluation of 10 repeated measurements of elements content in a single extract and was expressed as percentual value of RSD. The selected extraction reagents were  $2 \text{ mol dm}^{-3} \text{HNO}_3$  and  $0.05 \text{ mol dm}^{-3} \text{EDTA}$ , which enabled measurements at two concentration levels. Before the repeatability calculation itself the Grubbs' test was applied to exclude outlying values from each batch. The results of the statistical evaluation of repeatability for the elements concerned are presented in Tables 4 and 5. The RSD values in the tables correspond to the statistical evaluation of 10 repeated measurements in individual extracts.

**Table 4** Relative standard deviation values obtained by statistical evaluation of 10 measurements of elements in one extract -  $\text{HNO}_3$

Extract No. Element	RSD / %										Average
	1	2	3	4	5	6	7	8	9	10	
<b>Cu</b>	1.17	0.84	1.62	0.76	0.91	1.22	1.03	1.56	1.31	0.58	1.10
<b>Pb</b>	2.58	2.60	1.77	2.41	1.20	2.86	1.39	1.93	2.47	2.00	2.12
<b>Zn</b>	6.44	6.03	4.22	2.38	3.71	3.60	5.33	4.30	3.03	3.23	4.23
<b>Cd</b>	20.48	18.58	16.73	19.75	18.28	12.83	20.39	10.38	16.52	16.89	17.08

**Table 5** Relative standard deviation values obtained by statistical evaluation of 10 measurements of elements in one extract - EDTA

Extract No. Element	RSD / %										Average
	1	2	3	4	5	6	7	8	9	10	
<b>Cu</b>	1.33	0.84	1.22	0.94	0.93	0.69	1.02	1.09	1.17	0.70	0.99
<b>Pb</b>	4.23	2.49	4.57	4.34	3.28	2.76	3.12	2.19	3.36	1.99	3.23
<b>Zn</b>	5.29	4.56	1.69	1.66	1.67	3.33	3.58	4.81	2.73	5.81	3.51
<b>Cd</b>	52.34	31.06	40.11	24.54	22.03	39.78	28.66	25.66	25.35	28.08	31.76

The calculated RSD values allow us to state that the determination of copper, lead and zinc in EDTA and HNO<sub>3</sub> ultrasonic extracts using the FAAS method is burdened with lesser error than the determination of cadmium. High RSD values valid for cadmium determination can also be accounted for by its low content in the extracts, which is below the limit of detection of the analytical method applied. For this reason, the results of cadmium determination in ultrasonic extracts by the said method are not relevant. The analytical method applied (FAAS) is suitable for determining Cu, Pb and Zn in HNO<sub>3</sub> and EDTA ultrasonic extracts. With regard to the high values of relative standard deviations in cadmium determination it has to be established that for direct determination of cadmium in extracts a method with a lower limit of detection has to be applied. For this reason, the ICP-MS method, being one of the available methods with lower level of detection, was used for cadmium determination. Table 6 presents the average concentration levels for the whole statistical set of 10 repeated analyte concentration measurements in 10 extracts, the standard deviations and the relative standard deviations calculated from these parameters.

**Table 6** Statistical evaluation of element measurements in 10 HNO<sub>3</sub> and EDTA extracts using the FAAS method

Element	HNO <sub>3</sub>			EDTA		
	$\bar{x}$	$s_e$	RSD / %	$\bar{x}$	$s_e$	RSD / %
<b>Cu</b>	37.387	0.3742	1.00	17.690	0.6262	3.54
<b>Pb</b>	2.1754	0.0515	2.37	0.8894	0.0348	3.91
<b>Zn</b>	7.478	0.3145	4.22	3.467	0.1719	4.96
<b>Cd</b>	0.0247	0.0027	10.93	0.0154	0.0040	25.97

From Table 6 it follows that the RSD values for Cu, Pb and Zn extraction are lower than 5% and at the same time much lower than the RSD values for Cd extraction. Table 7 shows RSD values for both types of repeatability being screened.

**Table 7** Relative standard deviation values obtained by statistical evaluation of 10 measurements of elements in a single extract (RSD<sub>m</sub>) and analyte measurements in 10 extracts (RSD<sub>e</sub>)

Extraction reagent Element	HNO <sub>3</sub>		EDTA	
	RSD <sub>m</sub>	RSD <sub>e</sub>	RSD <sub>m</sub>	RSD <sub>e</sub>
<b>Cu</b>	1.10	1.00	0.99	3.54
<b>Pb</b>	2.12	2.37	3.23	3.91
<b>Zn</b>	4.23	4.22	3.51	4.96
<b>Cd</b>	17.08	10.93	31.76	25.97

The presented relative standard deviation values suggest that extraction burdens the total fractionation analysis result by a larger error than does the analyte content measurement in HNO<sub>3</sub> and EDTA extracts by the FAAS method itself.

If we compare the obtained results of both types of determination repeatability in ultrasonic extracts with determination repeatability values in conventional extraction extracts [4, 5], then the application of ultrasound resulted in the lowering of RSD values as regards FAAS measurement for Cu and Cd determination in EDTA extracts. The remaining RSD values were

higher in ultrasonic extraction; however, with the exception of cadmium, they were within the acceptability limit (up to 5%). As regards the extraction, RSD values for Cu and Zn determination in HNO<sub>3</sub> ultrasonic extracts and for Pb determination in EDTA extracts were lower in comparison to conventional extraction.

Due to the effect of ultrasound there was a marked reduction of RSD value with regard to Cd extraction into both extraction reagents used, but in spite of this reduction the required acceptability of results in Cd content determination was not achieved in ultrasonic extracts. One of the possibilities of Cd determination in these extracts is the application of a method with a lower limit of detection. We therefore applied the ICP-MS method which meets this condition for HNO<sub>3</sub> extracts analysis. The results of statistical evaluation of measurements of element content using the said method, with regard to the instrument used and the extraction process applied are presented in Table 8. Outlying values were eliminated from the data sets by the Grubbs' test. The results suggest a marked improvement of RSD values not only as regards the determination of element content in extracts by the method employed, but also as regards the RSD values which are contributed to by the extraction. Výsledky poukázali na výrazné vylepšenie RSD hodnôt nie len vzhľadom na stanovenie obsahov v extraktoch použitou metódou ale aj na RSD hodnoty, ktorými prispieva extrakcia. The ICP-MS method is applicable to the determination of all elements in ultrasonic extraction extracts.

**Table 8** RSD<sub>m</sub> a RSD<sub>e</sub> values obtained using ICP-MS for HNO<sub>3</sub> extracts analysis

<i>Extraction reagent Element</i>	<i>HNO<sub>3</sub></i>	
	<i>RSD<sub>m</sub></i>	<i>RSD<sub>e</sub></i>
<b><i>Cu</i></b>	0.96	1.34
<b><i>Pb</i></b>	1.11	1.79
<b><i>Zn</i></b>	0.62	1.81
<b><i>Cd</i></b>	1.69	3.19

## ROBUSTNESS



The measure of the robustness of a method is its capability to preserve its performance even under less stable conditions. In the evaluation of robustness we monitored the impact of changes in ultrasound activity conditions during extraction with 0.05 M EDTA and 2 M HNO<sub>3</sub> on Cu, Pb, Zn and Cd extractability in extracts. The parameters monitored were generator power and extraction time.

In the extraction of all elements into EDTA, generator power affected element extractability values in ultrasonic extracts and reduced the robustness of the method. Extractability values of elements in HNO<sub>3</sub> extracts were not affected by generator power and the method can be considered as being robust in this case. The relative element extractability values related to generator power are shown in Fig. 9.

**Table 9** Effect of generator power on the relative extractability of elements in HNO<sub>3</sub> and EDTA extracts

<i>Power/%</i>	<i>Relative extractability / %</i>					
	<i>HNO<sub>3</sub></i>			<i>EDTA</i>		
	<b><i>Cu</i></b>	<b><i>Pb</i></b>	<b><i>Zn</i></b>	<b><i>Cu</i></b>	<b><i>Pb</i></b>	<b><i>Zn</i></b>
<b>70</b>	96.2	83.8	86.1	45.2	37.2	38.7



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<b>80</b>	95.2	85.7	79.9	58.4	42.7	55.4
<b>90</b>	94.3	81.9	86.1	71.9	66.4	73.1
<b>100</b>	94.5	86.4	85.1	58.1	53.6	65.7

**Table 10** Effect of extraction time on the relative extractability of elements in HNO<sub>3</sub> extracts (immersion depth = 4 cm)

<b>Extraction time / min.</b>	<b>Relative extractability / %</b>		
	<b>Cu</b>	<b>Pb</b>	<b>Zn</b>
<b>2</b>	81.2	73.5	69.9
<b>3</b>	94.3	81.9	71.8
<b>4</b>	97.4	83.8	74.9
<b>5</b>	100.4	96.8	100.5
<b>6</b>	100.5	101.2	101.9

**Table 11** Effect of extraction time on the relative extractability of elements in EDTA extracts (immersion depth = 4 cm)

<b>Extraction time / min.</b>	<b>Relative extractability / %</b>		
	<b>Cu</b>	<b>Pb</b>	<b>Zn</b>
<b>3</b>	71.4	56.3	70.7
<b>5</b>	92.5	83.9	83.4
<b>8</b>	113.8	131.4	120.7

## CONCLUSIONS

Optimization of extraction conditions (generator power, ultrasonic probe immersion depth, and extraction time) in ultrasonic extraction resulted in establishing conditions under which conformity of extractability in conventional and ultrasonic extraction was achieved for all elements being screened. These conditions are summarized in Table 12.

