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

PROCEEDINGS

of International Conference

„Global Environmental Changes and Environmental Health: Environmental and Economic Impact on Sustainable Development"

17th – 19th of November 2016
Budapest, Hungary

Impressum

For the Programme, Abstracts and Papers of the 7th ICEEE-2016 International Conference titled: „Global Environmental Changes and Environmental Health: Environmental and Economic Impact on Sustainable Development"

- The official language is English.
- The Programme and Abstracts of the Conference is provided to all registered participants in printed form and in USB format.
- All the received papers were reviewed by two of the members of the International Committee of the Conference.
- All reviewed papers for the **7th ICEEE-2016 International Conference** will be published in the Proceedings form with **ISBN 978-963-449-063-0** in CD-ROM format and online in the website of ICEEE: **www.iceee.hu**
- The selected high quality manuscripts will be also published in the online journal of **Óbuda University e-Bulletin with ISSN 2062-2872.**
- The scientific information and quality of the manuscript is due to the crosponding author.
- The Publisher of the Programme, Abstracts and the Proceedings of the International Conference is the ICEEE, Sándor Rejtő Faculty of Light Industry and Environmental Engineering, Óbuda University, Budapest, Hungary.
- Publication year of the Proceedings is 2017.
- Important Websites:
  - **www.iceee.hu**
- The Conference is organised in the framework of the Hungarian Scientific Season (Hungarian Scientific Festival).

Prof. Dr. Hosam Bayoumi Hamuda
President of ICEEE
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November, 2016.

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INTRODUCTION

Since 2010, International Council of Environmental Engineering Education (ICEEE) has taken around the world with hosting large number of participants from different countries. With the recent adoption of the Sustainable Development Goals by the United Nations, it is clear that in order to achieve the Goal of Environment and Sustainable Development, which need to be examined in greater detail and solutions to address, in concert with technological advances and after a great successful of the last 6 ICEEE International Conferences which brought together the world's professions and practitioners from different fields of environmental applied sciences and environmental engineering. It was a great honour of the ICEEE at Óbuda University in partnership with Technical University of Košice, Slovakia and University of Novi Sad, Technical faculty —Mihajlo Pupin from Zrenjanin, Serbia to organize the 7th International Conference titled: „Global Environmental Changes and Environmental Health: Environmental and Economic Impact on Sustainable Development" (7th ICEEE-2016). This partnership significantly improves the quality of Conference organization and contribution in area of regional cooperation with other universities and scientific institutions. The objectives of the Conference were: presentation of current knowledge and the exchange of experiences from the field Environmental and Economic Impact on Sustainable Development which is one of the major problems of modern civilization. The Conference was focusing on latest technological developments in viable solutions for a clean environment, and to find the practical applications to solve real global problems such as the environmental quantitative assessment of the climate change impact on urban inundation, drought indicators and drought forecasting, ecological indicators for river, ecology restoration, evaluating the effect of urbanization on diurnal temperature variations, food, soil and water security, climate change abatement, ecosystem, biodiversity protection, energy sustainability, etc. Another importance is gathering researchers from this field with aim of expanding regional and international cooperation, raising the level of professional and scientific work, expanding cooperation with institutions and encouraging young researchers within this field. Within this collection of papers are presented all accepted papers received for the 7th ICEEE-2016. The papers are belonging to: Environmental Consideration; Waste and Recycling; Ecological Sustainability: Engineering Change; Basic and Bioenvironmental Sciences; Global Change; Life Sciences and Biomedicine; Materials and ECO-Design, and Industrial Design Engineering; Sustainable Energy; Sustainable Agriculture; Sustainable Water Technology and Processing; Sustainable Soil Management; and World Population. As we reach the final issue of the 7th ICEEE International Conference for 2016, I wish to reflect on another successful year's achievements, and to thank all those who have contributed their time and effort to guarantee the high quality of our content. 2016 was a successful year for ICEEE. Total of 37 articles have been selected and published in the Proceedings of the 7th ICEEE Conference. I offer my sincere thanks to the authors who have contributed articles to the 7th ICEEE of 2016. The skill and dedication of all authors are critical to the continued publication of the Proceedings. The quality of published articles is also testament to the significant efforts of the peer reviewers, whose commitment ensures that the content of the Proceedings is held to the highest possible standard. We would like to thank the individuals who acted as reviewers for the 7th ICEEE in the last 12 months. In addition, we would like to thank the members of the members of the board of organization, who have acted as peer reviewers and authors. We take this opportunity to sincerely thank retiring the ICEEE president Professor István Patkó. The Organization of 9th ICEEE International Conference for 2018 in November at the Óbuda University (Budapest, Hungary) is well under way, and I'm looking forward to bringing you many high quality and authoritative articles over the coming year. We would like to express our gratitude to the all supporting authorities. Finally, we wish to thank all the authors of papers and participants in the Conference in hope that we will continue our cooperation successfully in the future and that each year will bring better ideas and solutions to help raise awareness of the responsibility we hold today for the well-being of future generations.

Prof. Dr. Hosam BAYOUMI HAMUDA
President of ICEEE
November, 2016.

Dear Distinguished Guests,
Dear Colleagues and Friends!

It's my great pleasure to welcome all of you to the 7th International Conference of ICEEE-2016 under the title: **„Global Environmental Changes and Environmental Health: Environmental and Economic Impact on Sustainable Development"***.*

The main approaches of the 7th ICEEE International Conference are to:

- *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, eco-design, eco-marketing, etc.*
- *Provide an excellent international forum for researchers and practitioners to continue research, characterize the global environmental changes and how they affect the life dynamics of global 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.

Dr. habil. Márta KISFALUDY
Dean
November, 2016.

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Accepted Full manuscripts of the presentation Reviewed by the Scientific International Committee of the Conference

ECO-DESIGN IN THE FUTURE OF SUSTAINABLE EDUCATION

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Received: November 2016

Abstract

An innovative product development became important to the current era following the full life cycle of the products and trying to reduce the natural and social adverse effects to the lowest level. Only the responsible and environmentally conscious designers can respond in an innovative way to social problems and environmental challenges of the 21th Century. For companies, the eco-conscious product development has a strategic importance to be able to meet the requirements that were set against them by not just lawmakers, but also by commercial and private customers, and all market participants. Through the training of young industrial designers and product engineering students, we put particular emphasis on raising the eco-conscious awareness and practical experimentation processing of different areas of light industrial wastes sets new tasks for the product designers. Our research focuses on mapping and creative reuses of the large amounts of unused waste, unnecessary objects, old household items etc. Basis on the theoretical background of this growing sustainable design philosophy fourth year students get a practical reuse project. They can use all the hand techniques and high technologies studied so far. Targeted solutions of project-oriented tasks are realized in new furnishings, fashion products and packaging which are promoted in exhibitions and fashion shows. This is a creative process which is a real design problem. All the experiences obtained through these reconstructions generate new ideas for future projects of the students.

Keywords: *Reuse, product design, reconstruction*

INTRODUCTION

Importance of the research work

One of the tasks of the eco-conscious strategy is to encourage designers to minimise the waste that is created in the industry. Industrial waste is produced by industrial activity which includes any material that is rendered useless during a manufacturing process such as factories, industries, mills, and mining operations.

Observing the life cycle of products one can found a number of economic and environmental development opportunities, including manufacturing and use stages as well as end-of-lifecycle waste recovery. The new thinking can also result cutting the costs, improve efficiency and increase competitiveness.

Eco-design means the introduction of the environmentally conscious way of thinking during the design and manufacturing processes. The eco-design aims to reduce the environmental impact of products throughout their entire life cycle.

It is a new responsible approach of the current design with new attitude and new philosophy. The eco-product design is a complex concept the criteria of which are:

1. the importance of protecting and balancing the nature.
2. the knowledge and use of new materials and technologies.
3. reinterpretation of craft traditions.
4. taking into account the real market needs, processes
5. reducing the "ecological footprint". (less water, chemicals, energy use)
6. innovation and creativity.

Reduce, reuse and recycle are the three essential components of environmentally responsible designer's behavior but we can add even repair from the point of view of the consumers. How can we meet the requirements? There are four ways:

- Slow design
- Design for long-life and short-life applications
- Zero waste cutting
- Design with enhanced aesthetic value

So through a one semester project work students learn to identify themselves with ecological, social and community consciousness. They do a research work on new and innovative ways to become more sustainable. They collect new designs of contemporary designers from all over the world as well as the works of Hungarian companies.

This research highlights the accumulated sources worth dealing with. After collecting information they

create innovative solutions even for industrial manufacturing. Our education has to prepare students for these kinds of conceptual ways of thinking integrated with engineering knowledge.

Photo 1 Photo 2 Photo 3

Photos 1, 2 and 3
Hungarian samples: Zip necklace from Gerdushi Design and reusable plastic bags from Medence Design

METHOD OF THE PROCESS

By knowing the theoretical background of the sustainable design philosophy fourth year students get a practical reuse project. The starting points can be all kinds of accumulated unused waste, unnecessary objects, old household items etc. They can make material-, form- and style combinations and can use all the hand techniques and high tech technologies studied so far.
We examine and analyse:

- structure, form and material of the chosen pieces,
- ways for deconstruction and reconstruction,
- the function of the new structure,
- the variability of the forms and materials,
- the possibility of their surface manipulations,
- style effects.

There are a plenty of purchasing sources all around the country and even in our personal home. We consider all the opportunities for further development and choose a few ways to start with. They collect their inspirations, all kind of similar shape solutions and colour suggestions on moodboards.

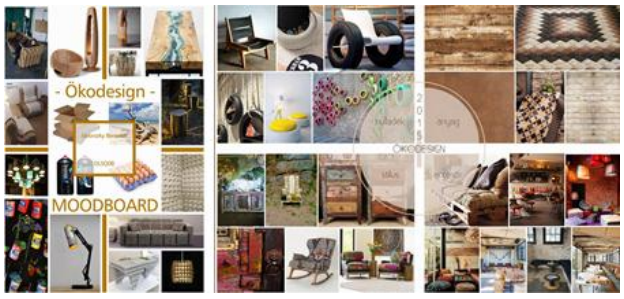

Figure 1
Inspiring moodboards (Benedek Jávorszky and Alexandra Baraksó)

Industrial wastes
During all types of production certain sizes of waste are generated, either of wood, or metal, fiberglass, leather, paper or textile. Students frequently use leather, wire and wood pieces to invent unusual demonstrating models and as many variations from their pieces gathered as they can.

The main question is what function will serve the reconstructed model from any kind of waste? The quality of the materials and the given sizes specify the form and the function.

Photo 4
Waste types: leather, wood, electric wire

As the students learn a lot of craft techniques and industrial technologies, as well they can choose their favourite type matching the best to the type of the waste. Study of the construction and technological solutions are essential for starting this project.

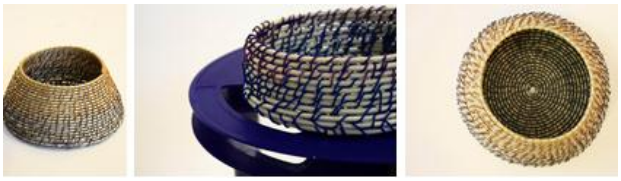

Photo 5
Bowls with basketry technique from electric wire by Kamilla Bihary

Photo 6
Patchwork from leather waste covering a seat made from two tires by Alexandra Baraksó

Photo 7
Chair from wood-waste by Zsófia Bagi

Electronic waste
Nowadays 20-50 million tonnes of E-waste are generated annually, of which only 12.5% are utilized, and these wastes contain high levels of valuable re-recoverable rare earth-metal elements (REE).
A student used an HDD (hard drive) as a desk clock. That was a 40GB faulty hard disk which he

transformed so that it has a new function as a clock thus prolonging its life. The small metallic elements evoke the classical futuristic way of the world of mechanical watches.

Figure 2
Reuse of E-wastes: desk clock by Dániel Végh

Unused and accumulated

People love collecting things and accumulate them in their homes, offices and cottages. The new generations are not emotionally attached to these household items, photos or games etc. so they just marvel at the old things and use them easily in another way. The most interesting ones are the chairs, space dividers, tables and all kinds of lamps, but objects with smaller sizes can have good functions, as well. The first step of the process is to deconstruct the object and survey it from the point of views mentioned above. The way of up-to-date reconstructions needs well-structured ideas.

Photo 8 Photo 9 Photo 10

Photos 8-9-10
A bar-chair from bicycle by Lőrinc Lipták. Glued and painted toy-parts as a table lamp. Vinyl records as a multi-levelled lamp and clock by Gerda Nagy

Reuse and traditions

Reuse is a good opportunity to rediscover the traditions of the society and this way of design enjoys a great popularity. To integrate the national tradition elements into the current design streams shows a fresh way to connect the new generations with the unforgettable values of the past.

Photo 11 Photo 12 Photo 13

Photos 11-12-13
A nightstand from an old basin stands by Lilla Molnár. Redesign of an old dining table by Eszter Németh. A practical kitchen stool with resin by Marietta Jobbágy

IMPLEMENTATION

This type of experimental work helps to strengthen the ability of assembling materials in a proper way while creating a new style. The project is based on innovative connection of different materials and shapes, meanwhile aiming to use the most suitable solutions. Mixing the different kinds of materials like the rigid and soft, resin/metal and wood, glass and leather, paper and textile etc. can cause problems in realizing the prototypes.

Creating a new form from waste materials or reconstructing an object can be produced mainly by using two or three different materials. Textile or leather patchwork from similar materials, but different sizes means an easier way of solution.

As new discoveries in material-science appear students would like to experience them in their works. Thus they focused on concrete and resin and three-layered sound insulating felt, as well.

Combinations and arrangements of these materials and form possibilities integrate all the knowledge students studied so far. Students combine high and low tech processes and use recycled materials to create expressive objects showing their engagement towards their responsible attitude for green design to develop a specific approach in design methods.

Figure 3
Experimenting with a new composite: chopped walnut shell in resin

The needed infrastructure for implementation is well equipped labs with: textile and leather sewing machine, laser cutter, 3D software, special machines for processing all kind of materials, handicraft tools etc. The final documentations and posters contain all the steps of the design process from the inspirations, drawings or photos of starting pieces, technological drawings, as well as sketches, and photos of the final products.

Figures 4

Figures 5

Figures 4-5
Two posters showing the results of design works (Gerda Nagy, Adrienn Rozsnyó)

CONCLUSIONS

Processing the waste originated from the different sections of light industry poses new challenges to the product designers. We educate our industrial product design engineer students with particular emphasis on eco-conscious awareness and practical experimentation. The main focus of our research is the mapping of the large amounts of unused waste and provides creative possibilities of further utilization.

The end-products present the intended creativity as well as the conscious thinking of the student. The prototypes of students demonstrate that the subject of these reusing studies is really thought provoking and leading to challenging solutions with the help of the method used.

All the experiences obtained through this creative deconstruction and reconstruction generates new ideas for their future projects. As the prototypes are unique we regularly present them to public, partly in the hall of our university and on the other hand during prestigious events, like Design week Budapest or Educatio exhibition etc.

Photo 14

Photos 15

Photos 14-15
Two public exhibitions

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A METHOD FOR ESTIMATING THE FIBRE WEIGHT USING FIBRE LENGTH ANALYSER

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Received: November 2016

Abstract

Paper is reality in our everyday life. The modern paper production technology is divided into several sections, roughly corresponding to the processes involved in making handmade paper. In this scientific work we have elaborated a new specific quantity, measuring the weight and number of pulp single fibres in aqueous medium. The measurement has been fulfilled in a Kajaani FS 100 fibre length analyser.

INTRODUCTION

The paper making processes cause the change of the length and weight of the cellulose fibres with a different order of magnitude. Fibre length is a fundamental property of pulp. The determination of the fibre length and fibre weight of pulp fibres is important in papermaking technology and environmental protection as well, because the effluents from paper mills contain solids and dissolved substances. Solids (fibers, fillers) are mostly removed from the effluent in a chemo-mechanical clarification process by the use of flocculants [1] [2].

It is important to emphasize the pollution in the wastewater of a paper mill depends on the type of raw materials and the paper production processes. The arguments given above prove that important to measure these properties. [1].

Paper is reality in our everyday life. The modern paper production technology is divided into several sections, roughly corresponding to the processes involved in making handmade paper.

Pulp is refined and mixed in water with other additives to make pulp slurry. In papermaking, a dilute suspension of fibres (Figure 1) in water is drained through a screen, so that a mat of randomly interwoven fibres is laid down. Water is removed from this mat of fibres by pressing and drying to make paper. The water is acting as a binding agent between the fibres by forming molecular bridges with hydrogen bonds.

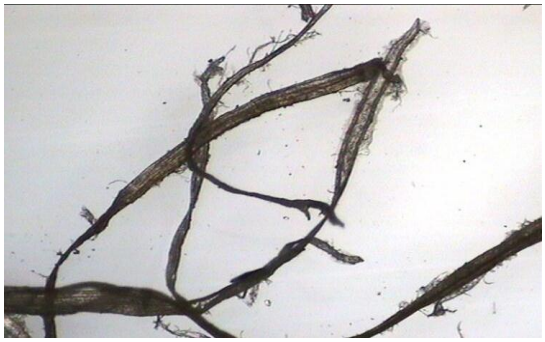

Figure 1

Pine (picea abies) tracheids fibres

The properties of papers are highly depended on the quality of the included cellulosic fibres.

Interfibrillar and intermolecular actions occur during the papermaking process.

The first interaction among the fibres is the felting occurring in the sieve section whereas the second one is the forming of hydrogen bonds among the cellulose molecules during drying. Such fibres are needed for the procedure in which the ratio between the length and the width of the fibre is 70:1. The mass (grammage) and the strengths of the produced paper are characterized by those of the included single fibres. So, determination of the fibre length and fibre weight of different pulp fibres is fundamental. The earliest method to measure the fiber length, width and coarseness was the microscopic method (Wilson, 1954). This procedure suffered from defects (fractionation of flat or collapsed fibers) that occur

during measurements on the fibers. We also studied the morphological properties of fibres using WAT-250 D (W96P) videomicroscope (Figure 2.) befor we used the fibre length analyser.

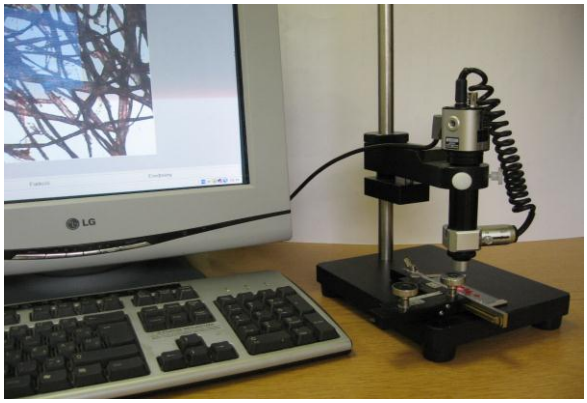

Figure 2
WAT-250 D (W96P) videomicroscope

Consequently new method has been elaborated by us for the measurement of the mass of the mentioned single fibres. The measurement has been fulfilled in a Kajaani FS 100 fibre length analyser. This analyser is consisting of a capillary tube (0.2 mm) through which an aqueous suspension (density of suspension: 1 per thousand) of the fibres is passed.

The pulp and paper industry started to use the Kajaani FS-100 in the 1980; this was the first automated fiber analyser [1]. "And is an optical device accepted as method for laboratory fibre length measurements (Tappi T271) to measure fibre length and coarseness" [3]. This tool is ready for quick and one simple measurement procedure [4].

MATERIALS AND METHODS

Pulp Fibres

In scientific research we studied different cellulose fibres of different origin:

- **sulphate pine** cellulose: bleached or unbleached and dried or undried,
- **mixed hardwood** semi-chemical pulp: dried or undried,
- **hardwood** cellulose: bleachedand and dried,
- **CTMP** (Chemical Thermo Mechanical Pulp) pine: dried or undried.

These pulp fibres are obtained by chemical pulping from softwood, hardwood, mechanical pulp is produced by mechanical defibrationof wood. Pulping represents the process by which wood or other lignocellulosic material is reduced to fibrous mass, denoted as pulp [5][6].

During chemical pulping, the most of the lignin is removed from the raw material.

The yield of the pulp is therefore only 45 to 55%. Two main industrial processesof chemical pulping are used:

- the **sulfate** process with sulfate pulp as product,
- the **sulfite** process with sulfite pulp as product.

The alkaline sulfate process uses sodium sulfide and sodium hydroxide as pulping chemicals. The acidic sulfite process is based on calcium, magnesium, and sodium or ammonium bisulfide. Worldwide, the sulfate process is used in up to 90% of cases.

Softwood is comprised of two types of cells: tracheids (90-95%) and ray cells (5-10%). Softwood fibres are by definition wood tracheids. Tracheids give the softwood mechanical strength (particularly thick-walled latewood tracheids) and transports water. Softwood fibres are closed at both ends.

The median fibre length of Finnish pine and spruce is approximately 3 mm. Due to their long fibres, softwood pulps are often referred to as long fibre pulps[7][8].

Kajaani FS 100 Fibre Length Analyser

The main part of the device a capillary tube (0.2 mm) through which the thin suspension of the fibres is conducted. On the one side of the capillary (Figure 3.) is positioned a lamp and on the other, opposite side is a detector. When a fibre go through the capillary, the polarized picture of the single fibre is transmitted into the detector and from this we can calculate the length of the fibre. "A low-pressure vacuum pump and chamber collect the analyzed fibres. The measurement range is between 0-6.79 mm, divided into 24 classes, of which the first 12 classes are resolved to 0.2 mm lengths and the last 12 have a resolution of 0.4 mm (for the 0-0.7 mm range)" The fibre counting is manually with a keyboard. The fibre suspension is diluted (0.0004% consistency). [9][10][11][12].

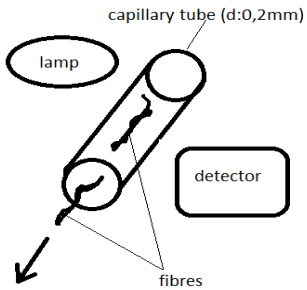

Figure 3
Fibre Length Analyser

A. Methods

In our method for the establishing of the mass of cellulosic single fibres the following 4 steps should be fulfilled:

1. Determination of the dry matter content of the sample
2. Cellulose sample with 0.1-0.2 g absolute dry fibre content should be pulped in 1000 ml distilled water

3. 100 ml of the above mentioned suspension should be diluted to 1000 ml by distilled water.
4. 100 ml of the suspension should be filled into the Kajaani 100 fibre analyser to determine the average fibre length (l_{af}) and the total number of the included fibres (tn).

Average single fibre mass (m_{asf}) can be calculated by dividing the included mass of the fibers (m_f) by their above gained number (tn):

$$m_{asf}(g) = \frac{m_{af}(g)}{tn} \qquad (1)$$

The above discussed data enable the calculation of the specific mass (m_{spec}) in g/mm of the single fibre:

$$m_{spec}(g/mm) = \frac{m_{asf}(g)}{l_{af}(mm)} \qquad (2)$$

Initially the impact of the grinding of different ECF bleached pine fibres in Jokro mill has been determined on the mass of the single fibre. 5 samples of different freeness (12, 18, 24, 32, 60 °SR) have been produced by grinding in Jokro mill.

5 Bauer McNett fractions have been separated (mesh: 14, 30, 50, 100, 200) from each mentioned samples of different freeness respectively. The average mass and length of single fibre of mentioned samples have been determined and compared with each other.

The average mass and length of single fibres of dried and never dried pine sulphate celluloses respectively after grinding in PFI mill have been determined and compared with each other thereafter.

Further experiments have been performed with Chemical Thermo Mechanical Pulp (CTMP) single fibres.

Finally the average mass and length of single fibre of 9 different cellulosic fibres of the same freeness have also been studied.

RESULTS AND DISCUSSION

Obtained data in the 1st set of experiments are summarised in Figure 4 and 5.

The first observation from the obtained data is that the grinding practically does not decrease the average length (Figure 6) of single fibres but it is significantly decreases their mass.

From this might be concluded that the grinding keeps the lengths of the fibre practically unchanged but it is sensitively decreasing its cross section.

Final conclusion is that in the length acting binding forces are strong primary ones whereas in the cross sections acting ones are much weaker secondary forces.

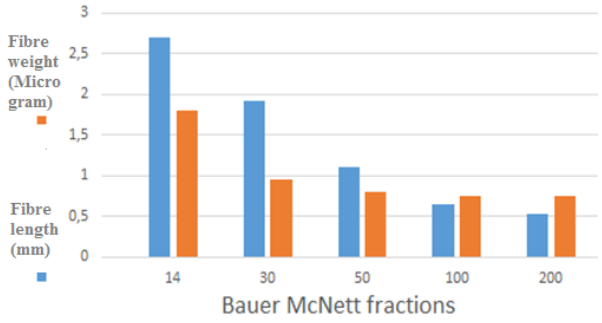

Figure 4
Average fibre length and weight of ECF bleached pine fibres of 12 °SR freeness (after grinding in Jokro mill) and 5 Bauer McNett fractions.