**Table 12** Optimal conditions

<b>Extraction reagent</b>	<b>0.05 M EDTA</b>	<b>2 M HNO<sub>3</sub></b>
<b>Generator power</b>	90 %	90 %
<b>Depth of immersion</b>	4 cm	4 cm
<b>Extraction time</b>	6 minutes	5 minutes

Analyte content in fractionation analysis extracts was at different concentration levels and depended on the type of bonding in dust particles. In many cases their total content in the sample was at trace element level and was even lower in the extracts. For this reason it was not possible to assess all validation characteristics.

When monitoring the effect of the time of extraction with HNO<sub>3</sub> under optimal conditions of ultrasonic activity (probe immersion depth = 4 cm, ultrasound generator power = 90%), the process can be divided into two stages with different robustness. The first stage of up to approx. 3 minutes for Cu and up to 4 minutes for Pb and Zn corresponds with the initial speed of the extraction process, when the influence on element extraction was significant and in this stage the method can be considered as having low robustness. In the second stage, the extraction



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process becomes more stable and therefore from 4th minute for Cu and from 5th minute for Pb and Zn the method can be considered as being sufficiently robust. The relative extractability values observed with the change of extraction time are presented in Table 10.

Contrarily, if we look at the effect of extraction time on element extractability in ultrasonic EDTA extracts under optimal conditions (Table 11), in this case method robustness has not been manifested as the extraction process did not become stable and the effect of ultrasound lead to the extraction of larger element content in relevant forms than with conventional extraction.

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## **PREPARING FUTURE TEACHERS OF ECOLOGY FOR NON-FORMAL EDUCATION IN UNIVERSITIES UKRAINE**

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Importance and actuality of preparation of future teachers-environmentalists is determined by two constituents: (1) foremost, by the structure of preparation of future specialists of ecology? (2) maintenance of professional preparation of future environmentalists? Carrying out purposeful professional preparation of specialists in industry of ecology, foremost, we gave an answer for a question that for today shows by itself ecological education and accordingly preparation of specialists of this industry? We examine modern ecological education as purposeful process and result of ecological studies, education of children and young people, in educational establishments of different types. Under preparation of environmentalists we understand preparation which provides the receipt of qualification “environmentalist”. It follows notices, that the modern, effective structure of preparation of environmentalists must include three constituents: vocational, professional and professional development. Career-oriented training - focused on cognitive and academic work involving children and youth in environmental professions, which is provided through non-formal education, after-school and secondary schools, community organizations. Professional preparation is directed on preparation of future environmentalists, receiving by them ecological qualifications in higher educational establishments. On this stage professional preparation of environmentalists in higher educational establishments of Ukraine is carried out after such educationally qualifying levels: it is a bachelor, specialist, master's degree. Preparation of bachelors for today is carried out by over 100 higher educational establishments. Thus a bachelor gets educational qualification level in direction ecology, guard of environment and balanced use of natural resources, and educational qualification level Specialist and master's Degree is Ecology and guard of environment. It follows notices, that an important value is acquired preparation of future environmentalists, where basic constituents are: (1) professionally oriented humanitarian and socio-economic preparation; (2) naturally scientific, professional preparation; (3) disciplines of independent choice of educational establishment. The important is a collaboration of organs of power, higher, general, out-of-school and vocational -technical educational establishments, public organizations, administrative structures, scientific establishments and enterprises for solving of ecological questions, in particular preparation and employment specialists. For achievement of this purpose was created the international association of environmentalists of universities. Creation of this association supported by the Ukrainian universities and foreign states: Poland, Slovakia. Consequently, completing the appearance, want to mark that, the effective mechanism of upgrading preparation of specialists of environmentalists consists in the collaboration of educational establishments, public institutions and public associations.

**Keywords:** education; non-formal education; future teachers; ecology; environmentalists

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## **ATOMIC PROJECT: HISTORY AND MODERNITY**

Victor Grigorievich BARYAKHTAR, Yaroslav Timurovich BYKOVSKIY

National Pedagogical M.P. Dragomanov University, Kiev, Ukraine

### **Abstract**

The paper presents the analysis of the creation of both military and civilian sections of nuclear energy. A relationship between the fundamental results of the German physicists Hahn and Strassmann (1939), World War II, competition between the United States and the Soviet Union, today's climate change and the problems of energy production and consumption in large quantities. We have presented the ideas of what should be done to reduce the probability of nuclear accidents at nuclear power plants.

**Keywords:** Atomic Project, nuclear energy, energy production, World War II, nuclear power plants

### **1. History of Nuclear Energy**

As you know, creation of the energy systems using new source of energy began from the elaboration of the atomic bomb. In 1934, O. Hahn and F. Strassmann began working over the irradiation of uranium with neutrons. They wanted to receive transuranic elements. The results of experiment showed that this brings to formation of elements with an atomic weight of about half of uranium. To explain the results Hahn presupposed that the core of Uranus "bursts". On December 17, 1938 they had a decisive experience - famous fractionation of radium, barium and mesothorium on the bases of which Hahn came to conclusion that uranium nucleus "bursts" decaying into the lighter elements. In such a way nucleus splitting was opened. The results of experiments done by F. Strassmann and O. Hahn being published on January 6, 1939, served as irrefutable proof of uranium decay into the lighter elements. Calculation of the energies involved in this nuclear reaction confirmed the results of experiment. Having made this discovery, O. Hahn immediately informed L. Meitner, who on February 11, 1939 together with his nephew Frisch published a theoretical explanation of this phenomenon in the British journal "Nature".

Great amount of energy, about 200 MeV, releases as a result of this cleavage reaction. It has become clear for nuclear scientists that uranium is belonged to the energy sources, on the basis of which weapon of enormous destructive power can be created.

It is worth of recalling that this was at the time, when Hitler started the Second World War. Before the War, German physicists had many outstanding results especially in nuclear physics. As a result of Hitler's anti-Semitic policies, many scientists in Germany, Italy and other European countries were forced to immigrate, mainly into the United States.

Physicists understood that creation of a nuclear bomb in Germany is possible due to the highly developed industry and a large number of physicists and nuclear engineers. Scientists who immigrated were well aware of impossibility of any moral principles to stop Hitler from the wider use of nuclear weapons.

For this reason, L. Szilard, E. Wigner and E. Teller asked A. Einstein to write a letter to the U.S. President Roosevelt to initiate a work on nuclear weapons in USA as opposed to the possible development of nuclear weapons in Germany.



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Here is the text of Einstein's letter to Roosevelt:

Albert Einstein  
Old Grove Rd.  
Nassau Point  
Peconic, Long Island

August 2nd, 1939

F.D. Roosevelt,  
President of the United States,  
White House  
Washington, D.C.

Sir:

Some recent work by E.Fermi and L. Szilard, which has been communicated to me in manuscript, leads me to expect that the element uranium may be turned into a new and important source of energy in the immediate future. Certain aspects of the situation which has arisen seem to call for watchfulness and, if necessary, quick action on the part of the Administration. I believe therefore that it is my duty to bring to your attention the following facts and recommendations:

In the course of the last four months it has been made probable - through the work of Joliot in France as well as Fermi and Szilard in America - that it may become possible to set up a nuclear chain reaction in a large mass of uranium, by which vast amounts of power and large quantities of new radium-like elements would be generated. Now it appears almost certain that this could be achieved in the immediate future.

This new phenomenon would also lead to the construction of bombs, and it is conceivable - though much less certain - that extremely powerful bombs of a new type may thus be constructed. A single bomb of this type, carried by boat and exploded in a port, might very well destroy the whole port together with some of the surrounding territory. However, such bombs might very well prove to be too heavy for transportation by air.





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-2-

The United States has only very poor ores of uranium in moderate quantities. There is some good ore in Canada and the former Czechoslovakia, while the most important source of uranium is Belgian Congo.