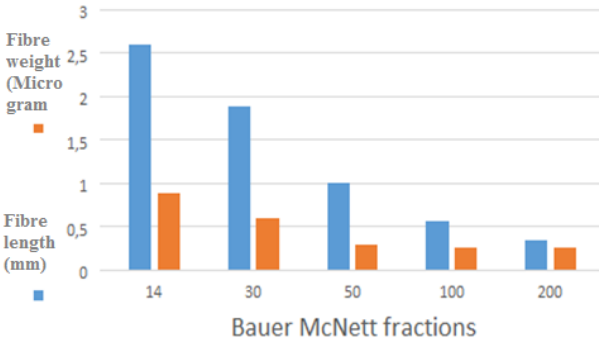

Figure 5
Average fibre length and weight of ECF bleached pine fibres of 60 °SR freeness (after grinding in Jokro mill) and 5 Bauer McNett fractions.

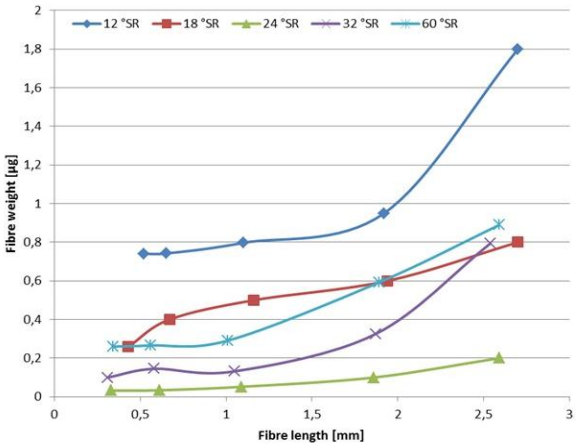

Figure 6
Average fibre length and weight of ECF bleached pine fibres of 5 different freeness and 5 Bauer McNett fractions of each freeness.

Obtained data in the 2nd set of experiments are summarised in Tables 1 and 2. Concerning changes in fibre length and fibre mass after grinding leading to freeness form 13 °SR to 57 °SR enabled the conclusion that small loss occurred in them as well of dried (Table 1.) as of never dried samples (Table 2.)

Table 1
Changes in average fibre mass, average fibre length and specific fibre mass of never dried pine sulphate cellulose single fibre in the function of freeness after grinding in PFI mill.

Bleached never dried sulphate pine ground in a PFI mill			
Freeness (SR°)	**Fibre length (mm)**	**Fibre weight (µg)**	**Specific fibre weight (µg/mm)**
13	2,27	0,303	0,133
22	2,26	0,298	0,131
33	2,23	0,295	0,132
47	2,21	0,295	0,133
57	2,19	0,289	0,131

Table 2
Changes in the average fibre mass, average fibre length and in then specific fibre mass of dried pine sulphate cellulose single fibre in the function of freeness after grinding in PFI mill.

Bleached never dried sulphate pine ground in a PFI mill			
Freeness (SR°)	**Fibre length (mm)**	**Fibre weight (µg)**	**Specific fibre weight (µg/mm)**
13	2,3	0,381	0,165
20	2,27	0,314	0,138
32	2,25	0,283	0,125
45	2,08	0,273	0,131
54	2,04	0,268	0,131

The changes in specific fibre mass (Table 3) are nearly neglectable in both samples because the loss in fibre length and fibre mass are proportional.

Table 3
Changes in average fibre mass, average fibre length and specific fibre mass of never dried Chemical Thermo Mechanical Pulp (CTMP) single fibre in the function of freeness after grinding in PFI mill.

Bleached never dried sulphate pine ground in a PFI mill			
Freeness (SR°)	**Fibre length (mm)**	**Fibre weight (µg)**	**Specific fibre weight (µg/mm)**
26	2,2	0,628	0,285
35	1,81	0,537	0,296
40	1,73	0,401	0,231
54	1,44	0,366	0,254
26	2,2	0,628	0,285

Both the length and the mass of CTMP (Table 4) single fibres decreased in the function of the increased freeness as well for dried as for never dried samples. No such tendency could be concluded in case of specific fibre mass data. Obtained data in the 4th set of experiments are summarized in Figures 6 and 7.

Table 4
Changes in average fibre mass, average fibre length and specific fibre mass of dried Chemical Thermo Mechanical Pulp (CTMP) single fibre in the function of freeness after grinding in PFI mill.

Bleached never dried sulphate pine ground in a PFI mill			
Freeness (SR°)	**Fibre length (mm)**	**Fibre weight (µg)**	**Specific fibre weight (µg/mm)**
23	2,31	0,607	0,262
30	1,96	0,342	0,174
42	1,71	0,299	0,174
52	1,36	0,246	0,180
26	2,2	0,628	0,285

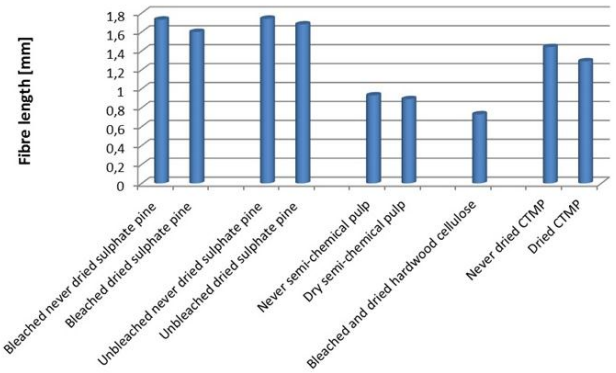

Figure 6
Changes in the average fibre length of cellulose single fibre of different prehistory at the same freeness (50 °SR).

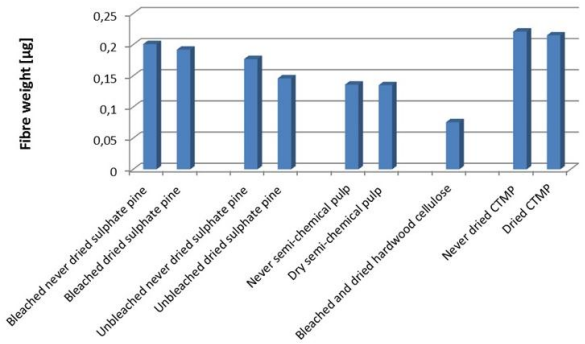

Figure 7
Changes in the average fibre mass of cellulose single fibre of different prehistory at the same freeness (50 °SR).

Comparing the average fibre length could be concluded that the unbleached never dried pine sulphate cellulose has the highest value and the bleached hardwood cellulose has the lowest one.

CONCLUSIONS

The elaborated by us method for the determination of the average single fibre mass for cellulosic fibre of different origin could be successfully used for a wide range of cellulosic fibres.
Comparing the results of average fibre mass could be concluded that the unbleached never dried pine

sulphate cellulose has the highest value and the bleached hardwood cellulose has the lowest one.

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PROTECTIVE EFFECT OF CALCIUM AND MAGNESIUM AGAINST THE INHIBITORY IMPACT OF TRACE METALS ON YEAST GROWTH

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Received: November 2016

Abstract

The pollution of the environment with heavy metals is one of the most serious global problems. Yeast (Saccharomyces cerevisiae) has received high attention due to its unique nature in spite of the mediocre capacity for metal uptake. In vitro, two strains of S. cerevisiae (GCB-Y-30-96 and GCB-Y-45-96) were investigated in order to estimate their tolerance to some trace metals. In this study two strains (GCB-30-96 and GCB-45-96) of Saccharomyces cerevisiae isolated from 30 and 45% sewage sludge treated sandy brown forest soil were used for the monitoring the effect of lead (Pb), cadmium (Cd) and copper (Cu) at different concentrations. The tolerance of S. cerevisiae strains against the trace metals in the contaminated YPD broth media was found to be up to 160 µM for Cu^{2+}, 320 µM and 640 µM for Pb^{2+}, it was 320 ppm for Cd^{2+}. The growth of two yeast strains in polluted growth media by Cu^{2+}, Pb^{2+} and Cd^{2+} were studied at 0, 5, 10, 20, 40, 80, 160, 320, 640 and 1280 µM. The toxicity decreasing order of the investigated trace metal salts on the experimental microbiome yeast strains was found to be $Cu^{2+} > Pb^{2+} > Cd^{2+}$. The addition of 100 mM $Ca(HCO_3)_2$ and 100 mM $MgSO_4$ in the growth broth medium before addition of different concentrations of Cu^{2+}, Pb^{2+} and Cd^{2+} illustrates a protective action against cell death and decreased the toxicity effect of the tested trace metals. The addition of alkaline earth metals reduced the effect all tested trace metals. The results obtained in the presented investigation exhibit the higher potentiality of S. cerevisiae strain GCB-45-96 than the strain GCB-30-96 to be used for decreasing the contamination of the tested trace metals of soil containing such as trace metal ions. Further task is going to examine the range of metal bioaccumulation in the yeast cells and the ability of these strains to be environmental bioremediators.

Keywords: *growth rate; yeast;, trace metals; synergistic effect; Ca, Mg*

INTRODUCTION

Heavy metal pollution represents an important environmental problem due to the toxic effects of metals, and their introduction in to the food chain leads to serious ecological and health problems. Microbiomial parameters in the ecosystem appear to be very useful in monitoring the pollution by high concentrations of trace metals. Since it is impossible to degrade those pollutants by any means, the only way to remove them from the ecosystem is to exclude metals from cycling through their concentration, with a possible recovery and reuse. The toxicity of trace metals cause serious problems to the environment, Nowadays, the most an important environmental problem is to correct the toxic impacts of these metals in contaminated ecosystem. Heavy metal pollution is a growing problem mainly caused by industrialization. Electroplating, surface finishing, metallurgy, mining, mineral and electronic processing are examples of industries that produce large wastewaters quantities containing high concentrations of heavy metals.

The problem of heavy metal pollution is basically associated with: (i) acute toxicity linked with particular metals (Cu, Hg or Cd), even in lower concentration; (ii) the fact that heavy metals are not degraded or destroyed and tend to circulate; thus, they remain for a long time in nature and are accumulated through the food chain, which creates a threat to public health [1].

Metals that present high affinity to react with sulfhydryl (thiol) groups are considered (1) Soft transition metals such as silver (Ag), cadmium (Cd) and mercury (Hg) have sulphur as their preferred

ligand. (2) Hard transition metals such as chromium (Cr), manganese (Mn) and molybdenum (Mo), and the metalloids arsenic (As), antimony (Sb), selenium (Se), tellurium (Te) and bismuth (Bi) prefer oxygen in their higher oxidation states, (3) An alternative is considered when metals are able to bind sulfur, oxygen or nitrogen atoms while they prefer sulphur in their lower oxidation states. Lead (Pb), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn) can use oxygen, sulphur or nitrogen as ligands [2]. In general, the above mentioned group of nonessential metals falls under the soft metal category and is highly related to cell toxicity, since the reaction with thiol groups may lead to functional impairment of many proteins. This chemical property is, nonetheless, explored by cells for metal detoxification [1].

Metal toxicity may be caused by oxidative stress, impaired DNA repair, inhibition of enzyme function and by disturbing the function of proteins that regulate proliferation, cell cycle progression, apoptosis or differentiation [3] (Figure 1) [1].

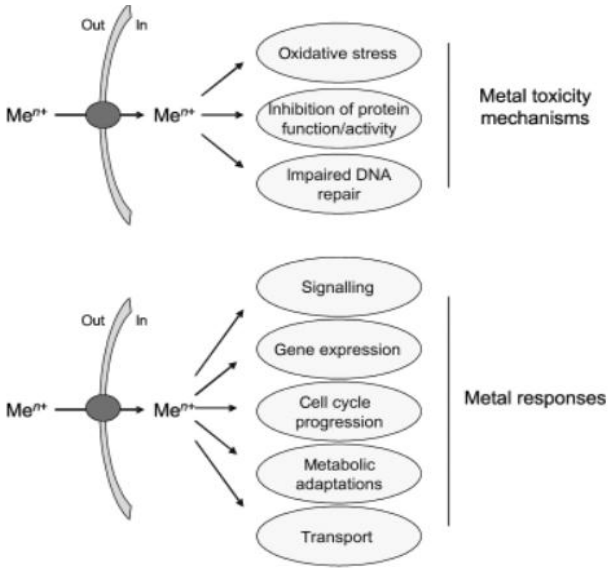

Figure 1
Metal toxicity mechanisms and metal responses. [1]

Heavy metal resistant microbiomes are often associated with acidic environments, since metals are easily solubilized in acidic solution. These metals usually have their cytosolic levels tightly regulated through homeostasis mechanisms and are typically maintained within a narrow range. On the other hand, nonessential metals are not necessary for cell function, are usually toxic in very low concentrations and lack homeostasis mechanisms. Nevertheless, excessive concentrations of both essential and nonessential metals can be cytotoxic and even cause cell death [4].

The conventional methods adopted earlier for this purpose included chemical precipitation, oxidation, reduction, filtration, electrochemical treatment, evaporation, adsorption and ion-exchange resins. These methods require high energy inputs especially when it refers to dilute solutions. Here microbial biomass offers an economical option for removing heavy metals by the phenomenon of biosorption [5].

Soares et al. [6] mentioned that the decreasing order of toxicity of select heavy metals on S. cerevisiae, in 10 mM MES (2-(N-morpholino)ethanesulfonic acid) pH buffer at pH 6.0, was found to be Cu, Pb, and Ni. Heavy metal (200 µM) induced a decrease in the number of viable cells by about 50% in the first 5 min for Cu and in 4 h for Pb, while Ni was not toxic up to a 200 µM concentration over a period of 48 h. The addition of 0.5 mM Ca, before addition of 200 µM Cu, showed a protective action against cell death and decreased the release of UV-absorbing compounds, while no effect was observed against Pb or Ni toxic effects. Cu complexation capacities of the filtrates of cells exposed for 2 h in 200 µM Cu and 24 h in 200 µM Pb were 51 and 14 µM, respectively.

Chen and Wang [7] demonstrated that the growth of *S. cerevisiae* in the presence of Pb^{2+} showed a lag phase much longer than that in the absence of Pb^{2+}. The inhibition was dependent upon Pb^{2+} concentrations. The Pb^{2+} at a concentration of 5 µM inhibited the microbial growth by approximately 30% with regard to control, whereas Pb^{2+} at concentration of 2 µM did not have a significant effect on the microbial growth.

Bioprocesses are an alternative to the traditional treatments. Algae, bacteria, filamentous fungi and yeast have the ability to remove heavy metals from solutions [8]. Among the different kinds of biomass available, yeast cells of *S. cerevisiae* constitute a good alternative wastewater treatment mainly because of the following reasons: (i) it is generally recognized as a safe microorganism and can be used without public concern; (ii) it is available in large quantities at a very low cost as it is a by-product of fermentation industries (brewing and wine); (iii) it has the ability to accumulate a broad range of heavy metals under a wide range of external conditions [8].

Some metallic elements have an integral role in microbial bioprocesses such as calcium (Ca), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na) and zinc (Zn) and serve as micronutrients. They are acting as components of different enzymes and regulate the osmotic pressure of the biomaterials. Calcium ions are required to ensure the correct conformation of the lectins present in the yeast cell wall [9]. The increase of cell surface hydrophobicity [10] or the presence of 3-OH oxylipins [11] has been positively correlated with the promotion of flocculation. It was shown that a flocculent strain of S. cerevisiae accumulated more Cu^{2+} than the isogenic, non-flocculent strain [9]. Heavy metals can occupy lectin Ca^{2+}-binding sites with the consequent increase of their uptake; thus, cell walls of

flocculent cells may provide additional metal-binding sites than the non-flocculent ones. Consequently, flocculent yeast cells have a higher capacity of metal accumulation than the non-flocculent cells [12]. Owing to these reasons, flocculent yeast cells are a promising low-cost biosorbent, which combines a better efficiency in the removal of metals with an inexpensive and rapid separation of biomass. This allows the use of different configurations of suspended biomass reactors without the risk of washout [13].

Calcium at a concentration of 0.5 mM is completely removed the inhibitory effect of Cu at concentrations up to 50 µM and considerably reduced it at higher concentrations (up to 150 µM). Mg exhibited a similar but weaker protective effect against the influence of Cu. The protective effect of Ca against 50 µM Cu was evident at low Ca concentrations (2.5–5 µM), whereas Mg was effective at ≥ 50µM. In order to prevent the inhibitory effect of Cu, it was necessary to add Ca or Mg to the cell suspension before Cu addition. It is concluded that the protective effect of Ca and Mg is mediated by competitive and stabilizing interactions at the cell surface as well as physiological functions of Ca and Mg [14]. It was concluded that a significant proportion of toxic effects resulted from free metal cations in solution, with protective effects like Ca and Mg resulting from competitive and stabilizing interactions at the cell surface [15].

Metal ions may play important roles as trace metals in sophisticated reactions of biochemical pathways and other metals like silver (Ag), aluminium (Al), cadmium (Cd), gold (Au), lead (Pb) and mercury (Hg) have no biological role, nonessential and to what extend are potentially toxic to microbial cells. At higher concentrations these heavy metal ions form unspecific complex compounds within the biomaterials, which leads to toxic effects, making them toxic for any physiological function. At high concentrations, both essential and nonessential metallic elements can damage cell membranes; change the enzyme specificity; disrupt cellular functions; and damage the structure of DNA [16].

The mechanism of heavy metal remove from the environment by microbial cells can be classified as extracellular accumulation or precipitation, cell surface sorption or precipitation, or intracellular accumulation, according to the location of the biosorption of the metal removal from solution [17].

The increases in the concentrations of the investigated trace metals within the yeast cell environment needs to be immediately signalled so that the cells can take the necessary steps for survival stress conditions or death. Because metal ions cannot be degraded or modified like toxic organic compounds, there are six possible metal resistance mechanisms exist: exclusion by permeability barrier; intra- and extra-cellular sequestration; active transport efflux pumps; enzymatic detoxification; and reduction in the sensitivity of cellular targets to metal ions [18]. One or more of these resistance mechanisms allows microbiomes to function in metal co-contaminated environments.

Ruta et al. [19] mentioned that *S. cerevisiae* cells can easily act as cation biosorbents. Ruta et al. [20] studied the involvement of Ca^{2+} in the response to high Ni^{2+}, Cu^{2+} and Cd^{2+} in *S. cerevisiae* cultures which is responded through a sharp increase in cytosolic Ca^{2+} when exposed to Cd^{2+}, and to a lesser extent to Cu^{2+}, but not to Ni^{2+}. The response to high Cd^{2+} depended mainly on external Ca^{2+} but also on vacuolar Ca^{2+}. The adaptation to high Cd^{2+} was influenced by perturbations in Ca^{2+} homeostasis. Thus, the tolerance to Cd^{2+} often correlated with sharp Cd^{2+}-induced $[Ca^{2+}]_{cyt}$ pulses, while the Cd^{2+} sensitivity was accompanied by the incapacity to rapidly restore the low $[Ca^{2+}]_{cyt}$. It was indicated that the presence of high Cd^{2+} in the yeast cell environment is signalled through immediate and sudden waves of $[Ca^{2+}]_{cyt}$. Reports regarding the involvement of Ca^{2+} transporters in Cd^{2+} yeast tolerance are numerous [21] and described how these transporters are involved in Cd^{2+} transport and detoxification.

Ruta et al. [22] established that Ca^{2+} ions are versatile second messengers used by virtually all eukaryotic cells to transduce the signal towards either adaptation or apoptotic pathways. The role of Ca^{2+} in mediating the cell response to high Cu^{2+} was investigated in *S. cerevisiae* cell culture. It was found that the cell exposure to high Cu^{2+} was accompanied by elevations in $[Ca^{2+}]_{cyt}$ with patterns that were influenced not only by Cu^{2+} concentration but also by the oxidative state of the cell. When Ca^{2+} channel deletion mutants were used, it was revealed that the main contributor to the $[Ca^{2+}]_{cyt}$ pool under Cu^{2+} stress was the vacuolar Ca^{2+} channel [22].

Bioavailability is defined as the fraction of the total amount of a metal in a specific surrounding environment that, within a given time is either available or can be made available for uptake by microbial cells from the direct surrounding of the microorganism. Metal speciation and the resulting bioavailability rather than total metal concentration determines the overall physiological and toxic effects of a metallic element on biological systems [23].

Some strains of *S. cerevisiae* are high potential as bioremediation effectors [24]. Most bioremediation studies using *S. cerevisiae* involve the excellent biosorption capacity of yeast cells [25]. However, most of the bioremediation approaches that involved *S. cerevisiae* utilized either dead biomass [24] or live cells with improved biosorption properties [26] rather than metabolically active as hyperaccumulating cells. It is generally accepted that the ideal living bioremediator would be tolerant to high concentrations of the metal pollutant and at the same

time would be hyperaccumulate it, preferably in a cell compartment or sequestered in a chelated nontoxic form [27]. The property of nonliving biomass to accumulate heavy metals ions, called biosorption, has been known for several decades [28].

Yeasts are known for their ability to accumulate metal ions from aqueous environmental solutions by different physico-chemical interactions, through adsorption and absorption, or by a metabolism-dependent mechanism [29]. Brady et al. [30] proved that the cells of *S. cerevisiae* treated with hot alkali were capable of accumulating a wide range of heavy metal cations (Cu^{2+}, Pb^{2+}, Cd^{2+} and, Ni^{2+}). Some toxic metal ions studied in *S. cerevisiae* biosorption are Pb [31], Cu [32] and Cd [31. This kind of property makes *S. cerevisiae* useful not only for the bioremediation, removal and recovery of metal ions, but also for their analytical measurement [33]. Mapolelo and Torto [34] proved that biosorption of Cd^{2+}, Cu^{2+} and Pb^{2+} by *S. cerevisiae* is dependent on optimum pH values above 5. The optimal concentration of Cu^{2+} ion in the nutritive medium for the yeast growth is in the range of 1–10 μM [35] and over is also toxic [36]. Some trace metals are present in soil environment as natural nutrient, introduced to soil through weathering processes, and mostly originate from a variety of anthropogenic activities. However, the pollution properties of trace metals in the soils have become an important problem due to their toxic effects, accumulation, and concentration through the food chain [37].

The introduction of trace metals into the environment is capable of having ecotoxicological impacts on the natural environment including the biotic factors [38]. However, trace metal toxicity mainly depends on the metal speciation and bioavailability, as well as uptake, accumulation, and excretion rates of the living organisms [39]. Benson et al. [40] established that safe disposal of domestic sewage and industrial effluents should be recycled to minimize the level of metals introduced into coastal water ecosystems.

Trace metal ions play an important role in the bioprocesses of living organisms. Depending on the living organism type, its age, physiological developmental phase, habitat conditions (e.g., temperature, pH, etc.), the physic-chemical properties of the trace metal and the co-occurrence of other metal ions and chemical compounds, the toxic contents of the trace metals may be varied. The accumulation of metal by yeast is affected by several factors such as pH, redox potential (Eh), presence of anions, cations and soluble organic compounds. Some of these factors can act at different levels simultaneously. For instance, pH of the solution affect the percentage of ionized groups of yeast cell wall; at low pH, the increase of protonation of yeast cell wall ligands decrease metals adsorption [41]. Simultaneously, pH affects metal speciation [42] and consequently the available metal to be sequestered by the microbiomes. The presence of anions (carbonates, chlorides, fluorides, phosphates and sulphates) in solution can complex metal ions and thus reduce or inhibit their adsorption to *S. cerevisiae* [43]. Heavy metals can also be complexed by organic compounds and these soluble ligands can compete with the cells for the metals, reducing the efficiency of heavy metals removal [6]. Redox potential can also affect the speciation of a given element; for example, Cr exists as Cr(VI) or Cr(III) according to the Eh of the solution. The presence in solution of other cations besides the metals of interest can reduce heavy metals accumulation by biomass, by competition for binding sites on yeast cell wall [44]. Mapolelo and Torto [34] showed that trace enrichment of the metals with yeast, depends upon the amount of yeast biomass, pH and incubation time. Yeast biosorption largely depends on parameters e.g., pH, the ratio of the initial metal ion and initial biomass concentration, culture conditions, presence of various ligands and competitive metal ions in solution and to a limited extent on temperature. An assessment of the isotherm equilibrium model, and the kinetics was performed. Pasternakiewicz [45] mentioned that the negative effect of Cd^{2+} ions on the growth of *S. cerevisiae* was partly altered by supplementing the YM medium with Ca or Zn compounds.

The main reaction for heavy metal to be combined with the microbial surface can be described as an ion-exchange reaction between heavy metal and Ca^{2+}, Mg^{2+} or K^{+} in the cell wall. This reaction is also observed in yeast [46]. Temperature, pH, the number of yeast cells and their physiological activity as well as the presence of other ions in the medium may exert a significant effect on the dynamics of Mg biosorption by cells [47]. Mapolelo et al. [48] showed that the interaction between trace metals and yeast was dependent on the pH and available metal ions. Enrichment time of 30 min gave an optimum metal uptake. The presence of Na^{+}, K^{+}, and Ca^{2+} suppressed the uptake of Pb by less than 5%, Mg^{2+} suppressed the uptake of Pb by between 25 and 35%. For both Pb and Cd had the highest suppression of 35 and 30%, respectively for *S. cerevisiae*.

The aim of the present investigation is to examine the tolerance of two *S. cerevisiae* strains to the toxicity of Cu^{2+}, Cd^{2+}, and Pb^{2+}. Secondly, to study the functioning of divalent Ca^{2+} and Mg^{2+} metals to correct the negative impacts of heavy metals on yeast growth and multiplication and the ability of these strains to be environmental bioremediators.