In view of this situation you may think it desirable to have some permanent contact maintained between the Administration and the group of physicists working on chain reactions in America. One possible way of achieving this might be for you to entrust with this task a person who has your confidence and who could perhaps serve in an unofficial capacity. His task might comprise the following:

a) to approach Government Departments, keep them informed of the further development, and put forward recommendations for Government action, giving particular attention to the problem of securing a supply of uranium ore for the United States;

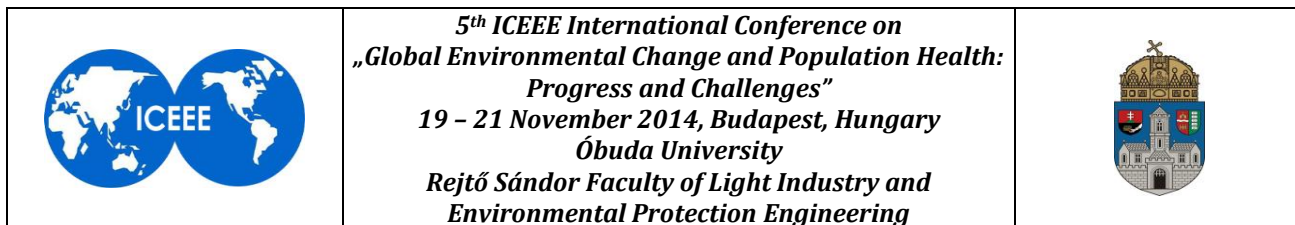
b) to speed up the experimental work, which is at present being carried on within the limits of the budgets of University laboratories, by providing funds, if such funds be required, through his contacts with private persons who are willing to make contributions for this cause, and perhaps also by obtaining the co-operation of industrial laboratories which have the necessary equipment.

I understand that Germany has actually stopped the sale of uranium from the Czechoslovakian mines which she has taken over. That she should have taken such early action might perhaps be understood on the ground that the son of the German Under-Secretary of State, von Weizsäcker, is attached to the Kaiser-Wilhelm-Institut in Berlin where some of the American work on uranium is now being repeated.

Yours very truly,

*A. Einstein*  
(Albert Einstein)

This letter marked a beginning of the Manhattan project. The main task of the Manhattan Project was creation of nuclear weapons. Distinguished American physicist Oppenheimer was appointed as a scientific project manager. Organization of work and secrecy were assigned to the General Groves. The USA built two bombs till 1945. One of them was based on Uranium-235, and the



second one – on Plutonium-239. The nuclear tests that showed exceptional destructive power of a nuclear bomb were conducted in 1945.

The new type of weapon was deployed on August 6 and 9, 1945 when the atomic bombs were dropped on the Japanese cities of Hiroshima and Nagasaki. Total number of dead was about 120,000 people in Hiroshima and from 60 to 70 thousand people in Nagasaki. After these atomic bombings Japan decided to surrender. Thus, the USA having been conducted atomic bombing solved two problems. Firstly, at least 100,000 lives of American soldiers and the same number of Soviet soldiers were saved. Secondly, the military capabilities of the new type of weapon, which only Americans had at that time, were demonstrated to the world (The impact of the A-bomb, Iwanami Shoten, Publisher, Tokyo, 1985 year, 19 and 48 pages).

Creation of the nuclear weapons by the American physicists stimulated the real danger, if such weapons to be created by the Nazi Germany. One of the problems with the development of nuclear weapons, which naturally arise, was ethical problem of its application. This problem was widely discussed in the USA and the USSR. After Hiroshima and Nagasaki bombing, Oppenheimer, Einstein, Joliot-Curie as well as a number of prominent scientist and physicists expressed their negative attitude to the use of the bomb. In the USSR, a large campaign against the use of atomic weapons was organized in the post-war years.

However, the work on creation of the atomic weapons was launched in the USSR since 1942. The first atomic bomb was tested in 1949. Incentive of the USSR scientists and engineers to create nuclear weapons was caused by the desire to deprive the USA their ownership monopoly on this kind of weapons and thus prevent a Third World War.

After the creation of the atomic bomb, the Soviet Union started an intensive work over the hydrogen bomb creation. It is worth of recalling that the first thermonuclear charge was blown in the USA on November 1, 1952. The device tested in the U.S. in 1952, was not actually "bomb" and was a laboratory sample size of a 3-story house filled with liquid deuterium, made in the form of special construction. Soviet scientists have developed exactly bomb - complete device suitable for practical use. Creation of the Soviet hydrogen bomb was based on Ginzburg's idea of deuterium and tritium "cooking" by means of initial explosion of the atomic bomb was presented in 1949. At the same time in 1949 the Soviet army soldier O. Lavrentiev, regardless V. Ginzburg, expressed the same idea. He had only schooling. A letter containing Lavrentiev's offer was sent to Stalin by use of secret mail. Most apparently that the letter from O. Lavrentiev was lost, so as that year Stalin celebrated his 70 anniversary and thousands of letters with congratulations came at his name.

Namely, a "layered" structure was offered for hydrogen bomb. The uranium or plutonium nuclear bomb was placed in the centre with a layer of lithium deuteride around, followed by a layer of uranium-238. Explosion of the atomic bomb caused a large neutron flux. This neutron flux induced in irradiated lithium deuteride producing of tritium. Shell of uranium-238 restrained "scattering" of the whole construction. Sakharov A. carried supervision over the works on the hydrogen bomb construction. This hydrogen bomb was called "Puffs". The first Soviet transportable bomb was blown up in 1953. After its explosion American physicists discovered lithium in a trace of hydrogen bomb and "borrowed" the idea to create their transportable bomb.

Calculation of the parameters of the hydrogen bomb was made by several groups of scientists, in particular by the group of L. Landau.





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There is a photo of the first Soviet thermonuclear bomb RDS-1 that was tested at the Semipalatinsk nuclear test site at 7.30 of local time on August 12, 1953.

### ***Photo of the bomb testing***

The testing of the "Tsar-bomb", created in the Soviet Union, was held on October 30, 1961 in the New Earth. The volume of the bomb was 58 megatons. It was brought to the testing place by the bomber aircraft Tu-95. With the explosion 97% of the energy evolved as a result of the reaction fusion (the maximum value of all tested devices). It was the most powerful explosive device ever developed and tested in the world.

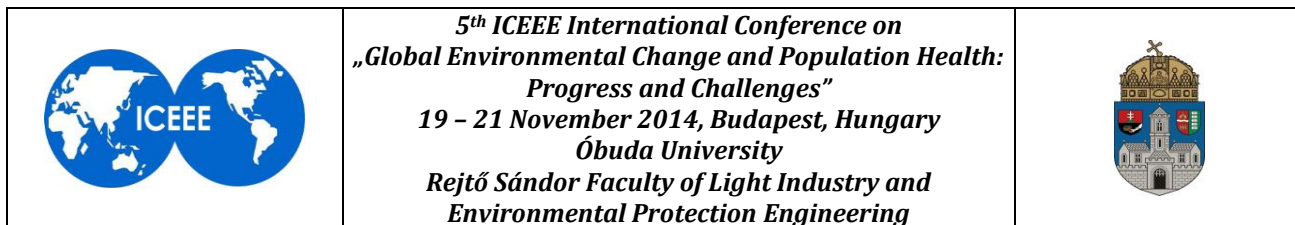
The creation of such weapons in the USSR and the USA demonstrated meaninglessness of the further research over the nuclear bombs and the need to prohibit the use of nuclear weapons. In other words, the creation of "Tsar-bomb" was one of the arguments to finish the arms race.

During the World War II, German scientists and engineers were not able to build the atomic bomb. Reasons are connected with the fact that neither project manager dealing with the creation of the atomic bomb W. Heisenberg, nor some other German physicists, could not understand how to get the necessary quantity of uranium-235 or plutonium-239. Later atomic weapon was created in Great Britain, France and China.

### **The use of atomic energy for peaceful purposes**

Nowadays the atomic energy (AE) has become an important source of electric energy. Today in 31 countries of the world at 194 nuclear power plants (NPPs) nearly 440 nuclear power units of different capacities are operational. Their total electricity capacity is 234,600 MW. AE share in the total world electricity production had maximum 17% in 1993 and decreased to 10% in 2012. In comparison with conventional energy sources, nuclear power plants have advantages such as: they are powerful point sources of energy, which is very important for large consumers such as steel, chemical plants, subways etc. Second positive advantage is dealing with the fact that NPP does not use oxygen to produce electricity. It is worth of recalling that oxygen was not used by TEC working on coal, oil or gas. To consume 1 kg of coal, oil or gas, it is necessary, accordingly, 2.7 kg, 4 kg, and 3.4 kg of oxygen. The next advantages of nuclear power plants is lower cost of kilowatt-hour of energy produced when compared with thermal power plants using coal, oil or gas. Cost of energy, which is produced by the wind power plants or stations using solar power semiconductors, is much higher. Specific details about Ukraine are presented. Thus, tariff for electricity generated by nuclear power plants is 22.2 kopecks. per kilowatt-hour; TEC for this indicator is 68 kopecks. per kilowatt-hour; for wind farms - 124 kopecks. per kilowatt-hour; for solar power - 511 kopecks. per kilowatt-hour. Price for HPP almost coincides with the value of kilowatt-hours at the plant and equals up to 20.6 kopecks per kilowatt-hour, but there are no financial recourses to build up the HPP in Ukraine.