MATERIALS AND METHODS

Yeast strains, medium and culture conditions

In vitro, from our gene bank, two strains of yeast belonging to *Saccharomyces cerevisiae* (GCB-30-96

and GCB-45-96) isolated from sandy brown forest soil amended with 30 and 45% sewage sludge were investigated in order to estimate their maximum and tolerance to metals (lead nitrate: $Pb(NO_3)_2$, cadmium sulphate: $3CdSO_4.8H_2O$, and copper sulphate: $CuSO_4$) as well as the synergistic effect of calcium hydrogen carbonate: $Ca(HCO_3)_2$ and magnesium sulphate: $MgSO_4.7H_2O$ at 100 mM. The strain cultures were maintained on a solid yeast medium (YPD) containing: 20 g D-glucose, 10 g bactopeptone, 5 g yeast extract and 20 g agar in 1 litre distilled water.

Inoculant preparation

For refreshing, the 2 strains were re-inoculated from agar slants into 50 ml YPD broth in 150 ml Erlenmeyer flasks.

The biomaterials were incubated at 28℃ and horizontally shake at 150 rpm for 24 h. Then 200 ml of sterile broth of YPD in 500 ml Erlenmeyer flasks were inoculated with 10% of the obtained inoculants. Flasks were shaken on a rotary shaker at 150 rpm and 28°C for 24 h. Such prepared inoculants were used in further experiments. The unities of the yeast biomaterials were adjusted to be 2.2 x 10^8 CFU ml^{-1} by measuring the absorbance of cell suspension at 570 nm (OD_{570}) to be equivalent to 0.3. To prevent metal contamination in further investigations, all glassware were soaked in 0.1 N HNO_3 and rinsed three times with deionized water before complete drying.

Preparation of cell suspensions

After the 24 h incubation, cells were removed culture broth by centrifugation (3000 × *g*, for 7 min), washed twice with 30 mM ethylenediaminetetraacetic acid (EDTA) solution (to remove the ions bound to the cell surface), once with deionised water and then with 10 mM MES-Tris (2-(N-morpholino)ethanesulfonic acid)-Tris pH buffer at pH 6.0. MES-Tris is a suitable pH buffer for heavy metal uptake studies, since it does not complex several metal ions [49, 50].

Also, the cell density was determined always using spectrophotometrical method at 570 nm, after dilution of the samples in 100 mM EDTA.

pH and biomass production

Yeast cultures were cultivated in YPD broth with different pH range from 4.0 to 6.0. The pH adjustment was done with HCl or NaOH.

Growth rate

In the course of cultivation, the yeast growth was determined at 48-hour intervals (0, 3, 6, 12, 24 and 48 hours) turbidimetrically, by measuring the optical density of cell suspension at 570 nm wavelength.

Impact of trace metals on tolerance and the biomass production

Similar to the method used for growth rate, the YPD broth media of the 2 yeast cultures were enriched with various concentrations (0, 5, 10, 20, 40, 80, 160, 320, 640 and 1280 µM) of Cu^{2+}, Cd^{2+}, or Pb^{2+} ions in their salt compounds. During the incubation, the growth of yeast strains was controlled by measuring the absorbance of the culture.

Synergistic effect of Ca and Mg

The addition of 100 mM $Ca(HCO_3)_2$ or 100 mM $MgSO_4$ in the growth broth medium before addition of different concentrations of Cu^{2+}, Pb^{2+} and Cd^{2+} illustrates a protective action against cell death and decreased the toxicity effect of the tested trace metals. Similar method of incubation and growth rate measurement was done as mentioned above.

Statistical analysis

Results are expressed as the average values of 3 replicates per each treatment. Application of Cu^{2+}, Pb^{2+}, and Cd^{2+} ions were established by different statistical methods.

RESULTS AND DISCUSSION

Rate of growth

The pH of the used media was established according to the maximum given at the investigated pH experiment. Figures 1, 2 and 3 illustrate the growth rate of 2 yeast strains in the YPD broth contaminated with Pb, Cd and Cu, respectively after 48 h incubation in horizontal shaking incubator with 150 rpm at 28°C.

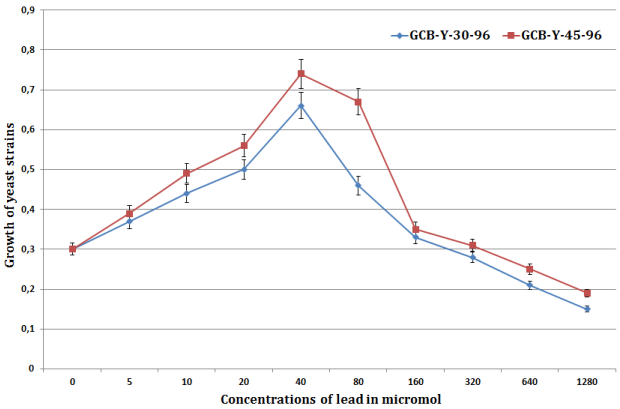

Figure 1

Effect of lead ions in $Pb(NO_3)_2$ at different concentrations on the growth of yeast cultures (at 570 nm) isolated from 30 (GCB-30-96) and 45 (GCB-45-96) % sewage sludge treated sandy brown forest soil.

The shape of the absorbance curve during the growth of the two cultures indicates the inhibition of yeast cell reproduction of both strains was started at at the concentration 160 µM (Figure 1) of Pb.

The maximum growth of both strains was detected at 40 µM while the strain GCB-45-96 can tolerate 320 µM of Pb and GCB-30-96 can tolerate 160 µM.

In Figure 2, the results indicated that maximum growth of both strains where found at 160 µM of Cd and both of them were inhibited at 1280 µM. Both strains can tolerate the Cd concentration of 320 µM.

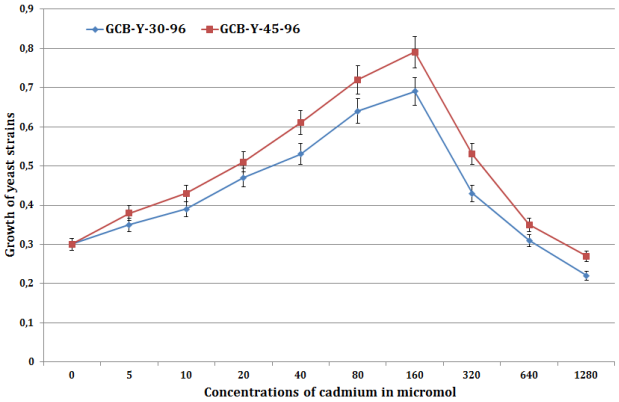

Figure 2
Effect of cadmium ions in $CdSO_4$ at different concentrations on the growth of yeast cultures (at 570 nm) isolated from 30 (GCB-30-96) and 45 (GCB-45-96) % sewage sludge treated sandy brown forest soil.

In Figure 3, it was found that maximum growth for both strains was at 40 µM and tolerated 160 µM as well as inhibited at 320 µM of Cu.
Figures 4, 5 and 6 show the effect of adding Ca before contaminating the cultures of the two strains.

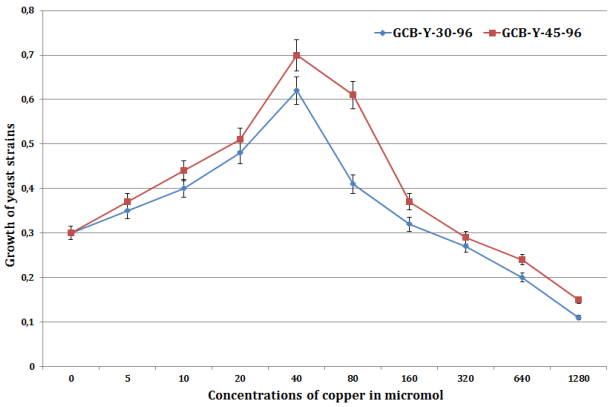

Figure 3
Effect of copper ions in $CuSO_4$ at different concentrations on the growth of yeast cultures (at 570 nm) isolated from 30 (GCB-30-96) and 45 (GCB-45-96) % sewage sludge treated sandy brown forest soil.

Figure 4 shows that maximum growth of both strains was found at 80 µM and both strains were inhibited at 1280 µM of Pb in the presence of 100 mM of $Ca(HCO_3)_2$ and can tolerate 640 µM of Pb under the effect of Ca ions.
Figure 5 illustrates the effect of adding $Ca(HCO_3)_2$ before contamination the growth broth media of both strains with cadmium salt.
It was found that maximum growth of both strains was found at 80 µM of Cd in the presence of Ca ions.

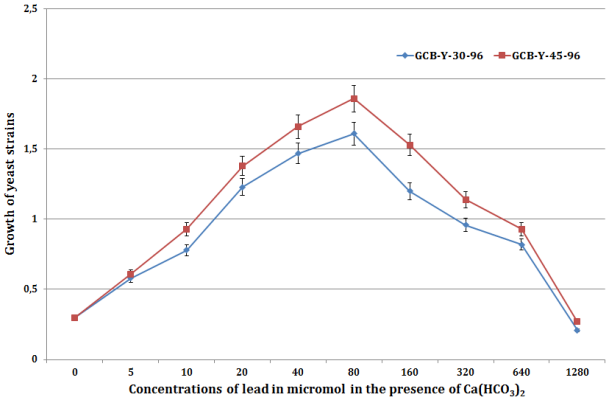

Figure 4
Synergism between calcium and lead ions in $Pb(NO_3)_2$ at different concentrations on the growth of yeast cultures (at 570 nm) isolated from 30 (GCB-30-96) and 45 (GCB-45-96) % sewage sludge treated sandy brown forest soil in the presence of 100 mM of $Ca(HCO_3)_2$.

Also, Figure 5 shows that both strains were inhibited at 1280 µM and can tolerate 640 µM of Cd salt in the presence of Ca salt.

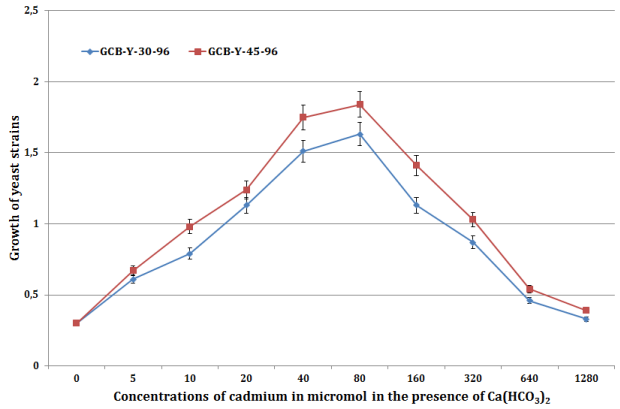

Figure 5
Synergism between calcium and cadmium ions in $CdSO_4$ at different concentrations on the growth of yeast cultures (at 570 nm) isolated from 30 (GCB-30-96) and 45 (GCB-45-96) % sewage sludge treated sandy brown forest soil in the presence of 100 mM of $Ca(HCO_3)_2$.

Figure 6 demonstrates that both yeast strains give the maximum growth at 160 µM of the Cu concentration. Meanwhile, the 2 strains were inhibited at 1280 µM and tolerate the concentration 640 µM of Cu salt in the presence of Ca salt.
Figures 7, 8 and 9 show the effect of Mg salt on the toxicity of Cu salt application in the broth media inoculated by yeast strains.
Figure 7 illustrates the protective effect of Mg salt against the effect of Pb salts on the growth of the yeast strains.
It was found that maximum growth rates of both strains were found at the concentration 80 µM while 1280 µM inhibit and decrease the growth of both strains lower than the control.

Also, it was found that both strains can tolerate 640 µM.

Figure 8 indicate that Cd at 160 µM both strains were at the maximum growth and inhibited when the concentration was increased to 1280 µM. Both strains can tolerate 640 µM of Cd in the presence of Mg ions.

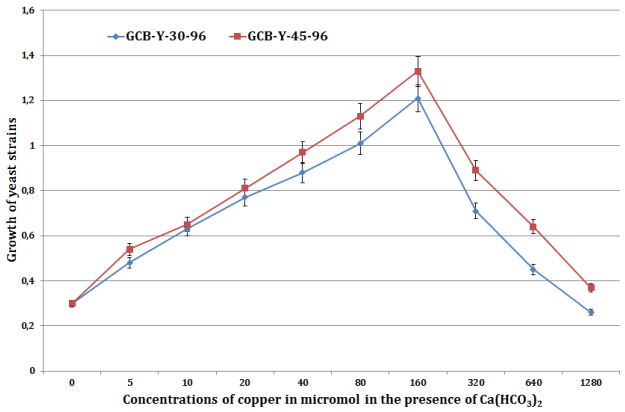

Figure 6

Synergism between calcium and copper ions in $CuSO_4$ at different concentrations on the growth of yeast cultures (at 570 nm) isolated from 30 (GCB-30-96) and 45 (GCB-45-96) % sewage sludge treated sandy brown forest soil in the presence of 100 mM of $Ca(HCO_3)_2$.

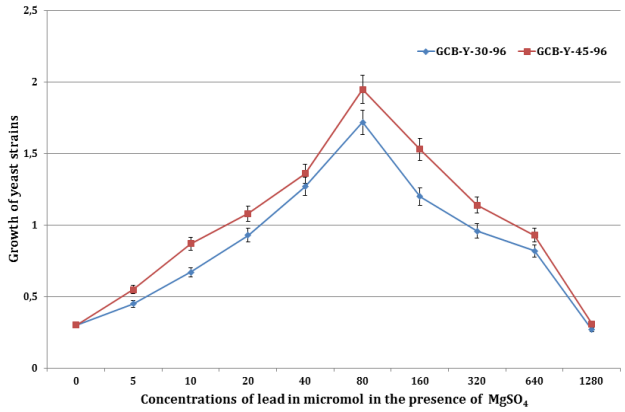

Figure 7

Synergism between magnesium and lead in $Pb(NO_3)_2$ ions at different concentrations on the growth of yeast cultures (at 570 nm) isolated from 30 (GCB-30-96) and 45 (GCB-45-96) % sewage sludge treated sandy brown forest soil in the presence of 100 mM of $MgSO_4$.

Figure 9 shows that maximum growth rates of the yeast strains were found at 160 µM of Cu salt in the presence of Mg salt and they can tolerate 640 µM while 1280 µM reduced the growth of both strains lower than the controls.

A second assay in the present study was performed to understand whether the addition of Mg or Ca (ions fron their salts) to the medium influenced growth of both strains.

It was found that 100 mM Mg concentration was tested with the different concentrations of different Pb, Cd and Cu concentrations.

The results indicated that both Ca and Mg extend the rate of growth, the tolerance and the inhibition degree to be more than their values as they are in the tubes of the trace metals only.

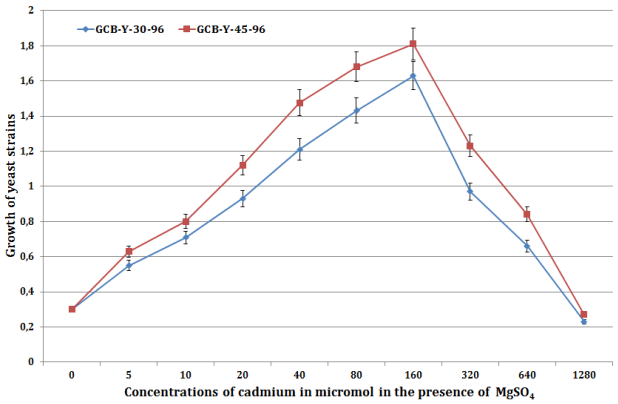

Figure 8

Synergism between magnesium and cadmium ions in $CdSO_4$ at different concentrations on the growth of yeast cultures (at 570 nm) isolated from 30 (GCB-30-96) and 45 (GCB-45-96) % sewage sludge treated sandy brown forest soil in the presence of 100 mM of $MgSO_4$.

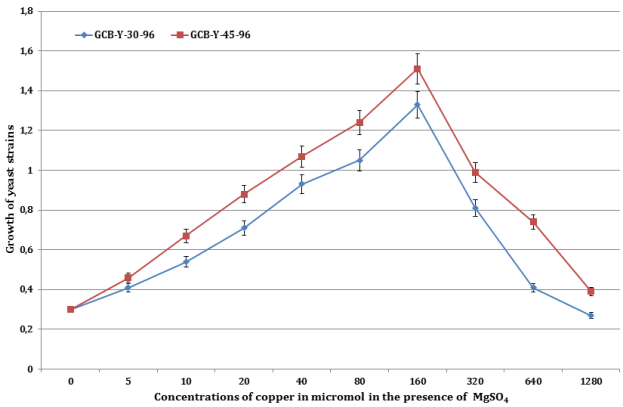

Figure 9

Synergism between magnesium and copper ions in $CuSO_4$ at different concentrations on the growth of yeast cultures at 570nm isolated from 30 (GCB-30-96) and 45 (GCB-45-96) % sewage sludge treated sandy brown forest soil in the presence of 100 mM of $MgSO_4$.

As heavy metal bioremediator, the yeast cells can act essentially in two ways: binding the cations to the cell surface (biosorption) and accumulation of cations inside the cell via metabolic transport.

Most of the bioremediation studies involving *S. cerevisiae* focused mainly on cell surface properties and biosorption by dead biomass [24] by living cells with improved biosorption capacity [26] or with engineered cell surface [51].

A similar upward trend in the yeast growth rate was found at 24, 48, and 72 hours after inoculation across treatments. The continuation of the growth rate was consistent and dose related.

Yeasts have ability to bioaccumulate minerals from aqueous solutions, from which they permanently incorporate these metal ions into own cellular structures owing to their high concentration of protein [52]. Yeast cells incorporate double-valence metals through mechanisms including production of metalloproteins, mineralization and capture of metals into vacuoles [53]. Numerous studies about the processes involved in the uptake of trace metals by the yeast *S. cerevisiae* as a model organism for investigating metal bioaccumulation in the cells have been conducted in recent years [54].

When Cu^{2+} ions increase further in the environment, they are accumulated in excess through a low affinity transport system [55]. In *S. cerevisiae* resistance to Cu^{2+} is associated with the production of a metal-binding protein mineralization [55] and sequestration to the vacuoles [56], leading to a reduction in the cytoplasmic concentration of a free Cu ion. Eide [56] established that metal ion uptake systems of cells are tightly controlled. Most importantly, studies of *S. cerevisiae* have identified a large number of genes that function in metal ion transport and have illuminated the existence of importance of gene families that play related roles in these processes in mammals.

A Cd-binding protein in the Cd^{2+}-resistant strain 301N of *S. cerevisiae* was induced by administration to 0.5 mM $CdSO_4$ [57].

The common yeast *S. cerevisiae* has been used to remove Pb [58] and Cu [59] from their aqueous solutions. The toxicity decreasing order of the investigated trace metal salts on the experimental microbiome yeast strains was found to be $Cu^{2+} > Pb^{2+} > Cd^{2+}$. Ca^{2+} was found to depress Cd^{2+} uptake strongly. Mowll and Gadd [60] reported similar findings and proposed that Cd^{2+} was accumulated via a Ca^{2+} transport system.

CONCLUSION

The addition of 100 mM $Ca(HCO_3)_2$, or 100 mM $MgSO_4$, in the growth broth medium before addition of Cu^{2+}, Pb^{2+} and Cd^{2+} illustrates a protective action against cell death and decreased the toxicity effect of the tested trace metals. The addition of alkaline earth metals reduced the effect of all tested trace metals.

Our results are consistent with data obtained for different strains of biomass which indicate that the cell surface is a complex, heterogenous matrix containing an array of possible different metal-binding sites. Further task is going to examine the range of metal bioaccumulation in the yeast cells and the ability of these strains to be environmental bioremediators.

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DETERMINATION OF HEAVY METAL CONTENT OF RIVER SEDIMENT AND ANALYSIS OF THE ACCUMULATION OF HEAVY METALS BY PLANTS

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Received: November 2016

Abstract

Heavy industrial pollution along the river bank of Danube had effected on the water quality. The heavy metal content of the industrial sludge and sewage water could pollute sediment on the bottom of the river Danube. The inflow of surface water can modify the heavy metal content of the water and the muddy sediment of the Open Beach in Dunaújváros. The main aim of this research is to analyse the heavy metal content of the sediment dump of Dunaújváros. The dump was created by excavation from the Open Beach of Dunaújváros in 2009, because the local municipality wanted to improve the water quality of the Beach with this process. In 2010 the whole sediment dump was planted with trees. The regular sediment analysis was made on four measuring points in the middle part of the dump every second weeks in April and November of 2015. Among the heavy metals iron, lead, cadmium, copper, zinc and nickel were measured. Results were compared to the standard levels of the Hungarian regulations. Results showed that seasonal changes can be observed in the concentrations of heavy metals and sometimes these values exceed the Hungarian standard levels both in the case of the sediment and plants growing on the dump.

Keywords: *heavy metal, river sediment, plant, accumulation*

INTRODUCTION

It is known that the floodplains and oxbow lakes along the rivers mean important ecological merits or corridors for the fauna and flora. They are often used for touristic purposes, so their protection or remediation is very relevant in these days because of the previous or recent industrial or communal pollution. In the case of river Danube, it was polluted mainly by the industrial plants. One of the most serious groups of toxic elements is the heavy metals, which are the focus point of this research.

The sources of the heavy metals are the natural inputs and anthropogenic emissions [1]. Heavy metal concentrations in waters have been analysed worldwide, but there are few publications on their concentrations in rivers of the Danube [4, 10] in Hungary.

The main aim of this research is to determine the seasonal changing of the heavy metals concentrations in the river sediment horizontally and vertically. Furthermore the heavy metal content of the plants which are growing on the sampling site is also analysed. The correlations or mobilization between the toxic elements of the sediment and plants and the accumulated quantity of the heavy metals were also determined. This method can be very useful for accumulate the toxic element from industrial or river sediment. It can be also adequate for the recycle of metals or rare earth metals from industrial sludge.

MATERIALS AND METHODS

The analyses were made on the sediment dump of Dunaújváros, which is located on the northern part of the town. This dump was made in 2009, when the local municipality wanted to rehabilitate this old Open Beach area of the town, therefore the sludge of this beach was dredged out into the floodplain which is located on the right side of the river Danube. In the southern part of the dump a stream flows, which is ended in the river Danube. In addition, a water channel surrounds the whole dump.

The regular sediment analysis was made on four measuring points (M1 - M4) in the middle part of the dump every second weeks in April and November of 2015. The measuring points are shown in the Figure 1.

The area of the sampling points was 1 m². The sediment samples were collected from the depth between 10 and 20 cm with a standard soil sampler.
The GPS coordinates of the measuring points are:

- M1: 46° 59' 22,8" N; 18° 56'31,4" E
- M2: 46° 59' 21,7" N; 18° 56'32,3" E
- M3: 46° 59' 20,9" N; 18° 56'33" E
- M4: 46° 59' 22,3" N; 18° 56'39" E

Figure 1
Automotive industry Foundry in Kikinda

The extraction of the heavy metal content of the river sediment was made with acidic destruction according to the MSZ 12739/4-78 Hungarian Standard [2]. At first, following the directions of the Standard, the organic parts were removed and the samples were dried. Thereafter, during the destruction process, the heavy metal content was extracted with concentrated nitric acid and hydrogen-peroxide of 35% from the dried samples in a rotating evaporator. After the filtration, the concentration was analysed with atomic absorption spectrometer (AAS, Perkin Elmer AAnalyst 400). Among the heavy metals iron, lead, cadmium, copper, zinc and nickel were measured. The flow chart of the destruction process is shown in the Figure 2.

From the concentration of the filtered samples, the extraction loss and the loss of the continuous heating the final concentration of heavy metals can be calculated in mg/kg with using the following equation (1):

$$c = \frac{c_0 \cdot V}{(1 - s \cdot i) \cdot m} \qquad (1)$$

Where

- c_0: concentration (mg/l) of the extracted and filtered samples, which is measured by the atomic absorption spectrometer
- V: volume of the extracted samples (l)
- s: quotient of the mass of the residue of the acidic extraction (g) and the mass of the calibration sample (g)
- i: quotient of the mass of the residue of the continuous heating (g) and the calibration sample before the continuous heating (g)
- m: mass of the sediment sample before the acidic extraction (kg)

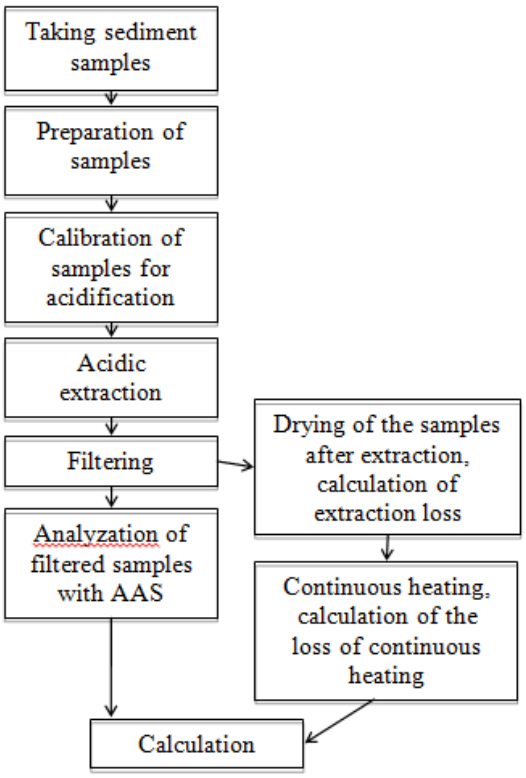

Figure 2
The flow of the extraction of heavy metals from sediment

For the determination of the heavy metal content of the plants the samples were also destructed with concentrated nitric acid and hydrogen peroxide [9]. For this analysis, perennial rye-grass *(Lolium perenne)* samples were collected from the four measuring points (M1-M4). During the preparation process the main parts of the plants such as roots and shoots were washed with deionised water, and then they were dried. After that the plants were cut into pieces which were smaller than 1 mm. These small parts were treated with concentrated nitric acid for 12 h on room temperature (20 ± 2°C). Finally, the samples were extracted with hydrogen peroxide during additional 3 hours on 110 ± 2°C, were filtered and completed to 50 ml. The heavy metal concentration of the samples was measured by atomic absorption spectrometer (AAS).

Beside the destruction and measurement of the heavy metal content of samples seedling growth test was also made with using white mustard seeds *(semen sinapis albae)* as test plant. For this experiment, dried river sediments were calibrated into Petri dishes. Moreover mixtures of the river sediment and chernozem soil

were also used in the rate of 20-, 40-, 60-, 80 and 100 %. In every Petri dish 20 pieces of seeds were dispersed. After the setting of the moisture content the samples were covered and incubated for 72 hours in a dark place. At the end of the experiment the number of the pullulated seeds and the length of radicles and plumules were counted.

RESULTS

Vertical cadmium (Cd) content of the sediment

Based on the Figure 3 it is determined that the cadmium content was exceeded the Hungarian standard level (1 mg/kg) [5].

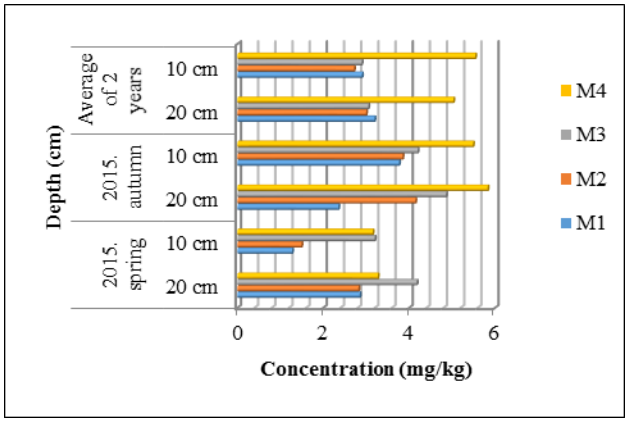

Figure 3
Cadmium content of the measuring places according to seasons

The cadmium concentration was higher in in the autumn season. The change of the concentration was not discovered between 10 and 20 cm. According to the horizontal distribution of cadmium, it can be said that higher concentration was measured in the case of M3 and M4 measuring points in autumn.
The cadmium content was similar to the average content of the previous years. [6, 7] The seasonal change can be shown in the Figure 3, the cadmium concentration increased until autumn.

Vertical lead (Pb) content of the sediment

The Hungarian standard level for lead content is 100 mg/kg [5]. Based on our previous research it is very important that in 2010 every layer contained lead, but in 2015 just in the upper 10 cm layer of the M1 sampling point was detected lead content in the sediment (Figure 4.). This value was twice as greater (222.5 mg/kg) than the standard level. In this case, among the four measuring points, the first, M1 was the most polluted place. According to our results, the lead content of the sediment was higher in April than in November. Additionally, the lead content was different from the average content of the previous years, because at that time lead was detected from every layer from every sampling point. The concentrations were higher than in 2015. [6,7]

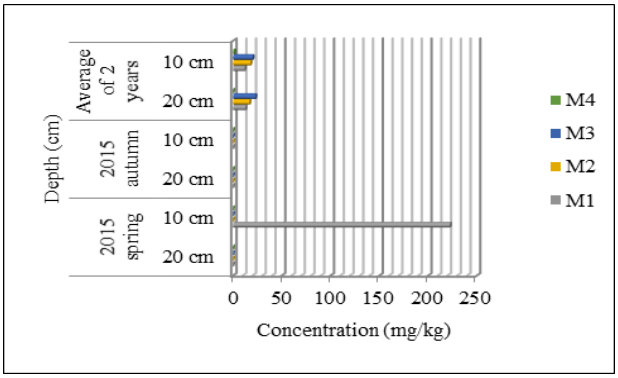

Figure 4

Lead (Pb) content of the measuring places according to seasons

Vertical copper (Cu) content of the sediment

Accordance with the vertical distribution of the copper content of the sediment it was obtained that the concentration in spring was higher than in autumn (Figure 5.).

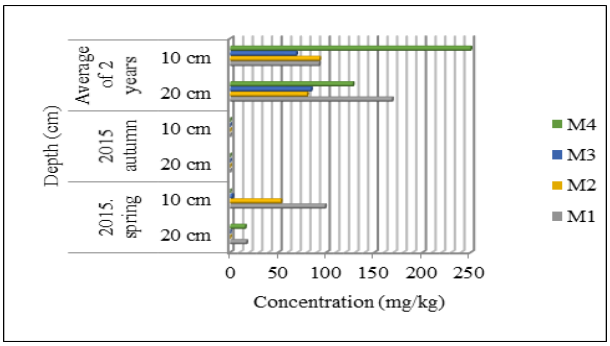

Figure 5

Copper (Cu) content of the measuring places according to seasons

Vertical zinc (Zn) content of the sediment

From results in Figure 6., it is clear that the zinc concentration of the river sediment was higher in April of 2015, than in November. The zinc element could be detected between the 10 and 20 cm depth in this time only. The layer of 0-10 cm did not contain any zinc. On the other hand, the distribution of this pollutant was changed until November, because it was measured just in the 0-10 cm layer at M4 point. The concentration here was 65 % of the zinc content of April of the same point. In the case of M1 and M3 points zinc content was not detectable.
The Hungarian standard level of the sufferable zinc concentration in soils is 200 mg/kg [5]. The given data

of the M1 and M4 measuring points exceeded this standard level, sometimes they were treble of the acceptable level.

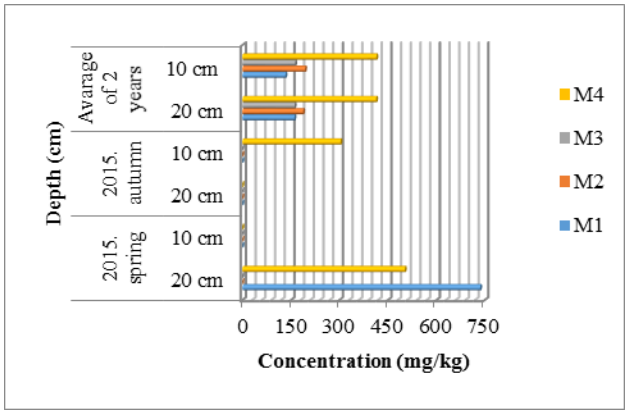

Figure 6

Zinc content of the measuring places according to seasons

The average of the previous years was higher [6, 7]. In the case of M1, M2 and M3 points zinc could be measured. On the other hand, the result of the M4 point was higher in spring and lower in autumn like the average.

Vertical iron (Fe) content of the sediment

When we analysed the iron content of the sediment, we could always detect this element in every layer at every measuring points (Figure 7). Hungarian standard level [5] does not contain standard level for the iron concentration of soils, so we could use the results of the Joint Danube Survey [4].

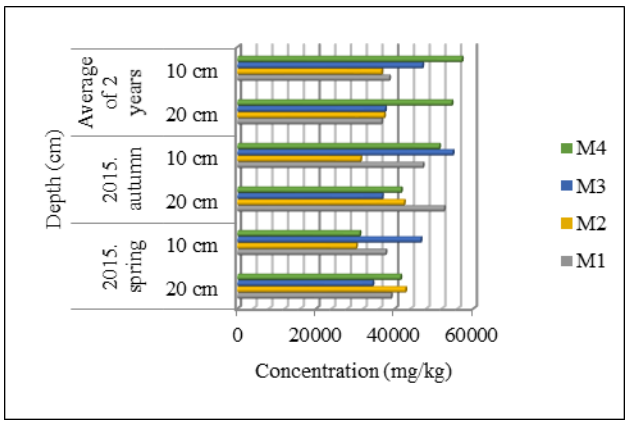

Figure 7

Iron content of the perennial rye-grass samples

This survey contained the iron content of the sediment of the river Danube according to river kilometres. Data were found at Adony and Dunaföldvár, which location are very close to Dunaújváros, so we compared our data to the concentrations, which were determined in these two places. Our results were around double (25 g/kg) of the results of the Joint Danube Survey [3]. About the Figure 7, we can see a seasonal increase of the iron concentration in the case of the upper layer. In the layer of 10-20 cm, same level was measured in spring and in autumn. The results of 2015 were similar to the average results [6, 7], remarkable change could not be observed among the data.

Vertical nickel (Ni) content of the sediment

Any nickel concentration was observed at every sampling point.

The heavy metal content of perennial rye-grass (Lolium perenne) samples

For the determination of the heavy metal content of the plants, we took samples from perennial rye-grass *(L. perenne)*, which grew on the measuring field.

The leaves of the plants were used for the analysis. After the destruction, the filtered liquid samples were measured in atomic absorption spectrometer (AAS) [9].

The sufferable standard levels of the element in plants were determined in the Hungarian Forage Codex [5].

At first the Cd content of the perennial rye-grass was measured. According to our results (Figure 8) the Cd could be detected in the M1, M3 and M4 samples. The samples of the M2 measuring point did not contain Cd. The standard level for Cd is 0.5 mg/kg in Hungary [5]. When our data are compered to this standard value, the samples of the M1 point is higher, the other results are lower than this level.

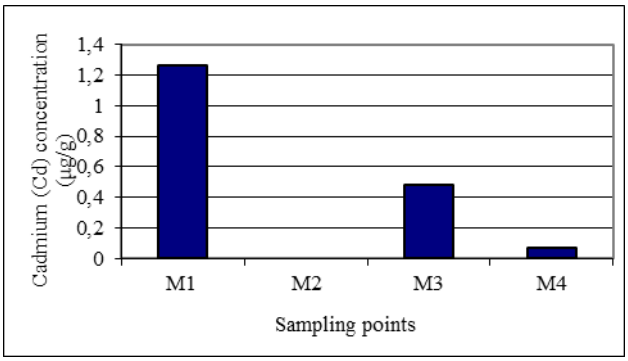

Figure 8

Cadmium content of the perennial rye-grass samples

Figure 9 shows that the copper content of the plants can be seen. Copper could be detected at every measuring point (M1-M4). Among the samples the M1 and M3 samples were higher. When these data were compared to the Hungarian standard value (35 mg/kg) [5], every sample exceeds this value except for the sample of the M2 point.

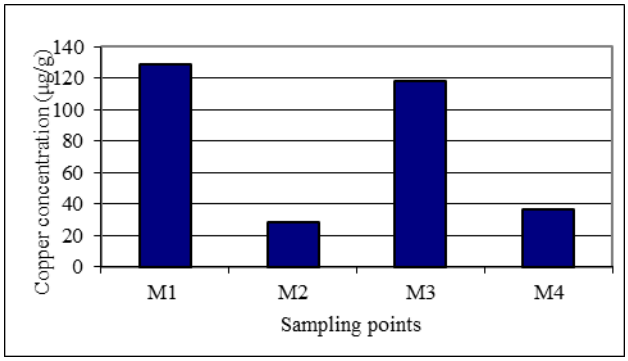

Figure 9

Copper content of the perennial rye-grass samples

The results of the measurement of zinc content were shown in Figure 10. The highest concentration of Zn was found in the sample of M3 point. The Hungarian standard value for this element is 250 mg/kg [5]. Based on our given data it can be seen, that the values of the M1, M3 and M4 points are higher than the standard level.

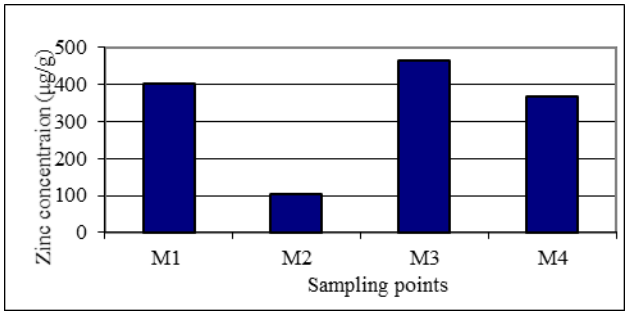

Figure 10

Zinc content of the perennial rye-grass samples

Finally, the iron content of the plants was analysed (Figure 11). The lowest iron concentration was detected in the case of the M2 point. The highest iron contents were measured at the other points.

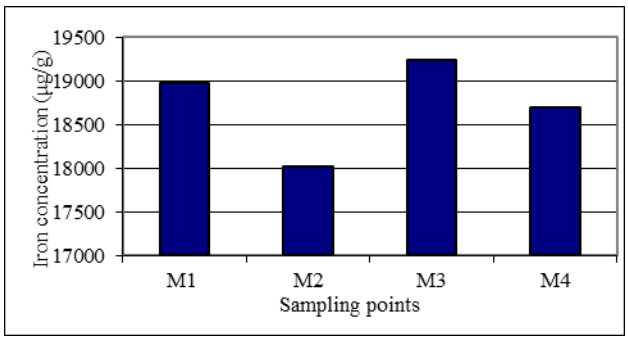

Figure 11

Iron content of the perennial rye-grass samples

Distribution of the heavy metal contents in the sediment and the prennial rye-grass samples

In autumn of 2015, both sediment and the perennial rye-grass samples were taken from the river sediment dump of Dunaújváros. After the determination of the heavy metal content of these samples we could calculate the distribution of the measured element between the sediment and the grass samples. The results of the depth layer of 10 cm of the sediment were applied in calculation. In the Figure 12, the ratio of the cadmium concentration is shown.

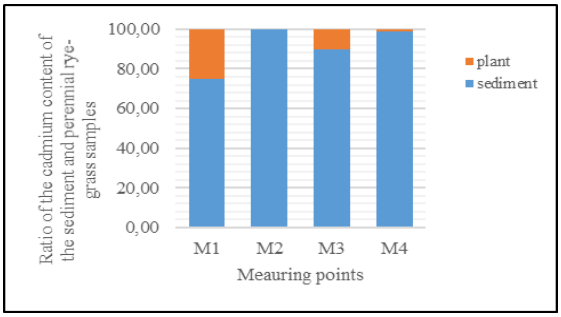

Figure 12

The distribution of the cadmium content

It can be determined that in the M2 measuring point the whole cadmium content was detected just in the sediment. In the case of the other sampling points the cadmium concentration could be measured both in the sediment and the plants. Between these points at the M1 place the highest concentration could be detected in the plants. At M3 and M4 places lower cadmium concentration could be accumulated in the leaves of the perennial rye-grass samples.

In the Figure 13, the accumulation of the zinc can be seen. Zinc accumulated only in the plants at the M1, M2 and M3 sampling points. Just in the sediment of the M4 point zinc could be detected. About half of the zinc could be accumulated in the leaves and the same content were measured in the sediment.

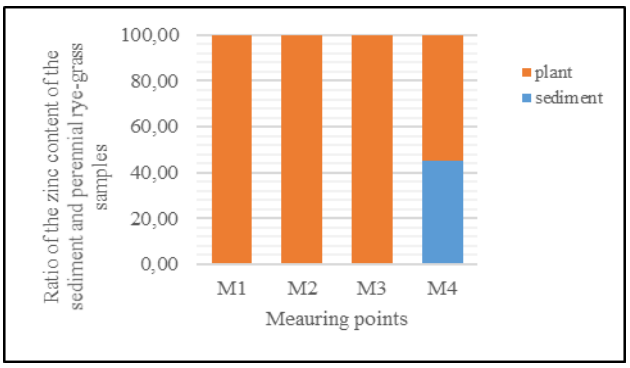

Figure 13

The distribution of zinc content

Based on the distribution of copper (Figure 14.) it is observed that copper was found just in the plants at every sampling point. In autumn of 2015 copper could not be detected in the sediment samples.

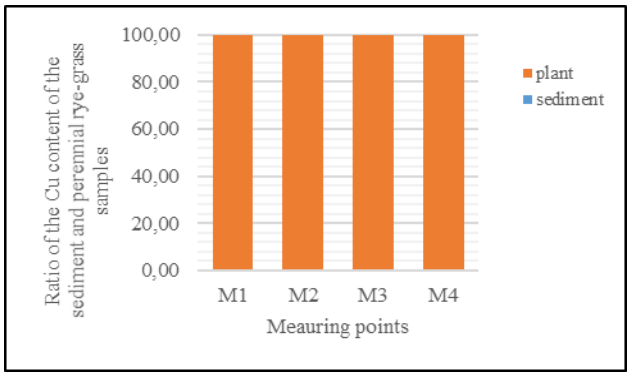

Figure 14

The distribution of copper content

At last the bioaccumulation of iron content can be seen in the Figure 15. Iron content could be measured at every point. In the basis of the results, 30-35% of iron was found in the leaves of the plants, and 65-70 % of iron was detected in the sediment samples.

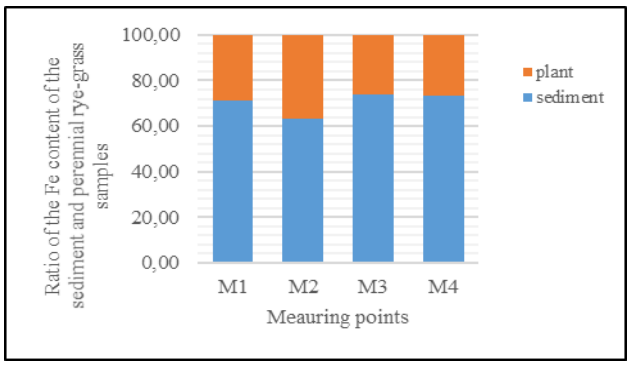

Figure 15

The distribution of iron content

The lead and the nickel could be not be detected neither in the sediment nor in the plants in the measuring time.

Seedling growth test with white mustard seed (semen sinapis albae)

The seedling growth test was made with white mustard seeds *(semen sinapis albae).* The number of the pullulated seeds were counted (Figure 16.) at the end of the experiment. [8]

It is determined that in average 17 pieces of seeds were came up from the potted 20 pieces.

During the experiment mixture of chernozem soil and river sediment was used. In these samples the mixing rate was 20, 40, 60, 80 and 100% of chernozem soil.

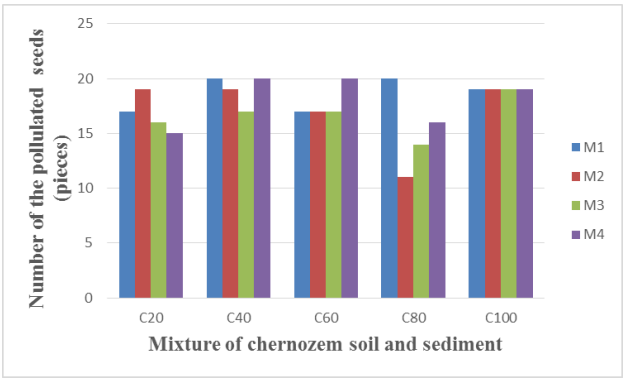

Figure 16

Number of the pollulated white mustard seeds

In the case of the M1 sampling point the highest number of pullulated seeds were measured in the C40 and C80 mixtures. The pullulated seeds of the M2 point were in the highest number in the mixture of the C20 and C40. According to the data of the M3 and M4 points, the most pullulated seeds were counted in the mixture of C40 and C60. The picture of this seedling growth test is shown in the Figure 17. The length of the radicles and plumules were also measured after the counting of the pullulated seeds (Figure 18-21.) for every measuring point. The length of the radicle was taller in the C20 and C40 mixtures when M1 sediment and the chernozem soil were mixed (Figure 18.).

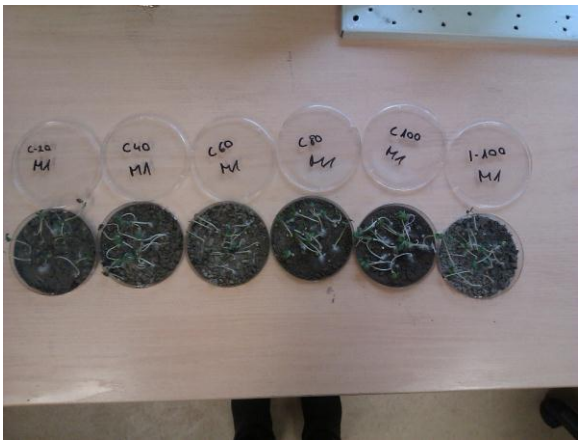

Figure 17

Picture of the polluted white mustard seeds

The tallest radicle was observed in the C100 mixture. The length of the radicle in C20 and C40 mixture was similar to the result of I100 (100 % sediment). The shortest radicles and plumules were measured in C60 mixture. The C60 mixture will be investigated later. In the case of the lengths of plumules similar results can be stated. When we used the M2 sediment samples for the seedling growth test the lengths were smaller than in the case of the sediment of the M1 point (Figure

19.). The length of the radicles and plumules decreased continuously from the C20 to the C80 mixture. It can be determined that the lengths were higher in the case of using the sediment of the M1 point.

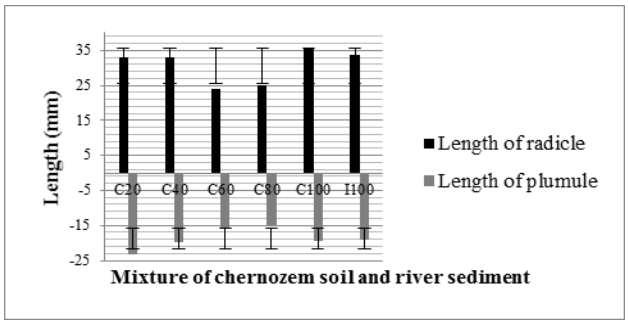

Figure 18

The length of the radicles and plumules of the M1 sampling points

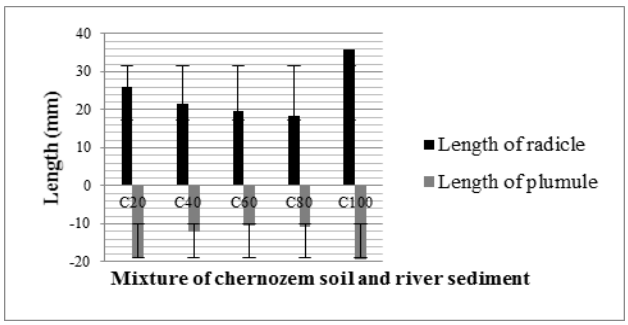

Figure 19

The length of the radicles and plumules of the M2 sampling points

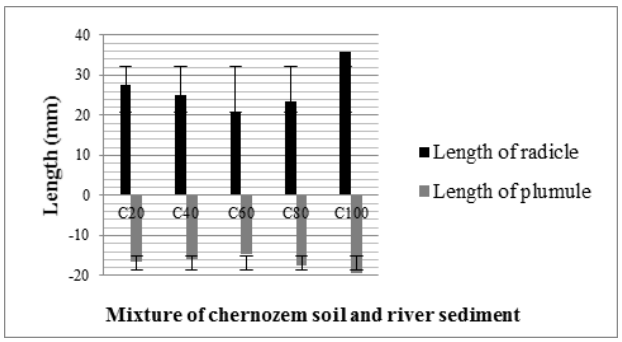

Figure 20

The length of the radicles and plumules of the M3 sampling points

The results from the mixture of the sediment of the M3 point and chernozem soil (Figure 20.) were similar to the case of the M1 point. The highest radicles were measured in the C20 and C40 Petri dishes.

On the Figure 21, the lengths of the radicles were very different from the other sediment samples. The highest lengths of radicles were observed in the mixture of C40 and C80. The length of the plumules decreased continuously from C20 to C80.

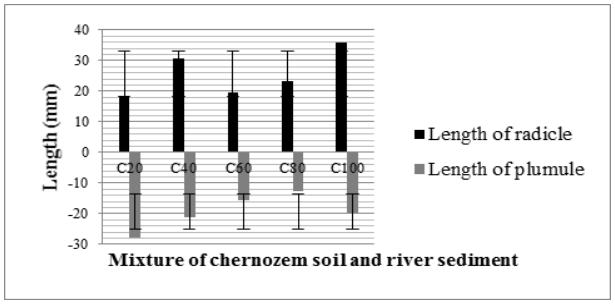

Figure 21

The length of the radicles and plumules of the M4 sampling points

The highest results were measured in the case of C100, which means 100 % of chernozem soil. It was more effective against the sediment (I100) or their mixtures.

SUMMARY

The main aim of this research is to determine the seasonal changing of the concentration of the heavy metals in the river sediment horizontally and vertically. According to our given data it can be stated that there is a seasonal change in the heavy metal content of the sediment. In the case of lead, copper and zinc the concentration decreased from April to November, 2015. Otherwise the cadmium and iron content of the sediment increased until autumn. When we compared our data to the Hungarian standard values, we could determine that the quantity of all of the measured pollutant was higher than the standard limit. In the case of lead, zinc and copper, the concentration was not detected in every month, but when we could measure these elements, the quantity exceeded the sufferable value. At least we analysed the vertical distribution of the heavy metal contents. The highest cadmium and iron concentration was measured at M3 sampling point. The highest zinc and lead content were detected at the M4 point. The highest concentration of copper was observed at M1 measuring point.