Let us consider specifics of the nuclear power production in other states. The greatest number of nuclear power plants and nuclear units are located in the U.S., there are 66 nuclear power plants where 103 nuclear power units are operating and produce nearly 20% of all electricity in the country.

In France, 19 nuclear power plants operate 58 units producing 74% of the electricity. Since the power of the modern nuclear power plants is unregulated, the total amount of electricity generated should be complemented by thermal electro stations capacity of which can be adjusted that is important for work at peak times. Consequently, a part of regulated powers in the production of the electricity is equal to 26 %.

In Canada, 19 reactors CANDU are in operation. A heavy water is used in these reactors as neutrons' moderator. This is the only country, which operate heavy water reactors.

### **The danger of the nuclear energy**

For the time since there are nuclear power plants, nuclear reactors, under-water boats, ships, research institutes, a huge number of accidents (several hundred) had happened. Analysis of the failures shows that the majority of these cases, about 70%, related to the human factor, about 20% belong to technical problems, and about 10% connected with a natural coincidence.

There are three largest nuclear accidents - it's the Three Mile Island in the United States, the Chernobyl disaster in Ukraine and the disaster at Fukushima in Japan. Analysis of these accidents as well as other smaller ones shows that accident from disaster are separated by short period of time, after which the process becomes irreversible.

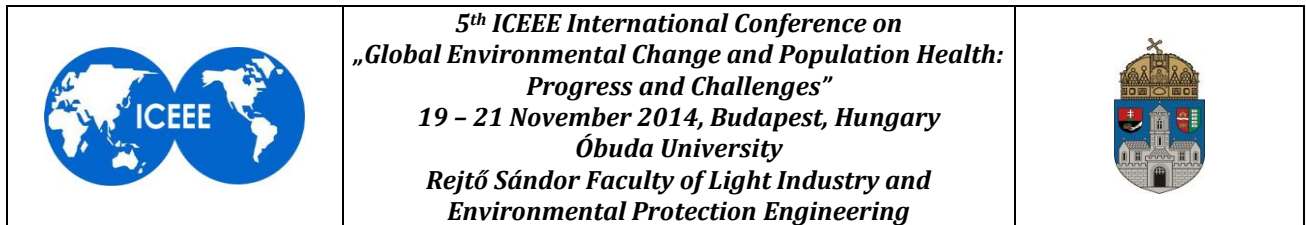
Accidents are called events after which the functions of the stations can be restored. Catastrophic events are called events after which the functions of the stations can't be restored. Besides the expenses for liquidation of consequences of the accident raise doubts as for the economic efficiency of the nuclear power use.

It is worth of mentioning that the accident at the Three Mile Island brought to the fact that the USA terminated construction of the new nuclear power stations. This is due to the fact that the costs on elimination of the consequences of the accident surpass all the economic benefits of the nuclear station.

After the Chernobyl disaster construction of the nuclear power stations was terminated all around the world. Expenses for the liquidations of the consequences of this accident amounted to approximately 12 billion of U.S. dollars. These costs are much higher than the income of all Ukrainian nuclear power stations.

More than 10 years after the accident, the rate of construction of the nuclear power plants in the world has been recovered. Impetus for NPPs' construction could be explained by the economic and physical benefits of their regular work. It is worth of reminding one of the problems that may be solved due to the NPPs. This problem deals with the climate change and greenhouse gas production by all thermal energy sources.

As it was already mentioned, a safe operation of the NPPs is primarily associated with the human factor, as well as the technical reliability of the power units. After the Chernobyl disaster, the labour community of the NPPs has recognized a need to prepare and stimulate the highly skilled personnel. This trend has been called "a culture of nuclear safety." Concept of nuclear safety culture is a very broad one and includes all elements as education of the workers of nuclear industry so as their high moral character. Nuclear safety culture is also important for the scientists to research nuclear reactors, soldiers and officers employed in the service of nuclear reactors in the army and navy. According to the statistics of nuclear accidents, a major role in reducing the number of accidents at the military facilities plays army discipline.



In our opinion the nuclear safety culture should be combined with a system of financial incentives and services. The team of specialists in nuclear energy, economists and psychologists should develop such system.

Unfortunately, until now in the world there are no programs specifically studying experience of liquidation of consequences of the NPPs accidents. Par example, the management of the Fukushima nuclear power plant did not know the experiences how consequences of the accidents at Three Mile Island and Chernobyl had been liquidated. They did not understand the danger of delay in cooling Fukushima nuclear reactors due to decay of radionuclides in them.

There is a need of in-depth examination of the nuclear accidents experiences. Special training programs for disaster recovery and regular trainings of personnel, at least once per a year, should be organised at each NPPs. It is necessary to inform public about the status of each nuclear unit in the country.

The accident at the Fukushima nuclear plant in Japan, provoked by the natural disasters, probability of which was not adequately evaluated the staff, confirmed that complacency and arrogance are incompatible with such source of danger as a nuclear power plant.

The accident at the Chernobyl nuclear power plant, the largest man-made accidents, was not the only fatal accident or a single simple handling error. Accidents at the nuclear power plants in the USA, Canada, England, France, Japan and the USSR, which could and should serve as a lesson and warn people against simplified approach to this complex problem of our time, had happened before the accident at the Chernobyl nuclear power plant.

### **Conclusions:**

- 1) The 21st century shows that science provides for new technical opportunities to reach the progress and improve human life. In particular, apart from nuclear energy, electronics, materials science, nanotechnology and information led to the qualitative change in the life of mankind.
- 2) New technical possibilities lead to the emergence of the new threats to human existence. The nuclear power plants vividly illustrate this.
- 3) Modern society uses and, without no doubt, will use the nuclear energy in the future - an efficient way to improve the quality of life.
- 4) Technical dangers of the nuclear energy raise requirements to the training and professional knowledge of the workers of the nuclear power plants and their skills to apply their knowledge quickly and in a proper way.
- 5) The moral as well as serious material stimulus should be implemented to ensure satisfaction of spiritual and material needs not only of the NPP's employees, but also their family members (at least two generations: fathers - children).
- 6) An important conclusion is that the large-scale accident may happen at any plant. Therefore, technical measures of emergency response and protection of the population from its effects should be developed at each NPPs. It is necessary to introduce these plans first to the NPP's staff and the population who lives in 30-km zone around the plant.
- 7) Regularly trainings on priority measures to be taken aftermath of the accident and protection of the population should be conducted. In particular, it is necessary to



disseminate information on protection activities provided by NPPs among the population, as well as to disseminate information about the general state of the NPPs and the level of radiation background.

The key persons of American nuclear project:



J. Oppenheimer      L. Szilard      E. Teller      E. Fermi      General Groves

Julius Robert Oppenheimer (April 22, 1904 - February 18, 1967) - American theoretical physicist. Commonly known as Scientific Leader of the Manhattan Project, in which during the Second World War, developed the first samples of nuclear weapons because of this J. Oppenheimer is often called "the father of the atomic bomb."

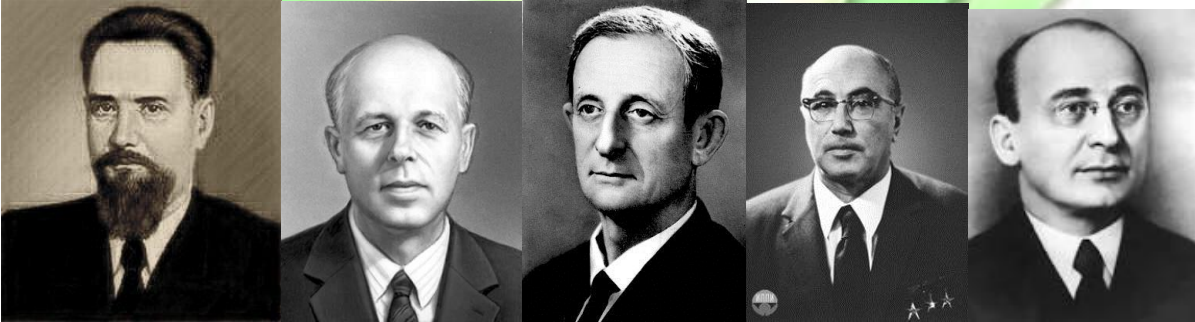
Leo Szilard (11 February 1898 - 30 May 1964) - together with Enrico Fermi has identified a critical mass of U-235 and participated in the creation of the first nuclear reactor.

Edward Teller (January 15, 1908 - September 9, 2003) - Hungarian and American physicist, head of the works on creation of the American hydrogen bomb (Father of the American hydrogen bomb).