On the other hand, we tried to find connections or mobilization between the toxic elements of the sediment and plants. It can be determined that the perennial rye-grass can accumulate cadmium. The average values 10-15% of this element was detected in plants. In the case of zinc 45-100 % of this pollutant can be measured in the leaves. According to the copper results, we could detect copper only in plants. At last, we calculated the distribution of iron content. The

plants could accumulate 30-35% of the total iron content. Further goals are to find additional plant species, which will accumulate these toxic elements in higher ratio.

In the basis of the seedling growth test we could determine, that the 85 % of the potted seeds came up. For this experiment, we used mixture of the river sediment and chernozem soil. Among the mixture the C40 was the most effective for the four sediment samples. When we measured the length of radicles, the highest results were given in the case of the sediment of the M1 measuring point. On the other hand, the highest plumules could be measured from the samples of M1 and M3 sampling points.

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ANALYSIS OF DISPERSION OF GENERATED PAH IN PROCESS OF CASTING PARTS FOR AUTOMOTIVE INDUSTRY BY USE OF ADMS 5 SOFTWARE

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Received: November 2016

Abstract

Polycyclic aromatic hydrocarbons are compounds that are highly toxic and have mutagenic and carcinogenic properties. They are formed in pyrolysis reactions and pyrosynthesis, in situations of incomplete combustion of organic substances which contain carbon and hydrogen. Incomplete combustion occurs in situations when the combustion temperature is low or the concentration of oxygen is low. PAH can enter the atmosphere by burning agricultural residues, in fires, during combustion of fuel in manufacturing processes, etc. Plants for production of coke, carbon fuels, aluminum, steel and iron represent the dominant source of PAH in industrial processes. This paper presents data on simulation of dispersion of PAH resulting from production process of casting elements for the need of automotive industry, using the software for dispersion of pollutants in urban areas under commercial name ADMS 5.

Key words: *Polycyclic Aromatic Hydrocarbons, PAHs, ADMS 5, Dispersion of pollutant*

INTRODUCTION

Polycyclic aromatic hydrocarbons are formed as a result of incomplete combustion of organic matter, or matter that primarily contains carbon and hydrogen [6]. Incomplete combustion occurs in conditions of combustion at low temperatures and without sufficient quantities of oxygen. In the atmosphere, these PAHs can react with other polluting components such as ozone, nitrogen dioxide, sulfur dioxide, building up nitro and dinitro-PAHs and sulfuric acid [15]. Depending on the location and conditions of combustion, sources of PAHs may be of natural and anthropogenic origin [8].

Natural sources of PAHs are accidental fires which cause burning of forest fires, agricultural residues and coal and crude oil. Anthropogenic sources of these pollutants are products of human activities, mostly in manufacturing industry sectors, pollutants resulting from traffic, as well as pollutants generated by burning different types of fuel for energy needed for indoor heating. Anthropogenic sources can be divided into two large groups; sources where polycyclic aromatic hydrocarbons are result of combustion for energy production and the other group burning of waste or incineration [7].

In industrial production the most important sources of PAHs are processes of coking coal and industrial processes in production of aluminum, steel and iron, production of cement, oil refining, production of tires, bitumen, asphalt, etc. Whether or not they will remain in the atmosphere depends on molecular weight. PAHs with five or more aromatic rings are heavy PAHs, and with less than five rings – light PAHs [7]. Heavy PAHs are adsorbed on dust particles, while lighter remain in gas phase and are subsequently removed by precipitation. Length of transport of emitted PAHs in the air depends on this fact and by

deposition in rainfall; they can become a significant source of pollution of surface waters [5].
In legislation there are 16 registered PAHs, which represent priority pollutants such as: naphthalene, acenaphthylene, acenaphthene, fluorene, phenantherene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perilen and indeno(1,2,3-cd)pyrene [5].
The most toxic and proven as cancerous is benzo[a]pyrene (3,4-benzopyrene, BaP), and the overall exposure to this group of pollutants is determined through concentration of BaP [5].
In this paper dispersion of benzo[a]pyrene generated in production process of steel casting in Kikinda Foundry is estimated by use of software under commercial name ADMS 5 developed at the Institute of Cambridge, to simulate dispersion of pollutants in the air. Applied software for forming simulation uses the adapted Gaussian distribution model.

METHOD AND INPUT DATA

Emission of pollutants in Kikinda Foundry and measuring the concentration of pollutants is carried out in three places

- Dust collector from smelter MM01
- Dust collector from emptying grid and crusher MM02
- Dust collector from core machines MM03

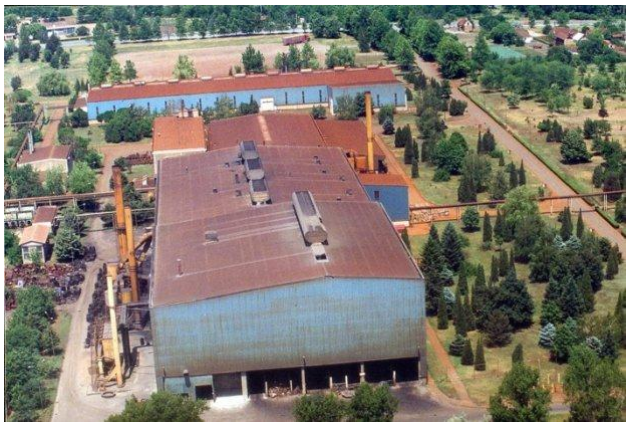

Figure 1

Automotive industry Foundry in Kikinda

At the source of emissions MM01 melting solid material of cartridge is performed in three medium frequency induction kilns to obtain liquid iron. In kiln number 1, capacity of 2,000kg, liquid steel casting is obtained for casting cast position INSERTA, in a kiln II and III capacity of 2,500kg casting for centrifugal casting molten tubes is produced for position of distribution ring. Electrical energy and natural gas are used as fuel in kilns for additional heating of pots in which materials are melted.
At the source of MM02 emissions located on the dust collector grid, crusher and transfer points, moulded masks are transported over casting conveyor to the bars emptier, where moulded clusters insert is shaken out and further cooled on a plate carrier. The cooled clusters are placed on a flow device which performs sanding of material by using steel buckshot in order to obtain a clean surface. Used buckshot is delivered to the reservoir into which air is blown using air, while all the impurities smaller than 0.2 mm pass the filter. Through exhaust pipes buckshot smaller than 0.2 mm is conveyed to the air filter for dust removal while larger buckshot remains in a tank.
Source of MM05 emission is the dust collector of core machines, where shells used for casting are formed. These shells are used in casting using hot CRONING process. Croning procedure was developed in 1940s by German engineer Johannes Croning [14].The process is reflected in the principle of making shells using chromite-olivine quartz sand coated with phenol resin. Sand is fed in heated core machine by a blowing process, where it is heated to a temperature of 250°C.
By heating, grains of sand are joining and creating a crust taking a form of core. Natural gas is used for heating, and after 3 minutes in core machine shell of sufficient thickness required for casting and the "cluster" is formed. For forming shells two machines are used so that the upper shell is made in one machine and the lower half in the other, which are later assembled by gluing and form a shell ready for casting.
Table 1 presents data on emission of PAHs at measuring points MM01, MM02 and MM05. Next to emission values, the table presents basic data required for creating simulations of dispersion of pollutants in ambient air.

Figure 2

Layout of pollutants emitters

Measuring concentration of PAH was performed three times, in 3-day intervals. Measurements were made on 25, 26 and 27 December 2013. Concentrations listed in the table represent mean values of measured concentrations.

Table 1
Emission data [2]

Measuring point	Pollutant concentration mg/m³	Stack height m	Mass flow of pollutant g/h	Waste gas temp. °C	Waste gas velocity flow m³/s
MM01	<0.00004	15	<0.0004	8	2.745
MM02	0.0001	18	0.0038	6	10.556
MM05	0.0001	12	0.0027	9	7.501

Measuring concentrations of PAH was performed in accordance with standard accredited method ISO 11338-1:2003 certified. This standard describes a method for determining mass concentration of PAH in flue gases from stationary sources such as aluminum smelters, waste incinerators, power plants, industrial and household appliances with internal combustion and others. There are three different standard methods of sampling and minimum requirements for effective sampling of PAH are defined. These methods are: 1 dilution methods, 2. heating of filter / condenser / adsorber method, 3. cooled probe – adsorber method. All three methods are based on representative isokinetic sampling, as PAH is associated with particles in the flue gas. Preparation of samples was performed according to standard ISO 11338-2:2003, and sample analysis was carried out by high compressive liquid chromatography – HPLC [3,4].

ADMS 5

ADMS 5 – *Atmospheric Dispersion Modelling Software* – was developed by consulting firm "Cambridge Environmental Experts Consultants" (CERC) and represents a dispersion model which can simulate a wide range of pollution from various polluting sources. ADMS 5 is a model of new generation which uses two parameters to define the boundary layer in the atmosphere – the height of the boundary layer and the Monin-Obukov length, as well as adapted Gaussian distribution of concentrations in order to calculate the dispersion in convective conditions. Figure 3 shows the layout of program window where data input on pollutant emissions is taking place and types of sources, concentrations of pollutants, exhaust gas velocity and spatial position of emitters in the analyzed field [1].

When forming a simulation of pollutant dispersion, meteorological parameters represent a very important element. Parameters that largely affect the dispersion of pollutants are wind speed and direction, air temperature, air humidity and cloudiness [11].

Since we are presenting long-term simulations of dispersion, as well as simulations for the days in which the sampling was done, meteorological data from automatic stations in Kikinda were used. Automatic weather station is within the jurisdiction of the Provincial Secretariat [13]. Figure 4 shows a graph of the wind rose formed on the basis of available meteorological data. For forming simulations, meteorological data for the entire period of 2013 were used.

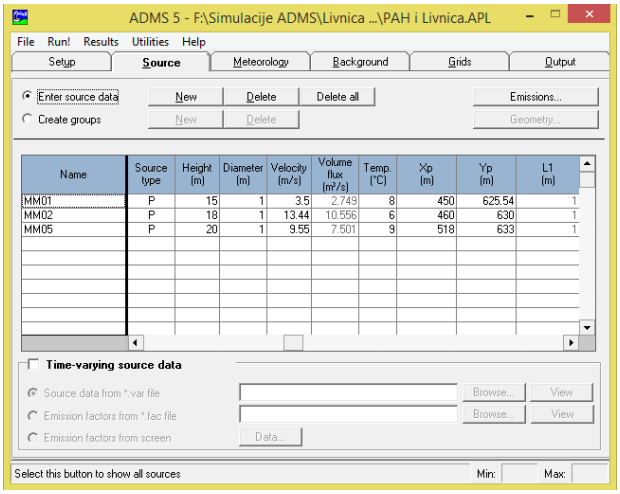

Figure 3
Model data input – ADMS 5 METEOROLOGICAL DATA

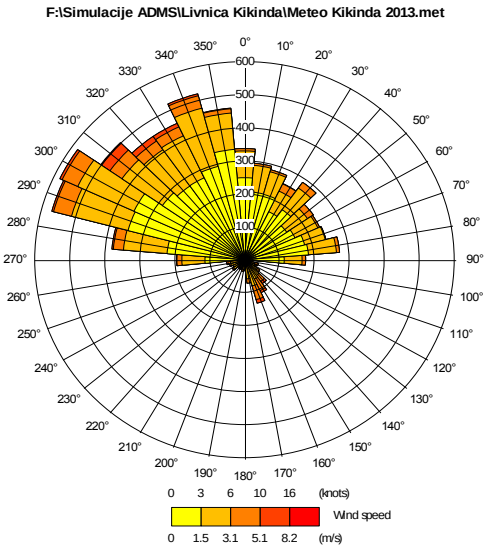

Figure 4

Wind rose – Kikinda 2013.

RESULTS AND DISCUSSION

Figure 5 shows the results of long-term simulation of dispersion of PAH resulting from Kikinda Foundry. The maximum concentration of pollutant for long-term simulation at one-year level is 0.0056 ng/m³.

Meteorological data parameters used for formation of long-term simulations
- Temperature in 2013 in the range: -7.9 to +37.27 °C
- Relative humidity: 17 – 99%
- Maximum wind speed: 8.87 m/s
- Wind direction: north-west wind is dominant

Concentration of PAH in the simulation is in the range from 0.0002 to 0.0056 ng/m^3. Caused by meteorological conditions and dominant northwest wind, pollutant dispersion is south of the town of Kikinda.

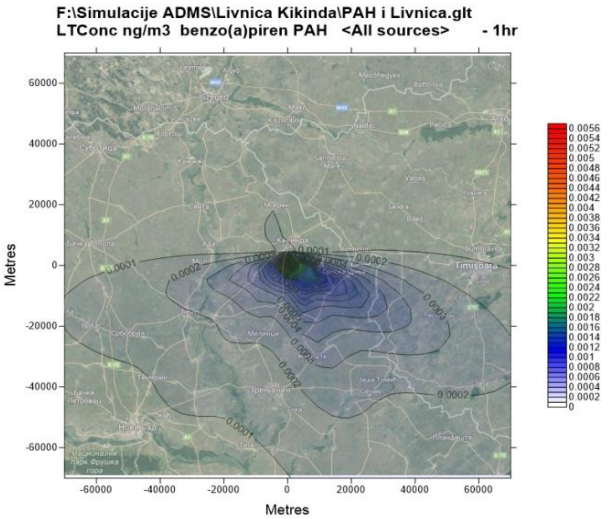

Figure 5
Results of Long Time Simulation – MAP 140x140km

Places exposed to the pollutant generated in casting process at the foundry of the automotive industry are: Kikinda. Zrenjanin, Jasa Tomic, Secanj, Vrbas and Srbobran. In the simulations cross-border impact of pollutants has also been noticed in the area of Timişoara and Jimbolia. Maximum simulated concentration of pollutants is 0.0056 ng/m^3. This concentration represents a much lower concentration than the defined limit values.

PAH concentration defined in the legislation of the Republic of Serbia is 0.05 mg/m^3 [12].

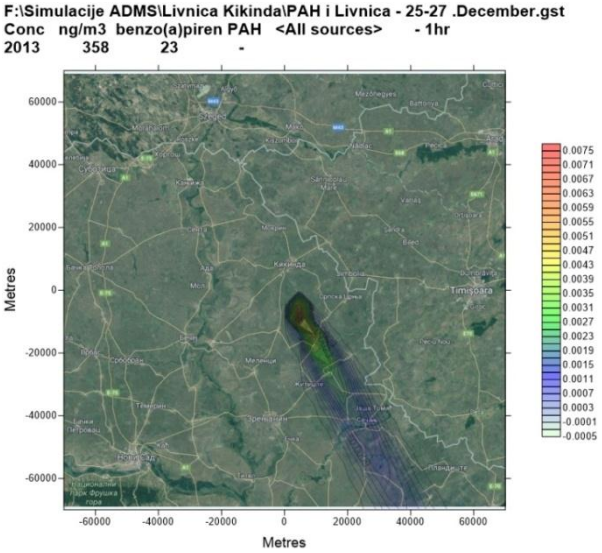

Figure 6
Results of simulation – 25. December

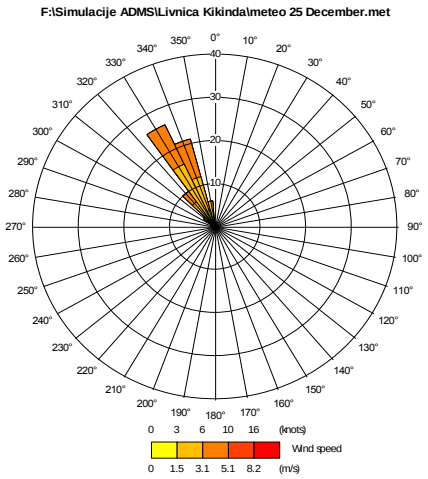

Figure 7
Meteorology data – 25th December

Figures 6, 8 and 10 show the simulations of dispersion of pollutants for each individual day when sampling procedure was performed, i.e. measurement of emissions of pollutants from the source. Meteorological parameters for a specific day affected the dispersion of pollutants. The wind rose formed on the basis of meteorological data for the specific dates when simulations were performed are shown in Figures 7, 9 and 11.

Figure 6 shows the simulation on 25 December, when the wind direction was north-west, at maximum speed of 3.15 m/s, and maximum concentration of PAH 0.0075 ng/m^3. Figure 8 shows simulation of dispersion of PAH on 26 December in conditions of north-west wind, at maximum speed of 5.07 m/s, when the biggest pollutant concentration was 0.0099 ng/m^3. Figure 10 shows simulation for the third and final day of sampling. Maximum concentration of PAH

in the investigated day was 0.0075 ng/m^3, with a maximum wind speed of 2.88 m/s.

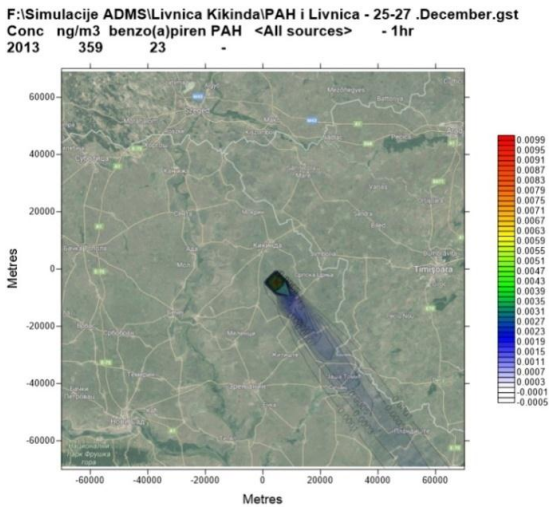

Figure 8.
Results of simulation – 26. December

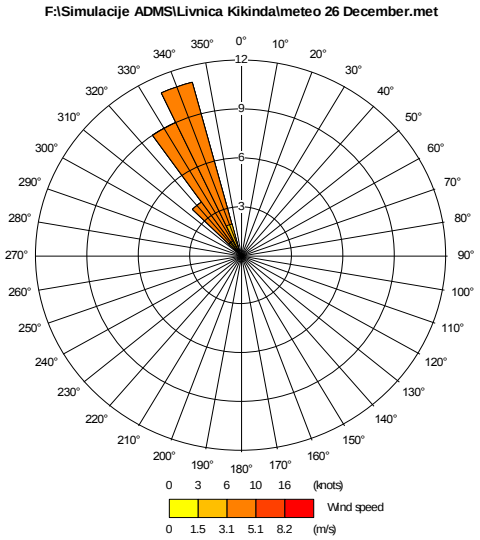

Figure 9
Meteorology data – 26th December

An important feature of PAHs is their transport over long distances or "long range transport". Dispersion of PAH in the simulations is noticeable at distances greater than 60 km and to this distance concentration is 0.0001 ng/m^3.

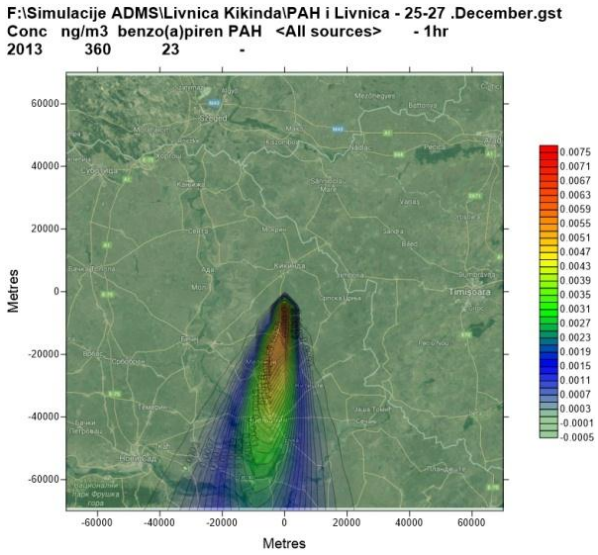

Figure 10
Results of simulation – 27. December

Figure 12 graphically shows the distance to which PAHs will expand from sources with data on concentration at certain distances as well as data where its concentration is zero, that is, at which final distance they will be deposited on the surface of the ground. For shown specific simulation, the distance from the source of emission to the point at which the concentration will be zero, is 90 kilometres.

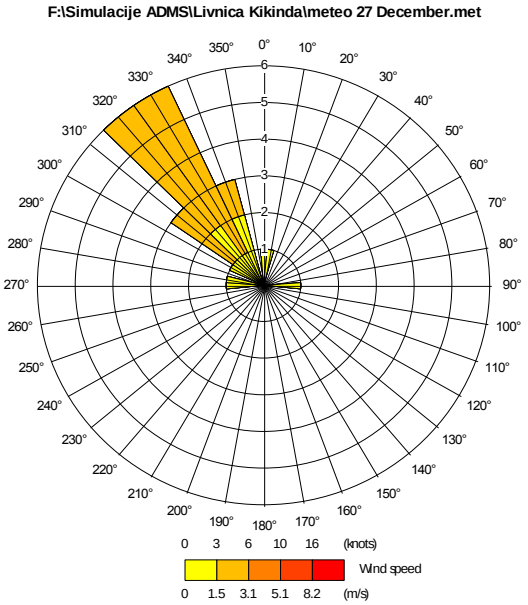

Figure 11
Meteorology data – 27th December

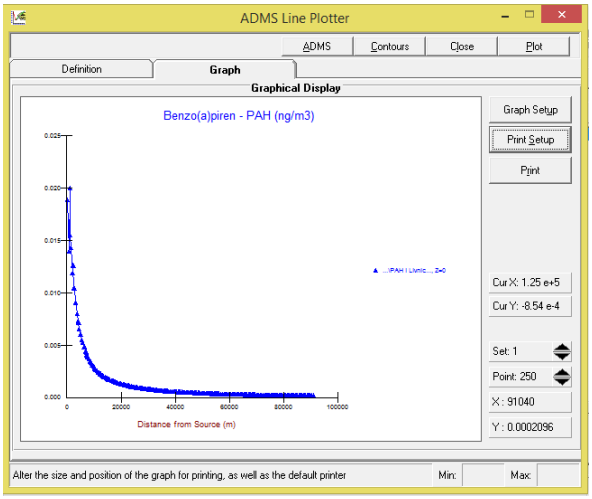

Figure 12
Distance from source – 27th December

CONCLUSIONS

Simulations of PAHs dispersion formed in the process of casting iron for automotive industry in Kikinda show that the projected concentrations are lower than the upper limit value both in domestic and European Union legislation requirements.

Maximum concentration for long-term projections for a period of one year using meteorological data for the year 2013, reached the value of 0.0056 ng/m^3, while in case of individual daily projection peak concentrations were in the range 0.0075 – 0.0099 ng/m^3. An important feature of the created simulation is the distance to which the pollutant stretched. In the long-term simulation of pollutant dispersion, pollutant transport length was greater than 60 km, whereas for individual daily concentrations distance to which the pollutant spread from the source was about 90 kilometres. In the future, validation of projected values of simulation should be carried out by checking official data about air quality and concentrations of PAHs in areas which are potentially affected by this pollutant. It is important to emphasize that the simulations showed that for long-term simulations there is a cross-border effect and impact on air quality in the region.

ACKNOWLEDGEMENT

This paper is a result of research activities and use of equipment and software purchased under the project "Sustainable development of a research centre in Banat region and Danube flow area through scientific research and environmental simulation tools to asses and evaluate potential threats", which is financed by the IPA CBC Romania - Serbia.

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BIOAVAILABILITY OF HEAVY METAL IN SOIL: IMPACT ON SOIL MICROBIAL PROCESSES AND POPULATION DURING LABORATORY INCUBATION

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Received: November 2016

Abstract

Predictions of heavy metal toxicity effects on organic pollutant biodegradation in contaminated soil environments is difficult since heavy metals may be present in a variety of chemical and physical forms. In our study; the presence and role of soil microbial interaction (in the form of log_{10} of bacterial population) in the brown forest soil was affected by the different concentrations of toxic ions of lead (Pb) and zinc (Zn). Their inhibitory effect was manifested both in the decrease of the number and the physiological activity of soil bacteria. Bacterial populations generally decreased similarly to the CO_2-production in response to the effect of the investigated toxic heavy metal ions. Also, the impact of different toxic heavy metal ions was studied on the CO_2-production in brown forest soil. The soil samples were amended by C, N and P in the form of glucose, sodium nitrate and potassium phosphate, respectively. The inhibitions appeared even after three weeks, but highly significant effects were detected after six week of incubation period. Lead has smallest effect on decreasing CO_2-production in brown forest soil after the different incubation periods. The strongest inhibition of the gas production was detected by the influence of zinc ions in the same soil samples. The fertility of natural soil ecosystem depends significantly on the rate of turnover of soil organic matter, mediated by the soil microbial biomass.

Keywords*: lead, zinc, CO_2-production, soil microbial activities*

INTRODUCTION

Nowadays, with growth of industrialization and extraction of natural resources, there has been a considerable increase in the discharge of industrial waste to the environment, mainly soil and water, which has led to the accumulation of heavy metals. Consequently, contamination of soils, groundwater, sediments, surface water, and air with hazardous heavy metals and toxic chemicals is one of the major threats facing the world, as they cannot be broken down to non-toxic forms and therefore have long-lasting effects on the ecosystem. According to recent study by [1], the need to remediate these natural resources has led to the development of new technologies that emphasize the destruction of the pollutants rather than the conventional approach of disposal because of their potential to enter the food chain. Some heavy metals play an extremely important role in biochemical reactions which are significant for the growth and development of microorganisms, plants and animals [2].

Ecologically, the accumulation of heavy metals in soils is extremely hazardous because soil is a major link in the natural cycling of chemical elements; it is also a primary component of the trophic chain, composed of soil– plants – animals – humans [3]. 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_2-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. It is well known that microbial biomass increases when organic materials are applied to soil.

However, [4] the study has showed that microbial biomass in soil from the classical Woburn Market-garden Experiment which had been supplied with anaerobically digested lagoon-dried sewage sludge was half that in soil that had received farmyard manure. Sludge application increased soil metal concentrations up to current limits with the exception of Cd which was three to five times the maximum limit [5]. However, in other studies with the same soils [6] there were no effects of metal concentration on respiration rate. Therefore, the respiration rate per unit weight of biomass was considerably greater in the metal-contaminated soil.

This response may not necessarily be detrimental, but could be explained because metal-sensitive species have been replaced by other more tolerant groups that respire at a higher rate. Alternatively, the effect could be interpreted as a metal-induced stress response. Soluble metal salts have been applied to soils often as a basis for assessing effects of heavy meals in sewage sludge on soil N transformation were summarized by Doelman [7]. It was concluded that, in general, increasing soil metal levels may reduce the composition and diversity of the total soil microbial population, causing a shift towards resistant strains that become dominant in such soils. Increasing abundance of resistant strains under elevated metal conditions enables the continuation of essential processes that maintain soil fertility [8]. The gradual increase in atmospheric CO_2 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 [9].

However, heavy metals affect the growth, morphology, and metabolism of soil microorganisms, through functional disturbance, protein denaturation or the destruction of the integrity of cell membranes [10]. Soil microorganisms are essential in the decomposition of soil organic matter; any decrease in the microbial diversity or abundance may adversely affect nutrient absorption from the soil for plant [11]. The elevated levels of heavy metals in soils had significant impacts on the population size and overall activity of the soil microbial communities.

Several studies, depending on the isolation-based techniques used, have revealed that heavy metal contamination gave rise to shifts in microbial populations [12]. However, isolation-based techniques are limited because they only represent a small component of the microbial community. This limitation could be attributable to the fact that only a small percentage of soil microbiomes are able to grow on laboratorial cultures.

A relatively improved procedure that may be useful in evaluating changes in microbial community structure is the determination of the metabolic profile of a particular system [13]. Also characterizing the functional capability of soil organisms to utilize specific carbon substrates [14], and also has been widely used in assessing the functional diversity, associated with the microbial community in soil samples from farmland and grassland ecosystems [15].

A variety of methods exists to estimate the size of the microbial biomass in soil. Of these methods, glucose was the most simple and rapid substrate induced respiration (SIR), which stimulates a maximal respiratory response from the soil biomass, measured conductimetrically as CO_2 evolution, and methods currently available are those involving direct counting in which microorganisms can be variously stained, and relates this respiration to biomass C [16].

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.

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 [17]. Therefore, it is important to determine and predict the adverse effects of heavy metals and other pollutants on soil microorganisms [18].

Doelman and Haanstra [19] carried out short-term and long-term effects of Cd, Cr, Cu, Ni, Pb and Zn on soil microbial respiration in relation to a biotic soil factors. It was found that in short-term effects of Pb in sand were distinct, while in sandy loam, the inhibitory effect was not significant, but after 43 weeks, it had increased significantly. In silty loam and clay, there were no significant inhibitory effects. In general, the heavy metals were found to be more toxic during the first eight weeks than after an extended period. It was concluded that toxicity of heavy metals in soil decreases with time, as well as a biotic factor was found to be the dominant factor in decreasing the toxicity of cd and to a lesser extent of Zn.

The objectives of present study were to: 1) measure soil respiration (CO_2 evolution) as bioindicator parameter of soil contamination. 2) study the effect of heavy metal on microbial survival and activity in heavy metal amended soil under laboratory incubations.

MATERIALS AND METHODS

Soil and treatments

The soil samples were collected from the upper 10 cm of agricultural region of the brown forest soil. The soil samples were air-dried. The bioavailability and the effect of heavy metals (Pb and Zn) on CO_2-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 3 groups according to the number of heavy metals used. Each group was divided into 3 sub-groups which were treated with three concentrations of Zn in $ZnCl_2$ (4, 8, and 16 ppm), or Pb in the form of $PbCl_2$ (40, 80 and 160 ppm). The treated soil samples were incubated for 6 weeks. The soil samples were collected for measuring the total bacterial counts and the amount of CO_2-production after 1st week, 3rd week and 6th week of incubation at 28 C the experiment was carried out in triplicates. For measurement of CO_2-production, a fixed plastic tube containing 50 ml 10 M NaOH solution for trapping the evolution of CO_2 was placed in the centre of 1.5 1 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_2 of soil respiration, which represented the respiration due to litter decomposition, root respiration, rhizomicrobial respiration (i.e. microbial respiration utilizing C directly derived from living roots), and microbial respiration utilizing native soil organic matter. Method of Erdey [20] was applied for simultaneous determination of NaOH and Na_2CO_3 content in the experimental soil samples. The Hungarian technical directive method [21] was used to detect Pb and Zn content in the soil samples. Five grams 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^3 1.5 M HNO_3 at 20°C for 2 h. The elemental analysis of the filtrate was performed by jobin-Yvon 24 type ICP AES. The study was carried out in 3 replicates.

Determination of total number of bacteria:

The total bacterial count was carried out in all soil amendment with different concentrations of Pb and Zn Under sterile conditions, serial dilution technique was used for this purpose. 10 g of fresh soil sample of each soil treatment was suspended with 90 cm^3 sterile distilled water. After shaking for 30 min., in rotary shaker, this suspension was diluted gradually to 10^{-3} and 10^{-5} and from each diluted suspensions 1 cm^3 was pipetted in 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

The effect of CNP resources as SIR and heavy metals (Pb and Zn) on CO_2-production and bacterial population of brown forest soil was studied in laboratory conditions. The results were detected during one, three and six weeks of incubation. It's clear from data presented in Fig. 1 and Fig. 2 that CNP treated brown forest soil showed higher rate of CO_2 production during all three different incubation periods (1st, 3rd and 6th weeks). Data recorded in Fig.3 and Fig.4 show that CNP treated brown forest soil have stimulated the population of bacteria representing in log_{10} of bacterial colonies (CFU/g dry soil). After week of incubation, the recovery of (Pb and Zn) concentrations added to CNP treated brown forest soils was determined in the nitric acid soluble fraction.

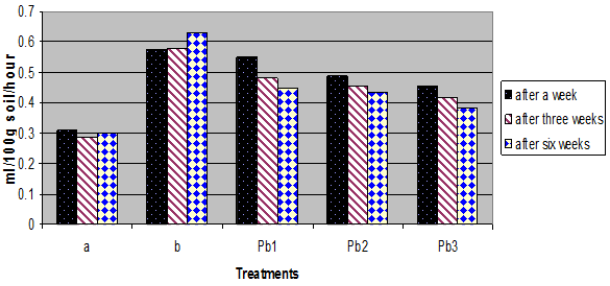

Figure 1

Average of CO_2-production volume at 25°C, 0.1 MPa (ml/100 g soil/hour) of brown forest soil treated by CNP and Pb for different three periods (a: CNP untreated soil, b: CNP treated soil).

Data showed that the addition of inorganic forms of Pb or Zn significantly increases the mobile (HNO_3 soluble) fraction of these metals but after one week incubation, their concentration does not reach the 100% recovery. Taking in the consideration that time can be an ecological factor; it was found that the amount of Zn recovery was increased by increasing the incubation time to reach a maximum recovery at the 6th week of incubation. Also, there were no differences between the recovery of the control soils and those activated with SIR and the soil samples incubated for one week.

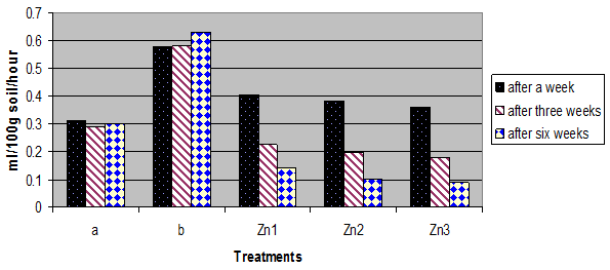

Figure 2

Average of CO_2-production volume at 25°C, 0.1 MPa (ml/100 g soil/hour) of brown forest soil treated by CNP and Zn for different three periods (a: CNP untreated soil, b: CNP treated soil).

But those soil samples incubated for three and six weeks were significantly with those mentioned early. Similar results were found in the soil samples treated with Pb, which indicated that the recovery was more than those of soils treated with Zn and incubated for six weeks were more significantly different than those incubated for three or one week comparing with the control or activated control soils with SIR.

It can be observed that the methods used for biomass, CO_2-evolution and total bacteria number, are both suitable to be indicators for biomass measurements through which we can have an idea about the soil fertility. It is well known that microbial biomass plays an important role in mineralization of soil organic matter due to the enzymatic activities.

The effect of heavy metal treatments on CO_2 reduction in CNP fertilized soil is showed in Figure 1 It is clear from data presented that CNP treated brown forest soil showed higher rate of CO_2-production, estimated by 0.75, 0.80 and 0.83 ml/100 g soil/h, and Figure 2. in brown forest soil comparing with 0.31, 0.29 and 0.30 ml/100 g soil/hour in CNP brown forest soil during all three different incubation periods (1st week, 3rd week and 6th week).

Data recorded in Figure 3 and Figure 4 show that CNP treated brown forest soil samples have higher bacterial population (which are representing in term of $\log_{10}$ of bacterial colonies) than in untreated ones during the three different periods (1st week, 3rd week and 6th week). These previous results are in accordance with the results found by [17] 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 beneficial effects of sewage sludge due to the extra organic matter N or P supplied may be short lived. These results are also in accordance with investigation of [22].

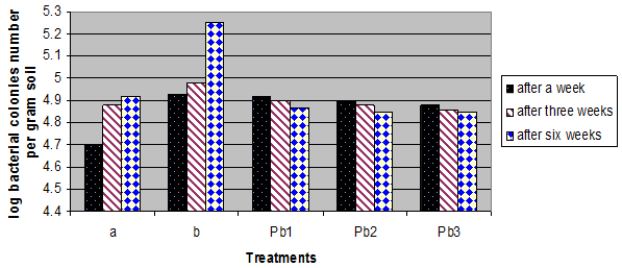

Figure 3

Average of log10 of total bacterial number of brown forest soil treated by CNP and Pb after different three periods (a: CNP untreated soil, b: CNP treated soil).

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. Microbial specific respiratory activity was higher in the unfertilized treatments [23]. Nannipieri et al. [23] stated that the changes in CO_2-evolution were related to glucose concentrations of mineral nutrients.

The results indicated that higher initial rates of CO_2-release 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 1 and Figure 2. Those heavy metals, Pb and Zn have significant effect on CO_2-production of tested brown forest soil samples at different incubation periods (1st week, 3rd week, and 6th week). It was found that Pb at different concentrations, 40, 80, and 160 mg/kg have the smallest effect on decreasing CO_2-production either in brown forest soil incubated at different periods.

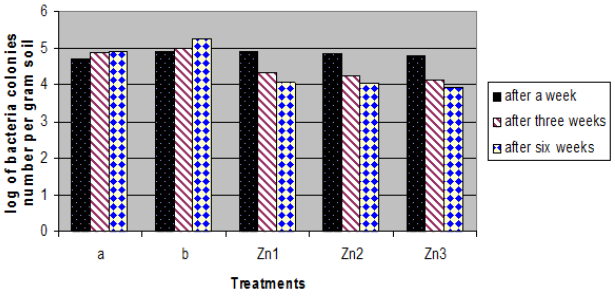

Figure 4

Average of log10 of total bacterial number of brown forest soil treated by CNP and Zn after different three periods (a: CNP untreated soil, b: CNP treated soil).

It can be shown also from data that Zn has higher effects in decreasing the amount of CO_2-production at the different concentration used, 4, 8, and 16 ppm for Zn either in brown forest soil at the three different periods. Baath [18] studied the effect of heavy metals in soil microbial processes and populations and had established that the relative toxicity of different metals decreased in the order Cd > Cu > Zn > Pb. These results of Baath [18] were similar to our results in which our investigation showed that the relative toxicity of tested metals decreased in the order Pb > Zn. A significant effect of heavy metals, Pb and Zn on bacterial population has been found in CNP treated or untreated soils (Figure 3 and Figure 4). It is shown that Zn 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 Zn cause decreases in total bacterial population. Concerning the effect of Pb and Zn on the CO_2-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 Zn), the highest CO_2-production was measured after the 1st week incubation followed by the 3rd and 6th week respectively. The same effect was found for the bacterial population. This result is in accordance

with the result of [10] who reported that the addition of Pb did not have any significant inhibitory effect on the level of microbial biomass C.

CONCLUSION

The present study clarify that the pollution of the environment with heavy metals is still one of the major global problems today. Heavy metals may inhibit biodegradation of soil organic matter by directly or indirectly interacting with enzymatic activities involved in biodegradation processes or involved in metabolism. The results indicated that Zn has much more significant effect in decreasing bacterial population than Pb that has a little effect It can be concluded also, that the incubation time is an important factor for metal recovery in soil as well as the heavy metals have the important concern in microbial populations in the investigated soil samples. It was found that Pb has the smallest effect on CO_2-production in brown forest soil after the different incubation periods. The strongest inhibition of the gas production was detected by the influence of Zn in the same soil samples. Finally, more investigations are needed on different soil types at different depth with various heavy metals at different concentration.

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IMPACT ASSESSMENT EXTRACTION OF MINERALS ON SOCIAL AND ECONOMIC SITUATION OF THE POPULATION IN SELECTED MICRO-REGION

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Received: November 2016

Abstract

This paper deals with impact of extraction of mineral resources for the social and economic situation of the population in selected micro-region Jelšava. Together with the city Jelšava as part of the selected micro-region were reviewed and adjacent villages Chyžné, Lubeník, Magnezitovce, Mokrá lúka and Revúcka Lehota. The selected micro-region have a combined population of 6 296 and is located on an area of 10 939 ha. For the impact assessment was necessary to assess the current state of socio-economic situation of the selected micro-region. In selected micro-region is currently being implemented and magnesite extraction company currently engaged in the extraction of magnesite has a decisive influence on the social and economic situation in the selected micro-region because they are crucial employers in this area. Any industrial activity in the region has the positive effects but also negative effects. Among the positive effects belongs increase in employment, an increase in average wages, improve the demographic situation etc. Among the negative effects we can include main impacts on the environment, human health, occupation of land, waste production, the emergence of environmental burdens etc. Extraction of raw materials is an area that brings with it a fairly significant negative impact on the environment. Therefore, it is necessary to connect these two areas and the area of socio-economic and environmental area. On the relationship between those two areas and a comprehensive assessment can be used chain of D-P-S-I-R. Just such chain can be used to assess state of the environment and know the causal-follow relations between human activities and the state of the environment.

INTRODUCTION

Extraction of mineral resources accompanies our company from the oldest historically dated period to the present. Any industrial activity brings with it a number of positive impacts in several areas, but and the quantity of negative impacts which impact on the environment and occupational environment people and thus affect their quality of life [1].

Extraction of mineral resources and mining industry is a global industry which brings relatively significant environmental impacts. On the other hand, are mineral resources and technological progress while irreplaceable inputs to production and thus the need for the objective reality. Therefore, the extraction of raw materials at the same time is promising sector of industry [3]. Of course the development of raw material extraction with them can contribute significantly to improving the socio-economic situation in the head area with high unemployment or regions with less developed infrastructure. Extraction of mineral resources brought to our country's prosperity, development of new urban agglomerations, development of technology and progress in drafting legislative codes [2]. In particular, for small municipalities and less developed regions are an important source of mining companies for development - as budget revenue, but also as a source of extra budgetary income (sponsor donations, help build infrastructure). Beyond the extraction can bring wider social and economic effects in the form of new jobs, increase in average wages, improvement of demographic trends, to improve infrastructure in the region [2].

CHARACTERISTICS OF THE REGION

One of the economically most important mineral resources in Slovakia is magnesite. The largest bearings of magnesite in Slovakia are situated in the carboniferous strata in the western Carpathians in Gemericum. Chemically pure, uncontaminated magnesite $MgCO_3$ contains 47.8% MgO and 52.2% CO_2. Following composition is usually rare. Most often it contains various additives such as carbonates, oxides, Silicate mainly calcium, iron, manganese and aluminum. Exploit magnesite deposit in Slovakia have relatively consistent quality with an MgO 40,2 to 43,5%, Fe_2O_3 fluctuate between 1,5-4%, CaO from 1,5 to 4,8%, SiO_2 0,7 to 2,5% MnO 0,1-0,4%. Currently, the extraction of magnesite carried out on two bearings underground manner. Bearing in Jelšava is the largest Magnesite deposits in the world. Among the most important and largest bearings are Jelšava - Dúbravský masív, which magnesite conquers from depths exceeding 400 m below the surface [5].
Jelšava city is situated at the interface of Slovak Karst and Slovak Ore Mountains. It has a rich tradition of mining and iron as well as artisanal production. [5] Jelšava is located on the international tourist route Gothic Road, is situated 12 km southeast of Revúca districts and belongs to the Banská Bystrica region.
Geographical location of the city is 48 degrees 37 minutes' north latitude and 20 degrees 14 minutes' east longitude, at an altitude of approximately 258 m. Jelšava the area has an area of 4 679 hectares, of which 296 hectares' urban area, rural area 4 383 hectares. Micro-region Magnesite voluntary association of municipalities, which was founded in 2003 [5]:

- Chyžné, Lubeník, Magnezitovce, Mokrá Lúka, Revúcka Lehota and Jelšava.

SLOVAK MAGNESITE WORKS, A.S. JELŠAVA

Slovak Magnesite Works (SMW) Figure 1 in Jelšava is the greatest mining and a processing magnesite plant in Slovakia and one of the world's largest producers of magnesia dead on.

Figure 1
Slovak Magnesite Works, a.s. in Jelšava

Today it is owned by the Slovak Magnesite Works, joint stock company, Jelšava. He has already completed more than 120-year history [6].

Magnesite Figure 2 is the most important mineral magnesium. It occurs in nature in crystalline and massive form. Both types of magnesite are mainly used for caustic clinker producing the refractory mass and insulation. It is used in the chemical industry for the manufacture of paper, rayon and like putty abrasive grinding wheels [6]. The most significant Bearings are located in a strip for about 70 km long from Podriečan (Banska Bystrica region) after Ochtiná, further in a section Margecany - Košice. Magnesite is currently mined outside the Košice region on bearings Lubeník, Jelsava et al., In the Kosice region undrawn deposits are located in Ochtiná and Košice - Bankov. Non-balanced occurrences of crystalline magnesite in the areas of Vlachovo, Gemerská Poloma, Mníšek and Hnilcom.

Figure 2
Magnesite

CHARACTERISTICS IMPACTS OF EXTRACTIVE INDUSTRIES ON THE ENVIRONMENT IN SELECTED MICRO-REGION

Mineral resources constitute the basis of production in metallurgy, electrical, chemical, construction, ceramic and glass industry, as well as in other industries. Essential part is of non-metallic extraction, construction and energy raw materials are magnesite, limestone, dolomite, gypsum, stones and others.
Essentially cover their domestic consumption. In Slovakia there are several sites which perform extraction of raw materials see Figure 3.

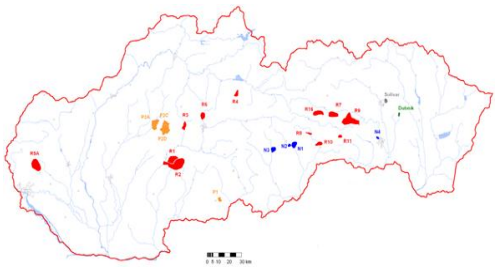

Figure 3
Intensely affected by the production site in Slovakia
Designation of locations: P1 – Veľký Krtíš, P2A- Nováky, P2C – Cígeľ, P2D – Handlová, N1 – Jelšava, N2 – Lubeník, N3 – Hnúľťa-Mútnik, N4 – Košice Bankov, R1 – Banská Horuša, R2 – Banská Štiavnica, R3 – Kremnica, R4 – Liptovská Dúbrava, R5A – Pezinok, R6 – Špania Dolina, R7 – Rudňany, R8 – Nižná Slaná, R9 – Slovinky, R10 – Rožňava, R11 – Smolník, R16 – Novoveská Huta

The right area of micro-region Jelšava is one of those areas [6].

TABLE I.
STATE AND DEVELOPMENT OF THE ENVIRONMENT IN THE SELECTED MICRO-REGION

State	The count deposit reserves	13.	Energy raw materials
		14.	Ore minerals
		15.	Non-metallic and construction materials
		16.	Non-reserved minerals
	Underground water	17.	Groundwater supplies
	Geothermal energy	18.	Geothermal energy
	Geological environmental factors	19.	Landslides and slope deformation
		20.	Tectonic and seismic activity area
		21.	Radon activity in the geological environment
		22.	River sediments
		23.	Stability of rock massifs
Consequence	Environmental burdens	24.	Old environmental burdens
		25.	Heaps
		26.	Tailings ponds
	Soil contamination	27.	Soil contamination
	Risks and diseases	28.	Accidents, injuries and occupational diseases in mining activities
	Air pollution	29.	PM2,5 emissions from industry
		30.	PM10 emissions from industry
	The waste water	31.	Wastewater discharges from industry
	Waste production	32.	Development of industrial waste

SOCIAL ASPECTS OF RESOURCE EXTRACTION

Slovak Republic on a global scale not one of the countries in which the extraction and processing of raw materials more striking is involved in the creation of employment. [4] In 1989 in the mining and mineral processing employed a total of 36 950 employees, including 14 305 in coal mining industry, 9 959 in ore mining, 5 068 in magnesite industry, 6 309 in mining of industrial minerals and raw materials for production of building materials and 1 309 in oil and natural gas, including underground storage.

Since 1990, the number of employees in this sector falling sharply, which is related to the realization of the program attenuator in extractive industries sector and transformation processes and the country's gradual transition to market economy principles. In 2003, the mining and mineral processing were employed a total of 15 455 employees, including 6 355 in the coal mining, 981 in ore mining, 3859 in magnesite industry, 3 246 in the extraction of industrial minerals and raw materials for production of building materials and 1 014 in oil and natural gas, including underground storage. When compared to 1989, the number of employees in the mining and mineral processing in 2003 fell by a total of 21 495 employees [4].

Location exploited mineral deposits is the geological conditions of their creation, and this implies the irregularity in distribution of employees involved in the extraction and processing of mineral resources in the regional breakdown. Compared to regions poor in raw materials there are regions of relative rich in their occurrence and it also corresponds to the regional infrastructure and employment. Market liberalization and transition to market economy principles after 1990 led to the decline of mining, respectively. to the closure inefficient of establishments, which was significantly reduced employment in the mining regions without a corresponding compensation for new jobs. This new trend in the use of raw material base in Slovakia significantly befell in particular regions with a long mining tradition (Spiš, Gemer, Banská Štiavnica). In view of the current trend in the use of domestic raw material base and without opening new deposits in particular non-metallic minerals cannot be assumed in the near future substantial increase employment in this sector. On the contrary, by opening inefficient mines can be expected to further decline in employment in this sector.

In Figure 4 are represented shares of the most important companies in the Banská Bystrica region from the perspective of number of employees. The graph shows that the company SMW Jelšava, a.s. and Slovmag a.s., Lubeník collectively contribute 13 % and currently represent the largest employers in the district Revúca.

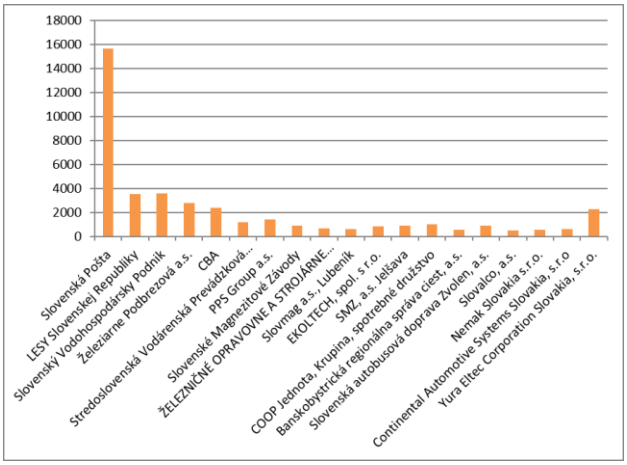

Figure 5
The largest companies with of view the number of employees in the Banská Bystrica region

The company SMW Jelšava, a.s. are among the most important employers in the district Revúca, which maintains about 1 000 direct job positions. At the same time as the road and rail transport, further in the services sector, goods and raw materials or produces. Keep more jobs, resulting in significant economic and social benefits for the region. [4]
The following Figures show evolution of the number of employees, educational and age structure of employees SMW Jelšava, a.s. In Figure 5 shows the development of average wages of employees SMW Jelšava, a.s.