Enrico Fermi (29 September 1901 - 28 November 1954) - a prominent Italian and American physicist. He created the world's first uranium - graphite nuclear reactor.

Leslie Richard Groves (August 17, 1896 - July 13, 1970) - Lieutenant-General of the U.S. Army in 1942-1947 military program manager to develop nuclear weapons (the Manhattan Project).



The key persons of the Soviet nuclear project:



I. Kurchatov      A. Sakharov      Y. Khariton      Y. Zeldovich      L. Beria

Igor Kurchatov (January 8, 1903 - February 7, 1960) – a "father" of the soviet atomic bomb. Founder and the first director of the Institute of Atomic Energy from 1943 to 1960, chief supervisor of the atomic problem in the USSR, one of the founders of the use of nuclear energy for peaceful purposes.



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Andrei Sakharov (May 21, 1921 - December 14, 1989) - supervisor of the works on creation of the Soviet hydrogen bomb. The father of the Soviet hydrogen bomb.

Yuli Khariton (February 14, 1904 -18 December 1996) – since 1946 the chief designer of soviet atom bomb and supervisor of the KB-11 (Arzamas-16) in Sarov. The best physics of the USSR were involved into the work on a nuclear weapons program under his leadership, for example N. Bogolyubov and his students.

Yakov Zeldovich (March 8, 1914 - December 2, 1987) - one of the creators of the atomic bomb and H-bomb in the USSR.

Lawrence P. Beria (March 17, 1899 - December 23, 1953) - head of Strategic Intelligence of the USSR, from December 3, 1944 he was assigned to "monitor the development of the uranium", i.e. he became the head of the Soviet atomic project.



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## **INVESTIGATION OF CHIRAL SELECTIVITY OF VARIOUS DERIVATIVES OF ENVIRONMENTALLY IMPORTANT MANDELLIC ACID**

Zoltán JUVANCZ, Dóra Jecsak MAKLÁRI



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Engineering, Environmental Protection Engineering Institute, Budapest, Hungary

The chiral selectivity structure relationships were measured to find the optimal derivative of mandala acid. Systematic gas chromatographic and capillary electrophoretic methods were used in the measurements. Our aim was to find a fast and robust chiral selective method, which can be applied for environmental samples.

The members of enantiomer compounds can show radically different biological effects. On many occasions only one enantiomer of agrochemicals show useful properties, but the other isomer has no effect (dichorprop, delthamethrin) or unwanted side effects may occur (bervomicine). A certain amount of enantiomerically pure agrochemicals can reach the same effect as using double amount racemic mixture of the very same agent. In this way the use of enantiomerically pure products reduce the burden to the environment. No universal chiral separation agent, chiral selector exists. A successful chiral selective separation requires tailor made interactions between the selector and selectand. Not only the chemical characters of interaction groups need be fit together, but their steric arrangements have to be same (three interaction points model). In several occasions, trial and error method is used to find the appropriate selectand selector pairs. Our research aims at to establish a better and faster method than trial and error. Our systematic study searches the interrelationship between the structure of the analyte and of the selector. The gained knowledge helps to find the appropriate selector selectand combinations for other enantiomer pairs too. We choose the mandelic acid as model enantiomer pair, because several derivatives can be synthesized from them. The mandelic acid its derivatives are broadly used as pharmaceutical and cosmetic products therefore it is potential environmental pollutant. We used  $\beta$ -cyclodextrin derivatives as selectors, because they have broad selectivity spectra. Very efficient chromatographic techniques (gas chromatography and capillary electrophoresis) were applied, to gain separations even for minute interaction energy differences of enantiomer pairs. The emphasized role of the H-bond interactions was established. More than 10 different derivatives have been tested. The measurements were made at least three different temperatures. The establishment of a  $1/T - \ln \alpha$  relationship helps to compare the energetic relationships measured in different temperatures. The emphasized role of the H-bond interactions was established.

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## **CHIRAL SEPARATION OF ENVIRONMENTALLY IMPORTANT PYRETHROID ACIDS**

Zoltán JUVANCZ, Zita LACZKÓ, András SZEDER

Óbuda University Rejtő Sándor Faculty of Light Industry and Environmental Protection  
Engineering, Environmental Protection Engineering Institute, Budapest, Hungary



Our aim was to establish structure selectivity relationships for pyrethroid acids on cyclodextrin based chiral selectors. Our results can be applied for environmental samples. The members of enantiomer compounds can show radically different biological effects. On many occasions only one enantiomer of agrochemicals show useful properties, but the other isomer has no effect (dichorprop, delthametrin) or unwanted side effects may occur (bervomicine). A certain amount of enantiomerically pure agrochemicals can reach the same effect as using double amount racemic mixture of the very same agent. In this way the use of enantiomerically pure products reduce the burden to the environment. The pyrethroid insecticide products are good examples for the different effects of enantiomers. This is the reason why recently the delthamethrin have been commercialized in an enantiomerically pure form.

The quality control of enantiomerically pure products and environmental samples requires fast, effective and robust analytical methods. No universal chiral separation agent, chiral selector exists. A successful chiral selective separation requires tailor made interactions between the selector and selectand. Not only the chemical characters of interaction groups need be fit together, but their steric arrangements have to be same (three interaction points model). In several occasions, trial and error method is used to find the appropriate selectand selector pairs. The  $\beta$ -cyclodextrin derivatives were used as selectors, because they have broad selectivity spectra. Very efficient chromatographic techniques (gas chromatography and capillary electrophoresis) were applied, to gain separations if members of enantiomer pairs have only minute interaction energy differences. The temperature effect of analysis temperature was also measured. The types and measure of chiral recognition forces can conclude from values of selectivity in function of temperature ( $1/T - \ln \alpha$ ).

It was established that the underivatized acids show higher selectivity than their methyl ester derivatives under gas chromatographic conditions. The ionized forms of pyrethroid acids have much higher selectivity than their protonated forms under capillary electrophoretic conditions. The steep  $1/T - \ln \alpha$  curve also suggests that the H-bond interaction is a key interaction of chiral recognition. The systematic study was made to establish main tendencies of the selector selectand interaction. Using these results a better and faster method development was established than the trial and error method.

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## **DEVELOPMENT OF A CHIRAL SELECTIVE ELECTROPHORETIC METHOD FOR ANALYSIS OF POPE-PEACHI DIASTEREOMERIC SALT RESOLUTION PRODUCTS**

Zoltán JUVANCZ<sup>1</sup>, Erzsebet VARGA<sup>2</sup>, Edit SZEKELY<sup>3</sup>, Rita BODANE-KENDROVICS<sup>1</sup>, Tamas SOHAJDA<sup>2</sup>, György BANSAGHI<sup>3</sup>, Béla SIMANDI<sup>3</sup>

<sup>1</sup>Obuda University Rejto Sandor Faculty of Light Industry and Environmental Protection Engineering, Environmental Protection Engineering Institute, Budapest, Hungary

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Obtaining enantiomeric pure compounds is possible via diastereomeric salt formation, even in supercritical carbon dioxide solution. It is important to evaluate the enantiomer excesses and the ratio of anions and cations in extracts and raffinates obtained using Pope-Peachy's method. The electro osmotic flow frequently enables the analysis of both anions and cations at the cathodic end in capillary electrophoresis from a single experiment. The simultaneous determination of anionic and cationic content of diastereomeric mixtures has not been reported using chiral electrophoretic separations so far. In this study, simultaneous determinations were achieved for the enantiomeric ratio and anion and cation content of the products of Pope-Peachy's resolutions in a single capillary electrophoretic run. The crucial point of the method is that both basic and acidic partners of the resolution mixtures must be in ionized form during the electrophoresis. This way the bases migrate before the EOF and the acids migrate after the EOF applying positive voltage. An effective method was developed for determination products of diastereomeric salt resolutions in supercritical media. The anion was (*R*)-1-phenylethylamine and cation various mixtures of *cis*-permethrinic acid enantiomers. Optimization study was done to find the optimal values of pH and concentration of permethylated- $\beta$ -cyclodextrin chiral selector. The method was also fully validated for these compounds.

The suitability of the developed method was demonstrated on various separation conditions. The composition of mixtures of (*R*)-1-phenylethylamine and isomers of *cis*-chrysanthemic acid were determined with methylated-(6)-monoamino-deoxy-(6)- $\beta$ -cyclodextrin chiral selector. The product salt of resolution of (*R*)-1-phenylethylamine and isomers of ibuprofen were successfully analyzed applying permethylated- $\beta$ -cyclodextrin as chiral selector. The method is also good to determine the composition of mixtures of (*R*)-2-(*N*-benzilamino)-butanol and isomers of chrysanthemic acid.