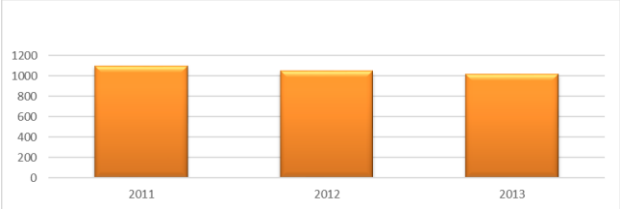

Figure 6
Number of employees

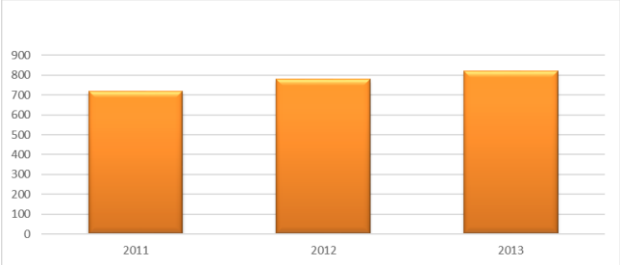

Figure 7
Average earnings (€)

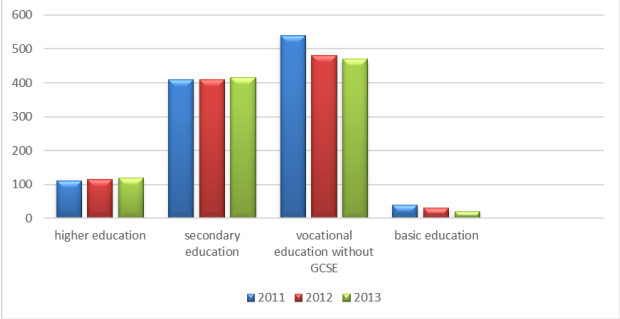

Figure 8
Employee education structure

In Figure 8 is presented in registered unemployment rate in the district Revúca. This indicates a significant reduction trend of unemployment in the district Revúca in the last three years.

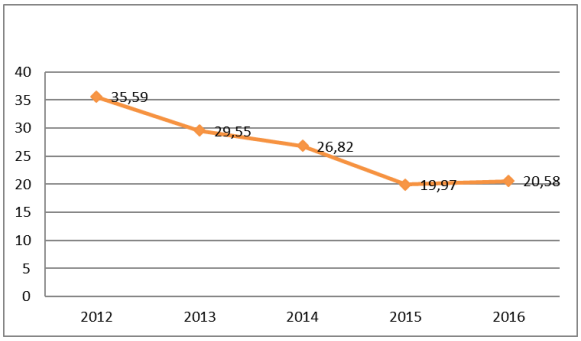

Figure 9
Unemployment in the district Revúca

In Figure 9, trends in the number of unemployed in Jelšava with a slightly falling trend.

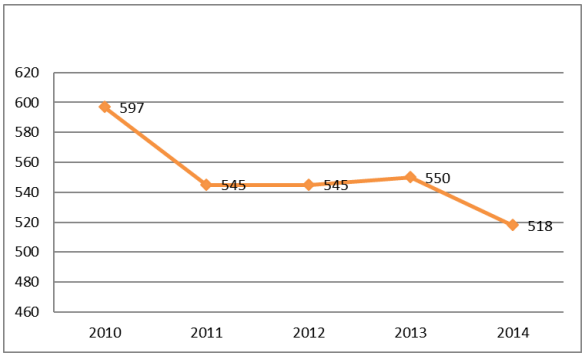

Figure 10
Development number unemployed in city Jelšava

In Figure 10 shows the development of average wages in the district Revúca, and now the amount is 784 €. Compared with an average height of payroll wages SMW Jelšava, a.s. is lower by about 60 €.

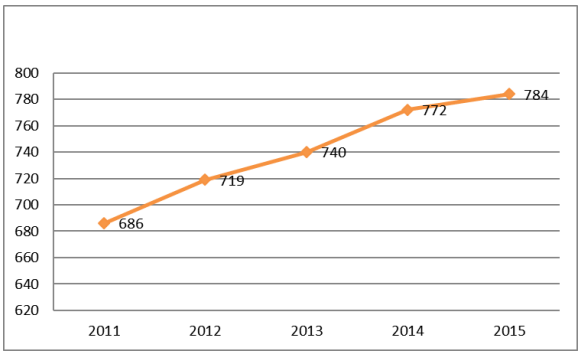

Figure 11
Height the average wage in district Revúca

CONCLUSION

The paper is aimed at assessing the impact of resource extraction on the environment and socio-economic situation of the population of the selected micro-region. For the purposes of preparing the article was elected region in Jelšava. The selected region has a long tradition in the extraction of magnesite, whereas this region contains up to 8 % of global reserves of

magnesite. The selected regions are among the less developed regions in Slovakia and it is mining industry has a dominant position in this region.

The presence of extractive industries in this region brings with it for particular micro-region positive and negative aspects. Among the positive aspects are, of course, economic benefits in the form of tax payments, employment, wage levels and the overall development of the region. Among the negative impacts we advise the main impacts on the environment and on public health. This negative impact cannot be total, but other side mineral resources are also present at technological progress irreplaceable inputs to production and therefore the need for the objective reality.

Therefore, the extraction of raw materials is essential at the same time from a global perspective and promising sector of industry.

ACKNOWLEDGMENT

This work was supported by the Slovak Research and Development Agency under the contract No. APVV- 15-0327 Research and development of optimization methodologies of the acoustic performance of domestic appliances emitting noise.

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BIODIVERSITY OF ALKALIZED SOIL IN THE EMISSION AREA OF MAGNESIUM FACTORY JELŠAVA - LUBENÍK (SLOVAKIA)

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Received: November 2016

Abstract

A strong alkaline reaction is caused by emissions from alkaline magnesium factory currently localized in Jelšava and Lubeník (Slovakia). The area Jelšava - Lubeník with specific alkaline pollutants, is one of the most devastated regions of Slovakia and with the alarming degree of environmental damage. The discovery of deposits of magnesite and its processing around Lubeník dates from 18097. Processing of magnesite raw materials began in the current Slovak Magnesite Works (SMZ) Jelšava in 1923 and Lubeník as early as 1903. Since then, both plants went through constant technological and volume-production alterations. Since 1990 there has been a reduction in production, the technological discipline was improved, the volume of solid emissions decreased by about 1/3. Even so, the pollution fallout remains enormous and devastating. The work examines the impact of alkaline deposition on soil and vegetation diversity in the emission field of magnesium factory Jelšava – Lubeník (Slovakia). The research was carried out in 2016 at the 12 research areas which are used as permanent grassland and is in emission field of magnesium factory Jelšava – Lubeník (Slovakia). Chemical properties of soil reaction were studied by potentiometric (pH/KCl). From the biological properties the functional diversity of soil microbiological communities have been monitored using methods Biolog® Eco Plates support device ELx808 ™ Absorbance Microplate Reader. The date one normalized parameter AWCD (Average Well Color Development) was calculated according to Garland and functional diversity of soil microbiological communities was calculated for BIOLOG data by classical Shannon diversity index (H') and Equitability index. Diversity of grassland communities was monitored at selected localities in the form of plots on the field of 16 m². Vegetation was assessed by Braun - Blanquet scale. Diversity of flora was assessed by Shannon index H´ and Equatibility index. The results of field and laboratory research were evaluated in the program Statistika and Past. In conclusion we can say that a spray particle of free magnesium oxide (MgO) has strongly influenced the reaction of the soil diversity and vegetation cover.

Keywords: *soil reaction, magnesium, microbiological communities, vegetation, Shannon diversity index.*

INTRODUCTION

Soil reaction substantially affects the characteristics of the soil and is one of the most important parameters of soil fertility. It is involved in many soil-forming processes and affects the solubility of many substances, accessibility of nutrients, biochemical reactions, soil structure and thereby all characteristics of the soil. Soil alkalinity is conditioned by the presence of alkaline salts which are easily hydrolysed and allow formation of alkaline. The fundamental reason of soils alkalinity is exchangeable sodium and content of Na_2CO_3 or $NaHCO_3$ in soil solution and worsens some soil processes like soil acidity. Strong alkaline reaction of pH / KCl > 7.7 is inflicted by air alkaline pollutants from magnesium factory currently located in the Jelšava and Lubeník. Magnesite air pollutants are a mixture of MgO and $MgCO_3$ due to which soil reaction can move above pH 8 [3, 13]. The area Jelšava - Lubeník with specific alkaline pollutants, is one of the most devastated regions of Slovakia and with the alarming degree of environmental damage. The discovery of deposits of magnesite and its processing around Lubeník dates from 1897. Processing of magnesite raw materials began in the

current Slovak Magnesite Works (SMZ) Jelšava in 1923 and Lubeník as early as 1903. Since then, both plants went through constant technological and volume-production alterations. Production of clink accompanies the enormous emissions of dust particles MgO into the air and the leakage of gaseous compounds, mainly SO_2 and NOx. The chemical compounds of MgO (75%), CaO (2.3%), Fe_2O_3 (6.9%), SiO_2 (0.6%), MnO (0.4%), Al_2O_3 (0.3%) were detected in the particles of toxic elements. The heavy metals are in the dust particles, in particular Cd, Pb, Zn, Mn, Cr. MgO emission of dust was raising with the volume of production; it was 44 t/yr in 1923 and 4898 t/yr in the 1980. Since 1990 there has been a reduction in production, the technological discipline was improved, the volume of solid emissions decreased by about 1/3. Even so, the pollution fallout remains enormous and devastating [1, 13].

The work examines the impact of alkaline deposition on soil and vegetation diversity in the emission field of magnesium factory Jelšava – Lubeník (Slovakia).

MATERIAL AND METHODS

Jelšava and Lubeník lie in the south central part of the Slovak Ore Mountains, in the valley Muran, in the district called Jelsava podolie. Jelsava podolie geomorphologically belongs to Revúca Highlands [5].

The research was carried out in 2016 at the 12 research areas which are used as permanent grassland and is in emission field of magnesium factory Jelšava – Lubeník (Slovakia), from A horizons the depth of 0.05 m to 0.15 m (Figure 1).

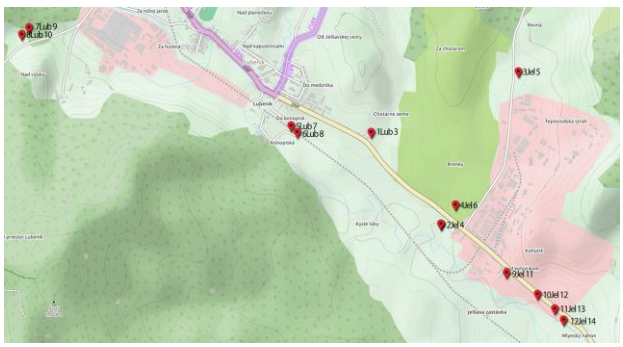

Figure 1
Location of research sites in investigated areas Jelšava and Lubeník (Slovakia)

Chemical properties of soil reaction were studied by potentiometric (pH/KCl) [11]. Diversity of grassland communities was monitored in the form of plots on the field of 16 m^2 during the growing season 2016. Vegetation was assessed by Braun - Blanquet scale [7]. Terminology is given in accordance with Marhold and Hindák [12]. The determination of species diversity of sites was according to Shannon index [2]

$$H' = -\sum_{i=1}^{s} \frac{xi}{N} log2 \frac{xi}{N},$$

which is sensitive to the different characteristics of plant communities, particularly the number and significance of the coefficient of all kinds. The results were evaluated on the basis of scales: 1 extremely low (< 0.5), 2 very low (0.5-1), 3 middle low (1 to 1.7), 4 low (1.7 to 2.5), 5 low to moderate (2.5-3.3), 6 medium (3.3 to 4), 7 half-height (4-5), 8 high (5-7), 9 very high (7-10) and 10 extremely high (> 10). In fresh soil samples we evaluated metabolic profiles of microbial communities using Biolog® Eco Plates [10].

Microtiter plates with 31 different organic substrates were incubated with 150 µl of the extract from the sample in 0.9% NaCl, at a 1: 10000 at 27°C for 7 days. During the incubation of the samples we used a device ELx808 ™Absorbance Microplate Reader to daily determining the value of the absorbance at 590 nm corresponding to the activity of microorganisms on various substrates. Diversity of functional groups of microorganisms was evaluated using the Shannon diversity index (H') and Equitability index.

The obtained data were processed statistically by means of the STATGRAPHIC software and Past.

RESULTS AND DISCUSSION

Major component of environmental pollution in Jelšava - Lubeník is magnesite powder belonging to aerosol particles, which is crucial for the deposition process of gravitational sedimentation. Most of the free magnesium oxide is in the finest dust fraction. These particles are highly active and are capable of chemical reaction with substances in the soil on the surface of plants and plant tissues. Considering the low wind speed, dust particles disposed in a relatively small area [15, 8]. Flue dust particle strongly influenced the dynamic properties of soils, especially pH. The continuous magnesite crust covers part of the soil; vegetation cover is considerably eliminated and reduces landscaping and environmental aesthetic function (Figure 2).

Figure 2
Soil covered with continuous magnesite crust in investigated areas Jelšava and Lubeník (Slovakia)

The research showed that the investigated sites are slightly acidic (pH to strongly alkaline (pH 7.7 to 8.8) (Table 1). We found alkaline to strongly alkaline soil reaction in seven investigated areas. This fact greatly affected the variability of species. Characteristic wild solanaceous as *Elytrigia repens*, *Chenopodium album*, *Equisetum arvense* were present on farmland. Permanent grassland were represented by species which are typical for wet and waterlogged sites as *Alopecurus pratensis, Lychnis flos-cuculi*, *Cirsium rivulare, Acetosa pratensis, Archangelica officinalis* and competitively strong species *Elytrigia repens, Phragmites australis* which creates monocultures (9Jel 11, 10Jel 12, 11Jel 13, 12Jel 14).

The communities of ruderal sites were recorded in areas 1Lub 3, 5Lub 7 near arable land and also on permanent grassland, for example *Tanacetum vulgare, Chenopodium album, Silene vulgaris* and rampant invasive taxon *Solidago canadensis*.

Species diversity of flora was investigated at localities evaluated by Shannon index H ', which is sensitive to the different characteristics of plant communities, particularly the number of coefficient of significance of all kinds.

Based on the results of Shannon index, we can conclude that diversity in investigated sites is extremely low (0.0) to middle low (1.5). Equitability values were in line with the index of diversity (Table 1).

TABLE 1

RESULTS OF MONITORED PARAMETERS IN INVESTIGATED AREAS JELŠAVA AND LUBENÍK (SLOVAKIA)

Location name	pH/KCl	*H´**	*J**	AWCD	*H´***	*J***
1Lub 3	6.23	1.54	0.86	1.85	3.37	0.98
2Jel 4	7.66	1.13	0.63	1.74	3.35	0.98
3Jel 5	6.88	0.55	0.39	1.84	3.33	0.97
4Jel 6	6.86	1.42	0,68	1.93	3.36	0.98
5Lub 7	6.36	1.34	0.98	1.79	3.36	0.98
6Lub 8	6.32	0.00	0.00	1.83	3.38	0.98
7Lub 9	8.16	0.69	1.00	2.25	3.40	0.99
8Lub 10	8.23	0.50	0.36	2.07	3.37	0.98
9Jel 11	8.71	0.00	0.00	1.52	3.25	0.95
10Jel 12	8.74	0.00	0.00	1.60	3.26	0.95
11Jel 13	8.76	0.00	0.00	1.30	3.00	0.90
12Jel 14	8.63	0.00	0.00	1.25	3.19	0.95

H´ * Shannon index H´ diversity of vegetation, J * Equitability J of vegetation, H´ ** Shannon index H´ diversity for ECO plates, J ** Equitability J for ECO plates, AWCD - Averages Well Color Development

Soil microorganisms play a vital and irreplaceable role in many soil processes. Present research has focused on the detection of the number of biomass and activity, while the investigating the diversity of soil organisms and in particular of soil microorganisms was initiated in the last years. Soil organisms are characterized by considerable diversity.

In general, the smaller organisms, the greater the diversity, which is related to the extreme heterogeneity of soil environment at all spatial levels and the limited ability of the migration of most of these organisms. Soil microorganisms depend on the metabolic products of primary producers, but it is questionable how the diversity of vascular plants affects diversity of soil microorganisms [6].

Functional diversity of microbial communities we evaluated using the Biolog Eco Plates. This method is well known for its sensitivity and quickness and was used among other for the ecotoxicological assessment of contaminated soils [14, 9].

To calculate Shannon diversity index, we used the absorbance at a given AWCD (Averages Well Color Development) in the samples investigated after 168 hours. We found that the absorbance in the soil sample located in emission field of magnesium factory Jelšava – Lubeník (Slovakia) reached low values (1.25 to 2.25) (Table 1, Figure 3).

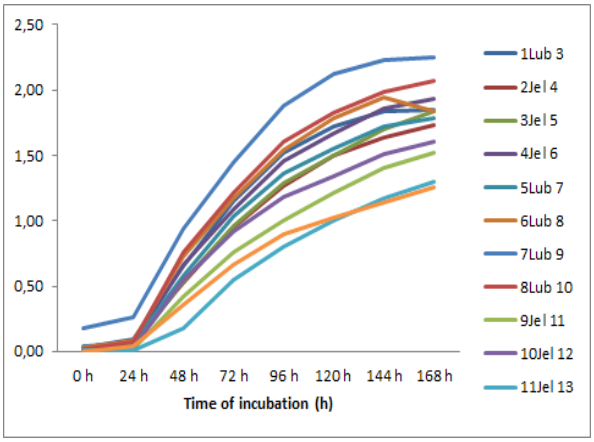

Figure 3
Averages Well Colour Development (AWCD) of Biolog® Eco Plates (31 substrates) in investigated areas Jelšava and Lubeník (Slovakia)

These correspond to low to moderate (3.0) and medium (3.4) diversity of functional groups of microorganisms (Table 1). At the same time, we found minimal differences between soils that are strongly alkalized and weakly acidic to neutral. Our research confirmed that plant diversity determines the activity and diversity of the soil environment [4, 16].

On this basis, we can conclude that the soil ecosystem in deteriorated environment is unstable, and its function is impaired.

TABLE 2
RESULTS OF MONITORED PARAMETERS EXPRESSED BY DESCRIPTIVE STATISTICS IN INVESTIGATED AREAS JELŠAVA AND LUBENÍK (SLOVAKIA)

Parameter	Min.	Max.	Mean	Standard error
pH/KCl	6.23	8.76	7.628	1.034037
H´ *	0.00	1.536	0.5977	0.618528
J *	0.000	1.000	0.408217	0.408283
AWCD	1.251	2.253	1.747	0.291597
*H´***	3.003	3.395	3.301	0.112714
*J***	0.901	0.989	0.965	0.025046

H´ * Shannon index H´ diversity of vegetation, J * Equitability J of vegetation, H´ ** Shannon index H´ diversity for ECO plates, J ** Equitability J for ECO plates, AWCD - Averages Well Color Development

ACKNOWLEDGMENT

VEGA 1/0127/16 Ecological and environmental risks of land degradation and management approaches to the elimination of their impact on the environment, KEGA 011PU-4/2016 Implementation of the new trends of environmental research into the education of natural and management courses in the study programme Environmental management.

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GC CHIRAL SELECTOR FOR SIMULTANEOUS SEPARATIONS OF ALPHA AND BETA PHENYLALANINE AND THEIR ENANTIOMERS

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Received: November 2016

Abstract

The paper shows a process control of transisomerisation α-phenylanine to β-phenylalanine, and simultaneous chiral purity test of compounds.

Key words: *Separations, Alpha and Beta Phenylalanine*

INTRODUCTION

The members of an enantiomer pair are mirror images of each other's (Figure 1). They are similar to each other as the right and left hands [1].

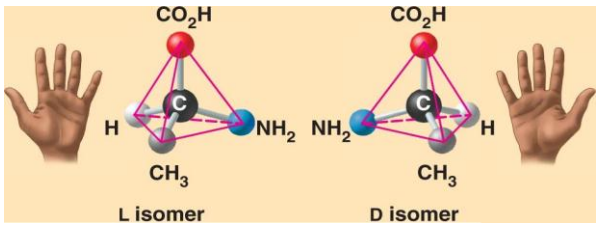

Figure 1

The structures of an enantiomer pair (alanine)

The members of the enantiomer pairs in spite of their very similar structures can show rather different biological effects; therefore the chiraly pure products (containing only one isomer) are basic requirement in pharmaceutical industry [2]. The separation of members of an enantiomer pair (chiral separation) is a rather hard job. Namely the chiral separations need tailor made (three points) interactions between the selectors and selectands [3].

The non-essential β-phenylalanine (Figure 2/b) is the raw material of some pharmaceuticals. The β-phenylalanine is synthetized from essential α-phenylalanine Fig.2/a) with enzymes [4].

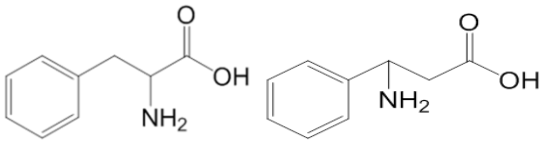

Figure 2

Figure 2a. The structure of α-phenylalanine

Figure 2b. The structure of β-phenylalanine

The gas chromatography (GC) is applied many cases for chiral separations [5]. The most popular chiral stationary phases of gas chromatography are based on cyclodextrin selectors (Figure 3).

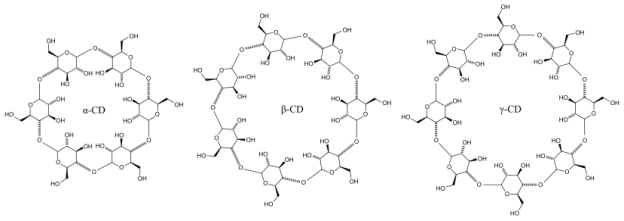

Figure 3

The structures of cyclodextrins (CDs).
The α- β- and γ-CD row 6, 7 and 8 glucose units [6].

On the other hand The Chirasil-Val valine containing selector is applied frequently for chiral separations of α- amino acids [7]. Therefore we tested various

cyclodextrins and Chirasil-Val chiral gas chromatographic stationary phases to solve our task.

MATERIALS AND METHODS

The β-phenylalanine, α-phenylalanine, trifluoro acetic anhydride, acetic acid anhydride, triethyl amine, N-Methyl-N-nitroso-p-toluenesulfonamid, ethyl acetate, diethyl ether, anhydrous Mg_2SO_4, were purchased from Sigma-Aldrich. Gas chromatographic silicone polymer columns were bought from different sources having various chiral selective contents: ALFA DEX 120 α-CD containing, 30 m x 0.25 mm x 0.25 µm (Supelco); CYDEX-B β- CD containing, 25 m x 0.22 mm x 0.25 µm (SGE); MEGA-DEX AC γ-CD containing, 25 m x 0.25 mm x 0.25 µm; µm (MEGA); Permabond Chirasil-L-Val valine containing, 50 m x 0.25 mm x 0.25 µm (Macherey-Nagel).

A GC-17A/QP5000 GC/MS (Shimadzu) instrument was applied for GC analyses.

The low volatility of amino acids make necessary for the derivatization of amino acids in GC analyses. The acidic groups were converted to methyl esters in every occasion. The amine groups transformed acetamide or trifluoro acetamide applying generally used derivatization procedures [8].

RESULTS

Appropriate simultaneous separations have been achieved with various selector-selectand combinations.

α-cyclodextrin

The permethylated α-cyclodextrin (TRIMEA) congaing silicone polymer proved to be a good selector (Figure 4).

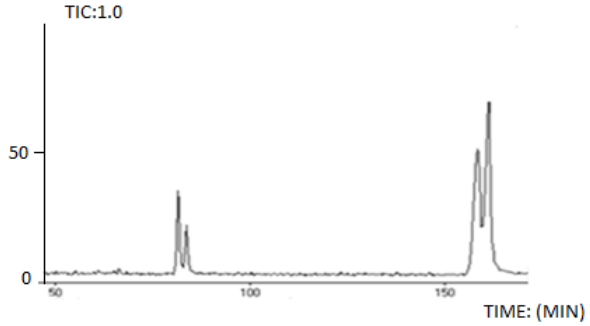

Figure 4

The simultaneous separations of α phenylalanine (first peak pair) and β-phenylalanine (second peak pair) and their enantiomers as methyl ester and trifluoro acetamid derivatives. Conditions: column, 25m x 0.25 mm x 0.25µm; stationary phase, permethylated α-CD containing silicone polymer (ALFA DEX 120); temperature, 100°C.

β-cyclodextrin

The permethylated β-cyclodextrin (TRIMEB) congaing silicone polymer proved to be also a good selector (Figure 5).