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## **CERTAIN METHODOLOGICAL APPROACHES TO THE ASSESSMENT OF CONTAMINATION OF AGRICULTURAL LANDSCAPES' SOIL**

Yurij DMYTRUK, Ol'ga STUZUK, Vasył' CHERLINKA

Chernivtsy national university, Chernivtsy, Ukraine

### **ABSTRACT**

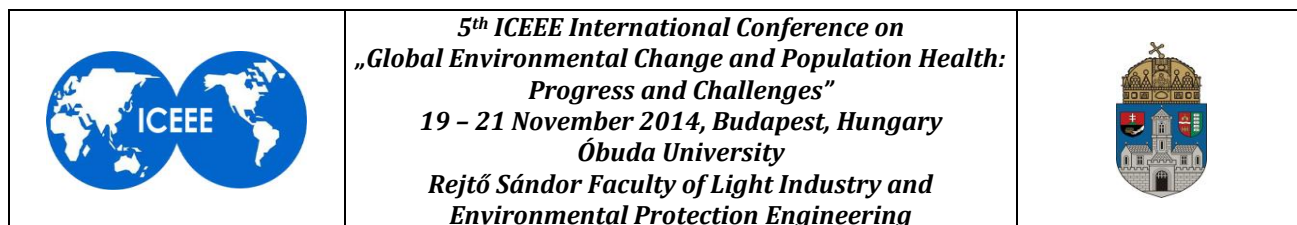
One of the main challenges for qualitative state of agricultural landscapes' soils are contamination, including pollution by heavy metals. The methodology of its evaluation on the regional level is remaining problematical. Therefore the aim of our research is to establish a approaches for the assessment of contamination on the basis of cartographic simulation of integrated indicators (in relation to heavy metal content). To analyze the spatial variability of heavy metals and integrated indicators were used SRTM data and analytical capabilities of GRASS GIS and R-statistic. In particular for the construction of spatial data models used interpolation based on inverse distance weighting, regularized spline with tension and some variants of Kriging. Geostatistical parameters were estimated in R-statistic packages geoR and gstat. Three-dimensional visualization of the obtained results was carried out in module NViz geographic information system GRASS. If the contamination is the multielement advisable to apply integrated indicators. Among them are two principal: soil saturation index of total forms of heavy metals and soil saturation index of mobile forms of heavy metals. The first one shows the general state of pollution and the other shows the possible risks of intake of heavy metals from soil to plants. Developed by us a gradation of indexes allows to distinguishing areas of background content of heavy metals and anomalous content (accumulation or scattering of heavy metals). Strictly for the last we need to choose the points of continuous monitoring in which we will hold sampling of soils and plants for a more detailed control. ).

We have created yet cartographic models which show the spatial distribution of heavy metals. However, the need to organize of monitoring is providing and a time reflection of all necessary parameters which may be created by sequential cartographic model. The visual comparison of such models immediately will allow detecting critical areas in relation to contamination. Hence, this methodology lets us to optimize the assessment of the soil quality and bringing us closer to direct division of the territory. The process of assessment based on the proposed algorithm is becoming significantly more efficient, and its verification provided by opportunities of mathematical processing of models. ).

**Keywords:** *assessment, soil quality, contamination, heavy metals, cartographic model*

### **INTRODUCTION**

A major problem for the quality for soils of agricultural landscapes are pollution, including pollution by heavy metals (HM). The methodology for its evaluation at the regional level remains problematic. The purpose of our research is to create approaches to the assessment of soils contamination of agricultural landscapes based on cartographic modeling of integrated



indicators (content HM). Our vision for assessing the quality of soil for possible contamination is a real comparative analysis of heavy metals in the soils of a particular agricultural landscapes with background content of these same metals. Background content can be found in two ways: 1) geochemical (empirical, based on an analysis of selected soil samples in areas of unaltered by anthropogenic activity); 2) the statistical (Matschullat et al., 2000; Roca et al., 2012; Tobías et al., 1997; Yay et al., 2008). For avoidance of doubt associated with different definitions of interpretation "background" the values of background content appropriate to use specifically-horologic, it means on local or most – on regional levels (Gałaszka, 2007; Dmytruk, 2012). Therefore, the best way to assess the state of soils contamination - with the use of cartographic modeling.

## **MATERIALS AND METHODS**

Data of remote sensing in the form of digital elevation models of different coverage widely used in research (Grohmann, 2006; Gorokhovich, Y., & Voustianiouk, 2006). One of the most common is a global digital elevation model Shuttle Radar Topography Mission (hereinafter - DEM SRTM) (Rodriguez et al., 2005; Reuter et al., 2007; Jarvis et al., 2008). For our study area it is represented in the resolution of 3 arcsec, which is quite suitable for the purposes of medium-mapping. However, due to existing uncertainties associated with the data acquisition technology, currently there are no distortions associated with the heterogeneity of the earth's surface (vegetation, buildings), high-frequency noise (fluctuation of the reflected signal) and a significant number of false basins: the cumulative effect distorts the picture of the terrain . Therefore, we conducted a pre-processing SRTM to remove gross errors and artifacts (Jarvis et al., 2008; Robinson et al., 2014). The area of research and modeling of the gross of heavy metals in soils located in western Ukraine, and is confined to the territory between the rivers Siret, Prut and Dniester (Fig. 1). This area is covered with pieces of data SRTM V4.1 42\_03 (C band), received by us from the directory CGIAR-CSI. Data imported to GRASS GIS (GRASS) using libraries GDAL/OGR (GDAL). From this fragment are allocated their own area of research, which is characterized by the following parameters: datum - wgs84 (EPSG: 4326); north: 48°40'32.5956"N, south: 47°56'11.066672"N; west: 25°06'31.32"E, east: 26°41'52.312727"E; rows - 887, cols - 1907. Since the SRTM data in the geographic coordinate system is not quite suitable for the analysis, we transferred them to the coordinate system designed by Pulkovo 1942/Gauss-Kruger zone 5 (EPSG: 28405) using GIS GRASS m.proj module and conversion options under (PROJ.4): + proj = tmerc + lat\_0 = 0 + lon\_0 = 27 + k = 1 + x\_0 = 5.5 million + y\_0 = 0 + ellps = krass + towgs84 = 23.92, -141.27, -80.9, -0,0.35,0.82, -0.12 + units = m + no\_defs.





Fig. 1. The sketch map of research area

Using the proposed (Grohmann, 2006) approaches, including interpolation based on RST-splines (Mitášová & Mitáš, 1993), we have eliminated most possible artifacts inherent in this SRTM, allowing us to optimize the usefulness of cartographic basis for further analysis (Fig. 2).

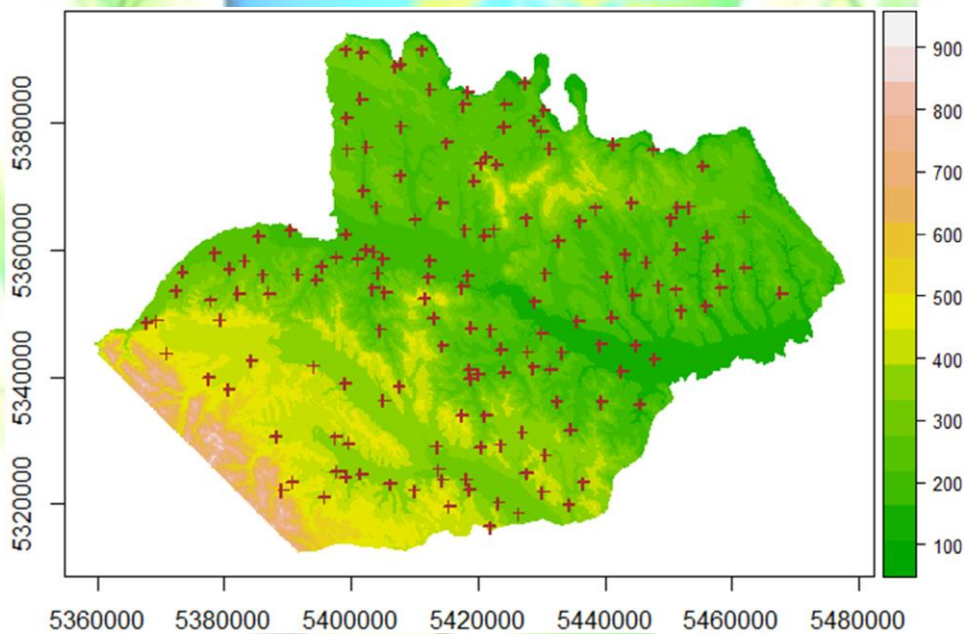


Fig. 2. SRTM data with superimposed surveys points

If contamination is advisable to apply complex multiple-indicators, including soil saturation index of gross forms of heavy metals that shows the general state of pollution regardless of the number of chemical elements that are investigated. Pre-designed and in details described the gradation of indices (Dmytruk, 2013) allows to distinguish between regions of the background of heavy metals and their abnormal content, it means accumulation or dispersion (Table. 1).

Table 1 Scale for evaluation of Saturation index (SI)

Value	SI
<0,70	Intense scattering

0,70-0,90	Scattering
0,90-1,10	Background
1,10-1,30	Accumulation
>1.30	Strong accumulation

## RESULTS

To construct the mapping patterns of spatial distribution of heavy metals, we used a set of data that are located to 156 points of observations in which there is information about the contents of the gross Pb, Cd, Cu, Ni, Cr, Zn. Based on gross heavy metal content was calculated integrated indicator of soils saturation with heavy metals (SI). Statistical characteristics of quantitative data are given in Table. 2 and a histogram of their distribution in Fig. 3.

Table 2 Statistical analysis of the gross content of investigated elements (n=156)

Investigated elements	<i>Pb</i>	<i>Cd</i>	<i>Cu</i>	<i>Ni</i>	<i>Cr</i>	<i>Zn</i>	<i>SI</i>
Mean	13,6	0,47	14,0	18,9	11,0	40,9	1,00
Standard error	0,29	0,01	0,40	0,37	0,20	0,94	0,01
Median	13,1	0,43	13,1	19,1	10,6	39,7	0,97
Moda	13,6	0,35	11,8	16,8	10,0	33,6	0,89
Standart deviation	3,61	0,18	4,93	4,66	2,44	11,7	0,17
Variance	13,0	0,03	24,3	21,7	5,93	136,3	0,03
Kurtosis	8,21	1,22	12,9	0,51	-0,53	0,63	0,08
Skewness	2,01	1,15	2,68	0,36	0,24	0,65	0,42
Iinterval	27,4	0,92	41,0	26,7	12,2	66,8	0,89
Minimum	7,60	0,20	5,47	8,20	4,95	13,2	0,56
Maximum	35,0	1,12	46,5	34,9	17,1	80,0	1,45

To construct models of the spatial distribution of heavy metals and saturation indices used 2 approaches: geostatistical and interpolational. Thus applied incorporated in Grass GIS tools like IDW and RST-spline interpolation (Mitášová & Mitáš, 1993; Neteler, Mitasova, 2008) and a wide range of geostatistical tools R-statistic (The R Project; Pebesma & Wesseling, 1998; Ribeiro & Diggle, 2001; Bivand, 2005). Although some authors have shown that the splines are formally equivalent to the universal kriging (Wahba, 1990; Cressie, 1993), the implementation model based on these approaches in some cases makes it very differentiated results. Since kriging assumes that the spatial distribution of geographical phenomenon can be modeled by implementing a random function, while the statistical methods used for data analysis and prediction. However, as indicated by (Journel, 1996), this process involves a number of subjective decisions, for example, to assess stationarity, choice of functions for Theoretical variography etc. In contrast to geostatistical approach splines are based on flexible physical model using the elastic properties of the interpolation function. However, most natural surfaces are not stochastic and the more resilient because they are the result of a number of natural processes. Therefore, each designed and proposed model has the following scope.

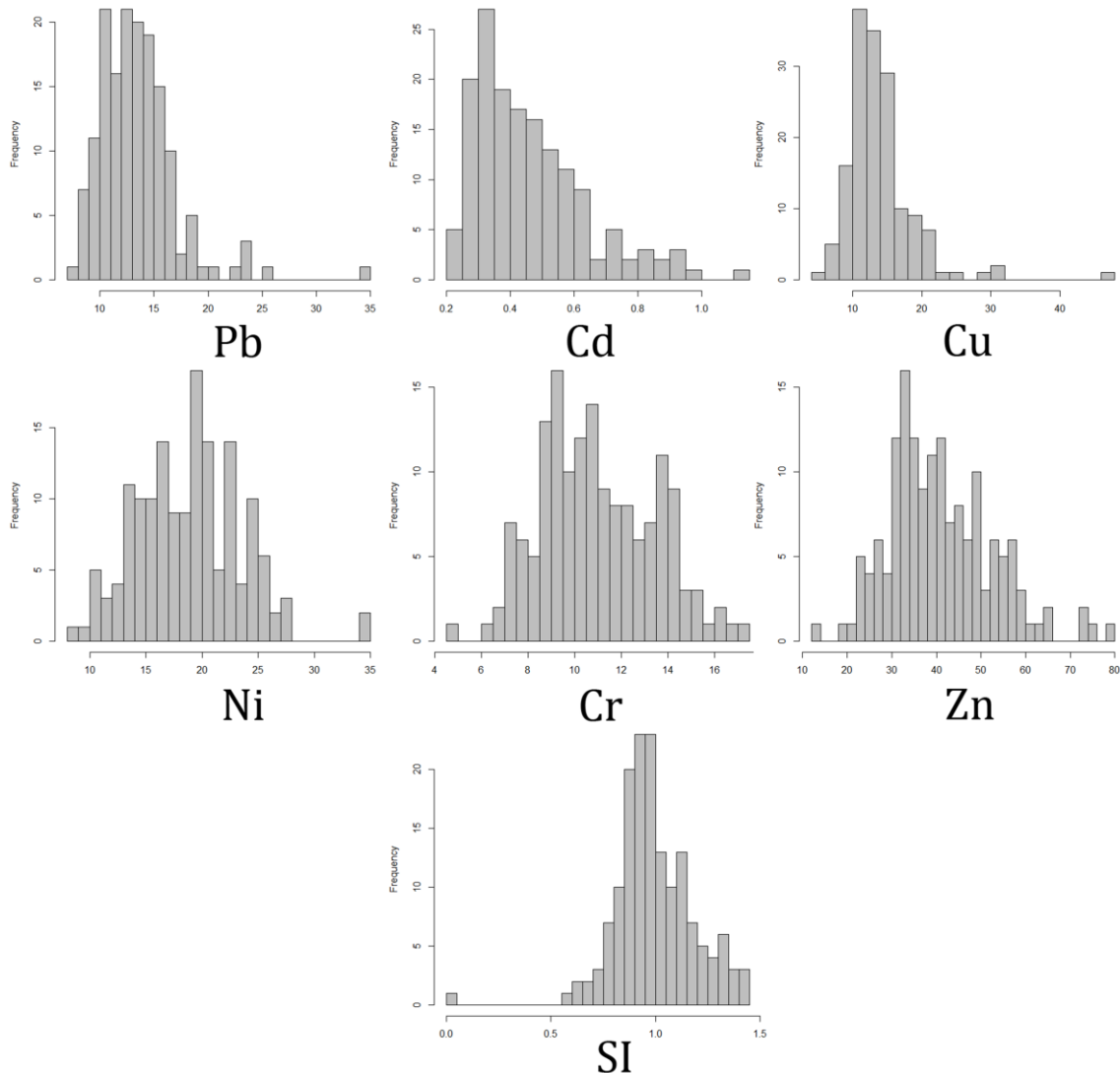


Fig. 3. Histograms of the gross distribution of heavy metals

## DISCUSSION

Analyze produced by our model of spatial spread index saturation gross forms of heavy metals. They are built based on interpolation inverse distance weighting (IDW), using regularized spline with tension (RST) and universal kriging. Using GRASS shell environment in the R-statistic was investigated conditions of construct of kringing-models based library gstat (Pebesma & Wesseling, 1998) and geoR (Ribeiro & Diggle, 2001). After a series of studies of trends in saturation index found that the best match based on the assessment variogram gives the exponential model. To minimize the error of prediction are investigated: the influence of spatial characteristics of the second derivatives and function of height. It was established that for the latter case, the square error is smallest. To verify this model was built in graph coordinates Elevation-Si (Fig. 4a). This last model we used for the prediction horologic changes



in the index SI research using universal kriging (Fig. 4b). Note that the possible predictive error increases with elevations region studies (Fig. 4c).

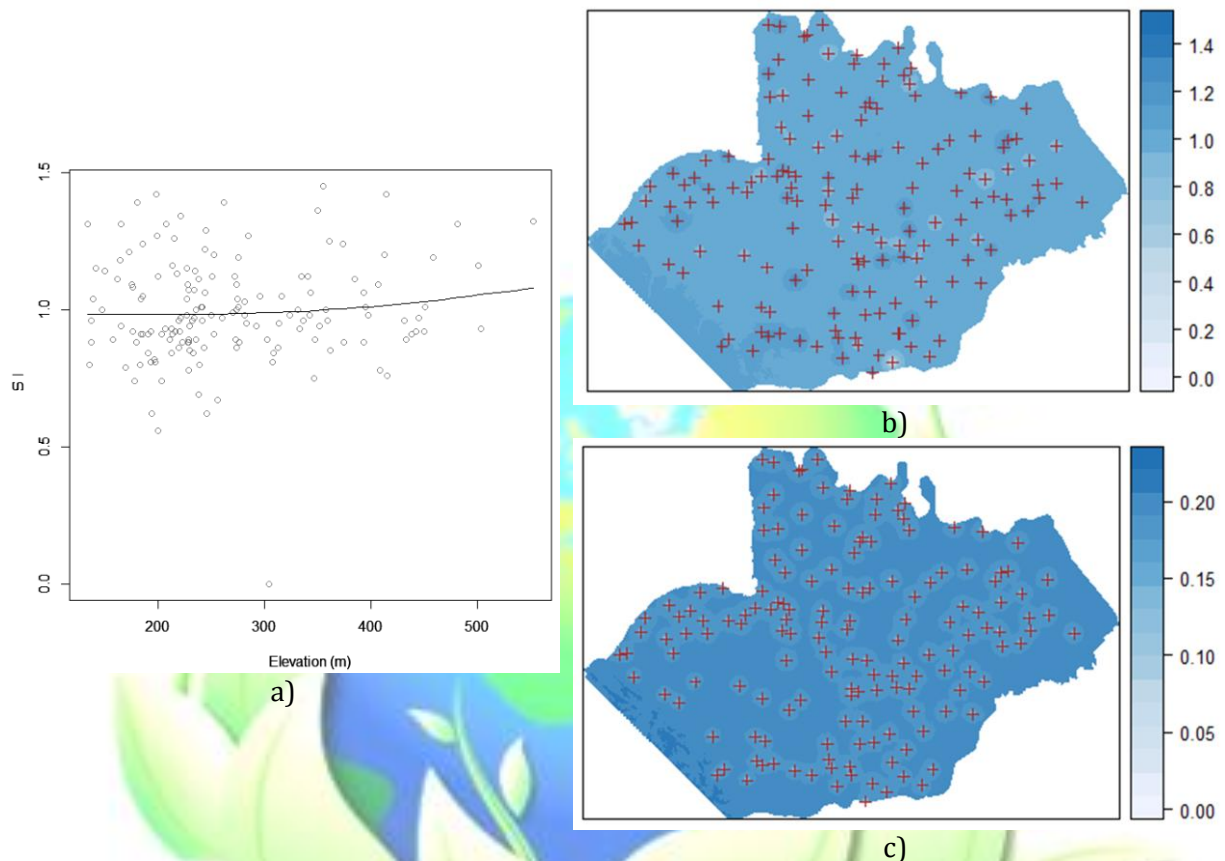


Fig. 4. Dependence of SI on the height of observation points (a) and the corresponding kriging-model: b) universal kriging of SI distribution: c) prediction error map

Comparison geostatistical kriging-model (reduced to standard color scale) with models of the spatial distribution of SI from IDW interpolations and RST- showed that between them there are significant differences. In particular IDW-interpolation gives a model that has a very low informative saturation (Fig. 5a). Model RST-based interpolation gives a high degree of overlap of data points in the observation and smooth gradients change the values in the intervals between them (Fig. 5b). This allows you to use it to clear zoning of the values of SI. Model based on universal kriging despite the incorporation of high-altitude component and under fairly good distribution of SI under relief (Fig. 5c), contains a large number of errors of the forecast. This indirectly indicates that the function of height despite his influence, is not a major factor in the spatial variation of SI. Identify the main factors affecting for use in kriging-models require additional research. Note also significant differences in the models and kriging-model based on RST-interpolation (Fig. 5 d).

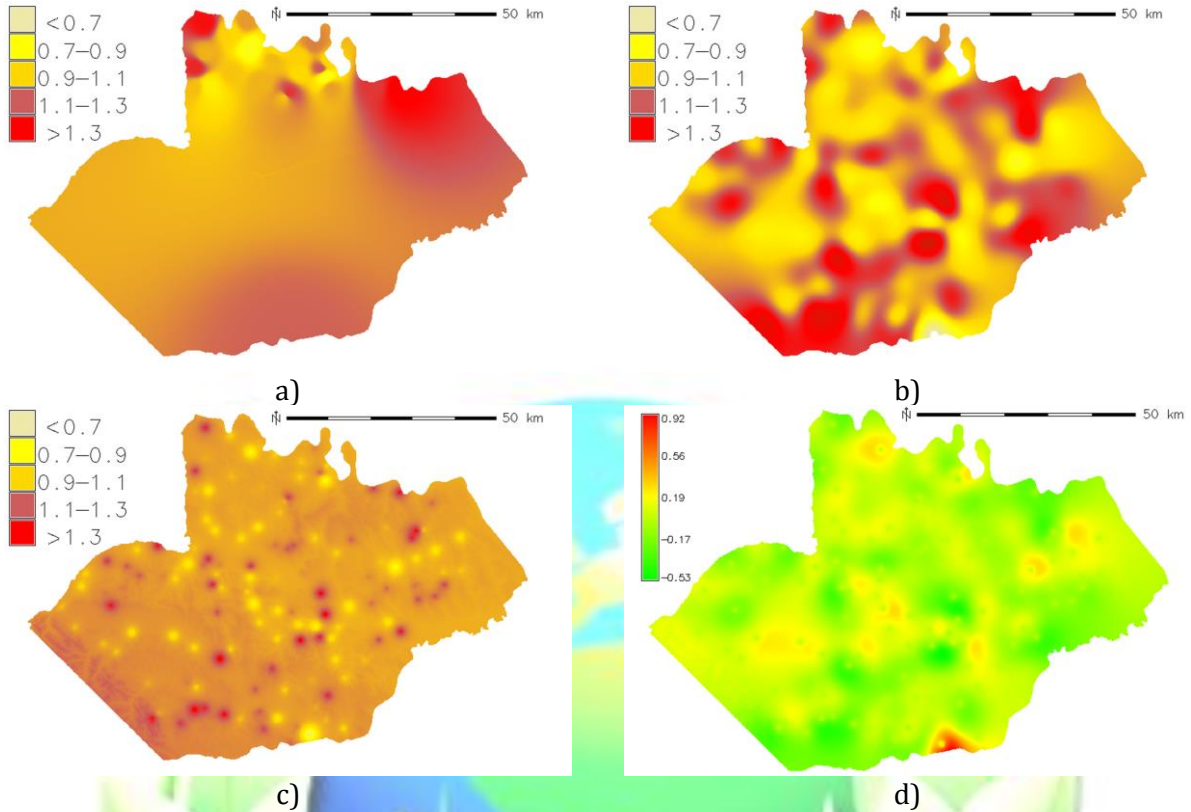


Fig. 5. Models of the spatial distribution of saturation index of gross forms of heavy metal: a) IDW; b) RST; c) universal kriging; d) map of the difference between the RST and kriging models

The basic model of the resulting spatial changes of heavy metals in soils obtained by three-dimensional visualization RST-model with clear zoning (according to the value of the index, Table 1) using the module GRASS GIS NViz (Fig. 6).

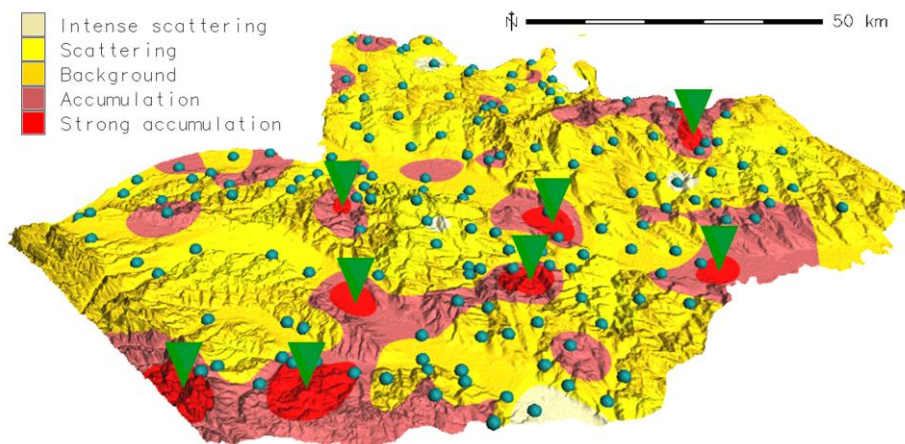


Fig. 6. Three-dimensional visualization of the zoning by RST-model NVIZ (hemispheres indicated sampling points)





Based on the analysis of the resulting model can be done some conclusions: 1) the major part of the study (56%) corresponds to the background of heavy metals in soils; 2) among habitats abnormal content of about 18% of the territory of the soils in which the gross amounts of heavy metals increased; the rest - it ranges scattering; 3) the points for monitoring the quality of soil pollution HM advisable to place in eight habitats (triangles ▲ in Fig. 6)

## CONCLUSION

So for assessing soils contamination HM and organizing appropriate monitoring is optimal RST-model that gives the minimum errors in the sampling points and compared with other models, including smooth gradients content of the studied parameters in the study area where no samples were taken. Even the visual analysis of geospatial models are based on our proposed algorithm can detect critical pollution areas. Extends the options for using the proposed models the possibility of their mathematical treatment. It optimizes the evaluation of soil quality for regions in which the potential problems associated with soils contamination HM.

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