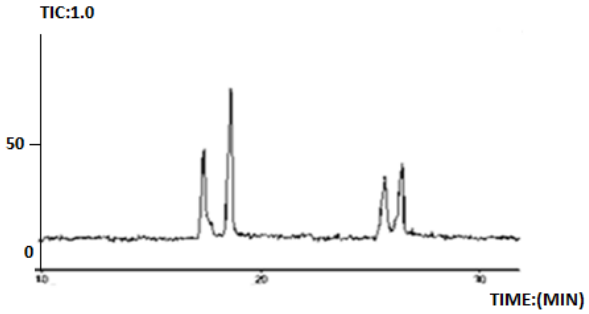

Figure 5

The simultaneous separations of α phenylalanine (first peak pair) and β-phenylalanine (second peak pair) and their enantiomers as methyl ester and trifluoro acetamid derivatives. Conditions: column, 25m x 0.22 mm x 0.25µm; stationary phase, permethylated β-CD containing silicone polymer (CYDEX-B); temperature, 130°C

γ-cyclodextrin

2,3-diacety-6-tercierbutylsilil γ-cyclodextrin (Ac G-CD) containing selector is excellent to separate enantiomers of β-phenyl alanine as methyl ester acetamide derivatives (Figure 6). No separation was achieved for α-phenylalanine.

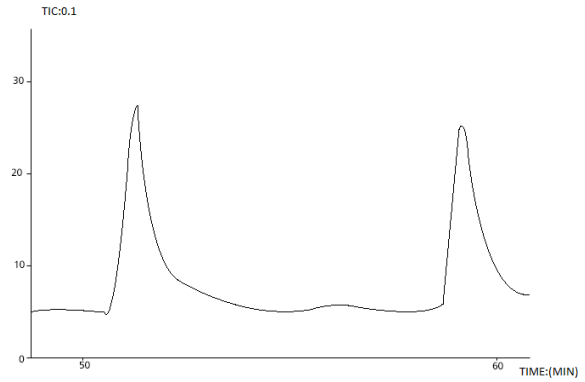

Figure 6

The chiral separation of β-phenylalanine as methyl ester and acetamide derivatives. Conditions: column, 25m x 0.25 mm x 0.25µm; stationary phase, 2,3-diacetyl-6-tercierbutyl γ- cyclodextrin containing silicone polymer (MEGA DEX DAC); temperature, 150°C.

Permabond Charasil-L-Val

The Chirasil-L--Val proved the best selector for the tested compounds. It can chiraly separate the enantiomers of β-phenylalanine, in spite of, it was designed for chiral separations for α-amino acids (Figure 7). Both derivatives (acetamide and trifluoro acetamide) of α phenylalanine and β-phenylalanine were chiraly well separated.

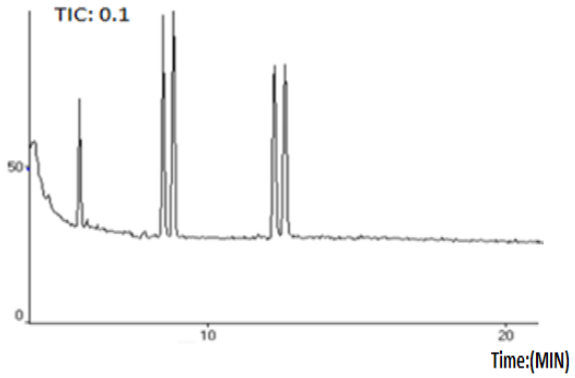

Figure 7
The simultaneous separations of α phenylalanine (first peak pair) and β-phenylalanine (second peak pair) and their enantiomers as methyl ester and trifluoro acetamide derivatives. Conditions: column, 50 m x 0.25 mm x 0.25µm; stationary phase, Valine (Charasil-L-Val) containing silicone polymer; temperature, 170°C.

The Chirasil-L-Val stationary phases have extra advantages. Both enantiomers of valine (L and D) containing selectors are commercialized as chiral stationary phases.
The elution order of member of enantiomer pairs can be reserved. The minor first elution order can be achieved according to the minor enantiomer choosing the appropriate chirality of valine selector. The best separations are summarized in Table I. The data of Table I show that some derivatives did not meet the recognition feature of every stationary phase.
The methyl ether trifluoro acetamides of derivatives α-phenylalanine and β-phenylalanine were separated on α-CD (TRIMEA), β-CD (TRIMEB) and valine (Chirasil-L-Val) containing stationary phases. The methyl ether acetamides derivatives α-phenylalanine and β-phenylalanine were separated only on γ-CD containing (AC G-CD) and valine (Chirasil-L-Val).

Table I
The best selectivity values of various derivatives of α-phenylalanine and β-phenylalanine.

Selector	Derivatives of amine	Selectivity	
		α-Phenylalanine	β-Phenylalanine
TRIMEA	TFA	1.0225 (100°C)	1.019 (100°C)
TRIMEA	Ac	/	/
TRIMEB	TFA	1.020 (110°C)	1.015 (120°C)
TRIMEB	Ac	/	/
AC G-CD	TFA	/	/
AC G-CD	Ac	1.046 (150°C)	1.156 (150°C)
Chirasil-L-Val	TFA	1.094 (140°C)	1.074 (160°C)
Chirasil-L-Val	Ac	1.150 (150°C)	1.041 (150°C)

Symbols: TRIMEA, permethylated α-cyclodextrin; TRIMEB, permethylated β–cyclodextrin; Ac G-CD, 2,3 diacety-6-tercierbutylsilil γ-cyclodextrin (Ac G-CD); /, no separation was recognized.

The acid functions were transformed to methyl esters. The amine functions were transformed trifluoro acetamide (TFA) or acetamide (Ac) derivatives.
The selectivity differences are caused by the different cavity sizes among the cyclodextrins.
The high selectivity values of analytes come from amino acid (valine) content of the stationary phase on Chirasil-L-Val. Namely the similar structures of selectand and selector give good chiral recognition ability.
The shake of the comparisons, the selectivity values of separated compounds were measured or extrapolated to 100°C (Table II).
The protruding chiral recognition feature of Permabond Chirasil-L-Val has become more obviously from the data of Table II. Even selectivity values greater than 2 were calculated for α-phenylalanine. Moreover, the tested compounds have rigid structure, which improves the chiral selectivity.

The chiral separations vs. temperature values
Selectivity values, measured in several temperatures, allow a deeper sight in the chiral recognition mechanism of a stationary phase. If the curve of ln α values is linear function of 1/T (absolute temperature) values, the chiral recognitions belong to one mechanism [7].

Table II
Shows the selectivity values at 100°C, using different selector-selectand combinations

Selector	α-Phea TFA	α-Phea Ac	β-Phea TFA	β-Phea Ac
TRIMEA	1.025	/	1.019	/
TRIMEB	1.025	/	1.011	/
AC G-CD	/	1.211	/	1.341
Chirasil-Val	2.058	2.306	1.273	1.207

Symbols: TRIMEA, permethylated α-cyclodextrin; TRIMEB, permethylated β–cyclodextrin; Ac G-CD, 2,3 diacety-6-tercierbutylsilil γ-cyclodextrin (Ac G-CD); TFA, trifluoro acetamide derivative; Ac, acetamide derivative; /, no

Every measured 1/T- ln α relation are linear suggesting that the chiral recognition mechanism belongs to one mechanism in the given stationary phase. This establishment is demonstrated in Figure 8. Of course the different stationary phases have different chiral recognition feature. This results in different selectivity of derivatives on various stationary phases.

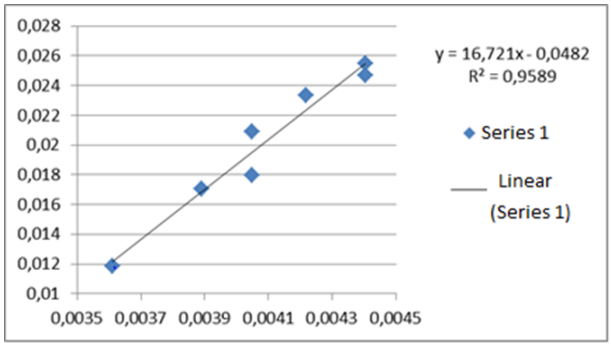

Figure 8
The dependency of natural logarithm of selectivity values (ln α) as function of inverse of absolute temperature (1/T). The measurements were done on Chirasil-L-Val coated columns (50 m x 0.25 mm x 0.25 μm) in the case of methyl ester trifluoro acetamide derivatives of β-phenylalanine.

CONCLUSION

The best GC chiral selector is the Chirasil-L-Val for the simultaneous separations of α-phenylalanine and β-phenylalanine and their enantiomers. The chiral selectivity of various derivatives of selectands belongs to their derivative forms and the selectors. Only one chiral recognition mechanism is responsible for the separation of the tested compounds in a given stationary phase.

ACKNOWLEDGMENT

Valuable help of András Szeder is acknowledged.

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APPLICATION OF MAXIMUM ENTROPY METHOD FOR EXPLORING SPATIAL POPULATION STRUCTURES

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Received: November 2016

Abstract

A method for modelling the spatial probability distributions of shoots in plant communities is proposed. The vegetation potentials at a given point depend on the distance r_i *of the nearest individual of species i:*

$U_f(v) = U_f(r_1, r_2,...r_s)$ *where s denotes the number of occurring species. We suppose the spatial means of these remain constant. The vegetation is in a stationary state if the corresponding distribution p(v) is the most likely, namely realized by the most of the possible configurations. An appropriate sampling procedure is proposed by which all spatial scales within the given area are considered at once. First, pick out at random a sample point. For each population studied, measure the distance between the chosen point and the nearest individual of the population. Take the measured distances down in a v vector of s dimensions, where s stands for the number of populations studied. So, in the course of sampling process v[i] holds by definition the distance between the last selected point and the i-th population. The concepts of scale-free floral diversity (entropy), distinctiveness, associatum and relative structural entropy are introduced. The latter contains an a priori probability density function. This accounts for the previously known spatial constraints and the architectural features of the studied plant species.*

The spatial structure of a plant community can be modeled in the framework of maximum entropy method. The maximum of relative structural entropy is considered with supplementary conditions (the spatial means of vegetation potentials are prescribed). The method was applied to a Bottle Sedge stand (Equiseto limosi-Caricetum rostratae). The distribution of Carex rostrata was independent on that of Equisetum fluviatile. The probability density function obtained for Carex rostrata can be interpreted that the sedge shoots take place according to a Poisson distribution on a fractal of dimension α*= 1.5494. The Lagrange parameter* β_1 *= 0.18166 is proportional to the shoot density on the fractal. Possible biological background of this result is discussed, and could be recognized as a self-organized critical phenomenon.*

Keywords: *Maximum Entropy Method, Population, probability density*

INTRODUCTION

The most important biological events in a plant community are the births and deaths of individuals (for clonal plants the individual corresponds to the ramet). So, the elementary processes of vegetation dynamics are the appearance and destruction of an individual at a given locality. We suppose these processes to proceed in a stationary state of the vegetation so that the spatial means of some vegetation potentials depending on the environment remain constant. The non-stationary vegetation left alone changes to approach the mean vegetation potential to the stationary one. The vegetation potential at a given point depends on some spatial variables r_i (specifying individuals of species i):

$$U_f(\underline{v}) = U_f(r_1, r_2, ...r_s) \quad (1)$$

where *s* denotes the number of occurring species. The vegetation is in a stationary state if the corresponding distribution *p(v)* is the most likely, namely realized by the most of the possible configurations. This means that the relative structural entropy S_r is at a maximum with the simultaneous fulfillment of conditions

$$\int p(d\underline{v}) = 1 \quad (2)$$

and

$$\int U_f(\underline{v})\cdot p(d\underline{v}) = \langle U_f \rangle, \qquad f = 1...m \qquad (3)$$

where *m* denotes the number of vegetation potentials. The procedure is similar to that of Jaynes building up the statistical mechanics on information-theoretical grounds, and known as 'maximum entropy method' [2], [3], [10].

The variables r_i, and therefore the vegetation potentials $U_f(\underline{v}) = U_f(r_1, r_2, ...r_s)$ depend on the sampling process used.

SAMPLING PROCEDURE

Let us suppose that the area is designated where the structure of populations is to be studied. Consider the following sampling procedure:

1. Pick out at random a sample point.
2. For each population studied, measure the distance between the chosen point and the nearest individual of the population.
3. Take the measured distances down in a *v* vector of *s* dimensions, where *s* stands for the number of populations studied. So, in the course of sampling process $\underline{v}[i]$ holds by definition the distance between the last selected point and the *i*-th population.

$\underline{v} \in \Omega$ is a probability vector variable, the distribution of which will be estimated from the sample frequencies. The Ω Euclidean vector space of *s* dimensions is determined by the area studied.

This procedure is a generalization of that proposed by Juhász-Nagy [4], [5]. The main difference here is that now all spatial scales within the given area are considered at once.

THEORY

According to the probability measure pertaining to *v*,

$$\int_{\Omega} p(d\underline{v}) = 1$$

With the knowledge of *p(v)* we can ask how to construct the probability distribution pertaining to any spatial scale point, i.e. how likely is that a given $i_1, i_2 ... i_k$ combination of populations occurs in any sampling circle of radius *r* placed out at random in the area studied. This is obviously the following:

$$P_{r,i_1...i_k} = \int_{\sigma} p(d\underline{v}),$$

where σ stands for that domain of Ω for which $\underline{v}[i_1] \le r, \underline{v}[i_2] \le r, ... \underline{v}[i_k] \le r$ relations are true in the case of populations involved in the combination specified, while in the case of all other populations $\underline{v}[i_s] > r.$

Here and what follows the notation of integral according to the probability measure is used. In the case of continuous distributions this corresponds to

$$P(r, i_1...i_k) = \int_0^r\int_0^r ... \int_0^r \int_r^\infty\int_r^\infty ... \int_r^\infty p(\underline{v}) dv[i_m]..dv[i_s]dv[i_1]..dv[i_k]$$

Here the populations involved in the specified combination are numbered from i_1 to i_k, while the populations not involved are numbered from i_m to i_s. Similar expression can be written for the discrete case, but sums occur instead of integrals. Our variable *v* is continuous in principle; it becomes discrete only because of the sampling process.

Hereafter we generalize the information quantities introduced in [4], [5].

The floral diversity pertaining to scale point *r*:

$$H = -\sum_f P(r, f)\cdot \log P(r, f),$$

where the population combinations are indexed by *f*. With the knowledge of distribution *p[v]* all information functions can be similarly derived, namely at any scale point. We can also say more than that, however. We can introduce the information quantities immediately on the basis of the distribution *p[v]*. The quantities obtained in this way are formally independent of the scale because they involve all scale points. So the scale-free floral diversity or entropy:

$$S = -\int \log p(\underline{v})\cdot p(d\underline{v}) \qquad (4)$$

The other information quantities can be similarly defined, e.g. the scale-free local distinctness:

$$L = -\sum_{i=1}^{s} \int \log p(r_i)\cdot p(dr_i),$$

where $p(r_i)$ is the probability density function of the *i*-th species' nearest occurrence in distance r_i from a randomly selected point:

$$p(r_i) = \int_{(i,r_i)} p(d\underline{v})$$

The integral is to be performed for those vectors *v*, according to which the *i*-th species occur at distance r_i.

The scale-free associatum represents the information that contradicts the hypothesis of independent occurrences of different species (information gain):

$$A = \int \log\left(\frac{p(\underline{v})}{\prod_i p(r_i)} \right) \cdot p(d\underline{v}),$$

where the product stands for those r_i which *v* depends on. This may be rewritten as follows [7]:

$$A = \int \log p(\underline{v}) \cdot p(d\underline{v}) - \int \log \prod_i p(r_i) \cdot p(d\underline{v}) =$$

$$= \int \log p(\underline{v}) \cdot p(d\underline{v}) - \sum_i \int \log p(r_i) \cdot p(d\underline{v})$$

First, we perform the integration at a fixed r_i, then according to r_i:

$$\int \log p(r_i) \cdot p(d\underline{v}) = \int \log p(r_i) \int_{(i,r_i)} p(d\underline{v})\, dr_i =$$

$$= \int \log p(r_i) \cdot p(dr_i),$$

so obtain

$$A = \int \log p(\underline{v}) \cdot p(d\underline{v}) - \sum_i \int \log p(r_i) \cdot p(dr_i) = L - S,$$

what is the same as the known relation between the corresponding scale dependent quantities.

It is worth mentioning that the scale-free information quantities cannot be written as the integrals (or in discrete case sums) of scale dependent ones, because the scales are obviously dependent.

The scale-free entropy (4) can be named as the structural entropy of the vegetation. By some modification of this, we can introduce the relative structural entropy:

$$S_r = -\int \log\left(\frac{p(\underline{v})}{p_0(\underline{v})} \right) \cdot p(d\underline{v})$$

where $p_0(\underline{v})$ is some a priori probability density function (in the special case $p_0(\underline{v})$=1 we obtain the S structural entropy). This accounts for the previously known spatial constraints and the architectural features of the studied plant species.

The maximum problem with the supplementary conditions (2-3) can be summarized by the method of Langrange-multiplicators in the following variation principle:

$$\delta \int \left\{ -\log\left(\frac{p(\underline{v})}{p_0(\underline{v})} \right) - (\lambda - 1) - \sum_f \beta_f \cdot U_f \right\} \cdot p(d\underline{v}) = 0 \qquad (5)$$

where λ and β_f (f = 1...m) are the Lagrange multiplicators.

By introducing the function

$$\Lambda = \left(-\log\left(\frac{p(\underline{v})}{p_0(\underline{v})} \right) - (\lambda - 1) - \sum_f \beta_f \cdot U_f(\underline{v}) \right) \cdot p(\underline{v})$$

,

the variation problem (5) leads to the (special) Euler differential equation

$$\frac{\partial \Lambda}{\partial p(\underline{v})} = 0$$

Solving this variation problem we obtain

$$p(\underline{v}) = \frac{p_0(\underline{v}) \cdot e^{-\sum_f \beta_f \cdot U_f(\underline{v})}}{Z}. \qquad (6)$$

The quantity $Z = e^{\lambda}$ can be named partition function by the above mentioned analogy with statistical physics.

According to Eq. (2),

$$Z = \int p_0(\underline{v}) \cdot e^{-\sum_f \beta_f \cdot U_f(\underline{v})}\, d\underline{v} \qquad (7)$$

The coefficients β_f are important quantities of intensity character, and may be obtained from the

auxiliary conditions (3), using (7) and solving the equations

$$\langle U_f \rangle = -\frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta_f}.$$

In the special case, when the species appear independently, the vegetation potentials can be associated with the single species:

$$U_i(\underline{v}) = U_i(r_i)$$

Now, the vegetation potential of the *i*-th species depends only on the distance of this species' occurrence. Hence the probability density function (6) can be written as the product of the probability density functions of each species' occurrences:

$$p(\underline{v}) = p_1(r_1) \cdot p_2(r_2) \cdot \ldots p_s(r_s),$$

where

$$p_i(r_i) = \frac{p_0(r_i) \cdot e^{-\beta_i \cdot U_i(r_i)}}{Z_i}$$

$$Z_i = \int_0^\infty p_0(\underline{r_i}) \cdot e^{-\beta_i \cdot U_i(r_i)} dr_i$$

In this case the scale-free (and also each scale-dependent) associatum is equal to zero.

EXAMPLE: BOTTLE SEDGE STAND (EQUISETO LIMOSI-CARICETUM ROSTRATAE)

The field data were compiled in Danube-Drava National Park, near the village Berzence, Hungary. The sample area was designated in the frame of a research program lasting several years and had a surface of 9117 cm². It consisted of four adjacent quadrangles. The coordinates of each above ground shoots were measured. The data were transformed into a unique coordinate system, using the edges and diagonals of the quadrangles. Six plant species occurred in the sample area (in brackets the number of shoots): *Carex rostrata* (306), *Equisetum fluviatile* (422), *Mentha aquatica* (5), *Rorippa amphibia* (1), *Agrostis stolonifera* (6), *Lythrum salicaria* (3). Due to the edge effect only the first two species were involved in further analysis. In particular, such a point that is nearer to the boundary than to any individual of the studied species in the designated area cannot be evaluated, because we do not know, how the shoots take place out of the sample area. Involving a third species would reduce unacceptable the area and shoot number, paying attention to a fourth species was impossible at all.

The scale-dependent associatum calculated from the empirical data proved to be negligible at all scales, therefore for each of the two species (i=1: *Carex rostrata*, i=2: *Equisetum fluviatile*) its own vegetation potential could be modeled. The model parameters were determined by the maximum likelihood method. After testing a number of possibilities, the following model seemed to be appropriate:

1. *A priori distributions*

For *Carex rostrata:*

$$p_0(r_1) = 2 \cdot r_1 \cdot \frac{\pi}{a} \qquad \left(r_1 \le a \cdot \frac{\sqrt{3}}{2}\right),$$

$$p_0(r_1) = \frac{r_1}{a} \cdot \left(2 \cdot \pi - 12 \cdot \arccos\left(a \cdot \frac{\sqrt{3}}{2 \cdot r_1}\right)\right) + \frac{\left(\frac{2 \cdot r_1}{a} - \sqrt{3}\right)}{\left(2 - \sqrt{3}\right)} \cdot \sigma \qquad \left(a \cdot \frac{\sqrt{3}}{2} < r_1 < a\right),$$

$$p_0(r_1) = \sigma \cdot \left(\frac{r_1}{a}\right)^{\alpha - 1} \qquad (r_1 \ge a)$$

a = 1.6045 cm, σ = 2.21215.

The function $p_0(r_1)$ is continuous and has the following sense:

When $r_1 \le a \cdot \frac{\sqrt{3}}{2}$, i.e. the sample point is close to a sedge shoot, the probability density function is proportional to the distance from the point to the shoot. This is a property of any finite, discrete point distribution in plane.

When $a \cdot \frac{\sqrt{3}}{2} < r_1 < a$, we take into account the property of *Carex rostrata* that this species develops several shoots in the immediate neighborhood of one another, and the shoots within these tufts appear in fairly regular distances due to intraspecific competition or correlative inhibitions. In the model a regular hexagonal lattice with lattice constant $a \cdot \frac{\sqrt{3}}{2}$ was taken into account (so the maximum point-shoot distance within the lattice is *a*). The last (linear in r_1) term appears because the tufts are bounded in space (and usually of small size), hence at their border the probability density function become again linear in

distance. The coefficients were selected so that the function $p_0(r_1)$ is continuous.

When $r_1 \geq a$ the sample point take place in the free space between tufts. In this case the probability density function of distance to the nearest shoot does not change linearly because the distances between tufts are varying and can also be fairly small. In the model this circumstance appear as a power function with an exponent (α-1) smaller than one. The notation will be explained later. The dependence on distances is expressed by a dimensionless ($\frac{r_1}{a}$) variable. Dimensionless variables will be used later too.

For *Equisetum fluviatile:*

$$p_0(r_2) = \frac{2 \cdot r_2}{R} \qquad (r_2 < R)$$

$$p_0(r_2) = \frac{r_2 + R}{R} \qquad (r_2 \geq R)$$

R = 1.6655 cm.

Here the hierarchic construction of *Equisetum* shoot system was taken into account:
The plagiotropic shoots are ready to develop shoot groups by monopodial branching and the secondary shoots tend to show the same pattern of branching. The radius of shoot group is denoted by R. When $r_2 < R$, the linear expression similar to that of *Carex rostrata* is valid.
When $r_2 \geq R$, a similar expression is supposed near the shoot groups. The coefficients were selected the function $p_0(r_2)$ to be continuous.

2. *Vegetation potentials*

Carex rostrata: $U_1(r_1) = \left(\frac{r_1}{a}\right)^{\alpha}$,

α = 1.5494.

Equisetum fluviatile:

$$U_2(r_2) = \left(\frac{2 \cdot r_2}{R}\right)^{\delta} \qquad (r_2 < R)$$

$$U_2(r_2) = \left(\frac{r_2 + R}{R}\right)^{\delta} \qquad (r_2 \geq R)$$

δ = 2.1413.

Power functions were chosen, in the case of *Equisetum fluviatile* with the above mentioned hierarchic structure.
In the case of *Carex rostrata* we obtain the following probability density function for $r_1 \geq a$:

$$p_1(r_1) = \sigma \cdot \left(\frac{r_1}{a}\right)^{\alpha-1} \cdot e^{-\beta_1 \cdot \left(\frac{r_1}{a}\right)^{\alpha}} \qquad (8)$$

This can be interpreted so that the sedge shoots take place according to a Poisson distribution on a fractal of dimension α= 1.5494. This can be easily seen if we take into account that the measure ('mass', according to [9]) of fractal objects in a circle of radius r_1, $M(r_1) \propto r_1^{\alpha}$. According to the Poisson distribution the probability of no shoot in that circle is $p(r_1) = e^{-\beta_1 \left(\frac{r_1}{a}\right)^{\alpha}}$. The probability density function of appearing a shoot at distance r_1 from the centre is the derivative of 1-*p(* r_1*)*, i.e. the expression (8). The Lagrange parameter β_1 = 0.18166 is proportional to the shoot density on the fractal (taking α=2 we obtain the analogous expression for the Poisson distribution in two dimensions). From the above considerations it follows also that $\sigma \propto \alpha \cdot \beta_1$.
We can unify the results obtained for the distinct species to get the probability density function for their community:

$$p(\underline{v}) = p_1(r_1) \cdot p_2(r_2) = \frac{p_0(r_1) \cdot p_0(r_2) \cdot e^{-\beta_1 \cdot U_1(r_1) - \beta_2 \cdot U_2(r_2)}}{Z}$$

β_1 = 0.18166, β_2 = 0.16753,

$$Z = \int_0^{\infty}\int_0^{\infty} p_0(r_1) \cdot p_0(r_2) \cdot e^{-\beta_1 \cdot U_1(r_1) - \beta_2 \cdot U_2(r_2)} dr_2 dr_1 =$$

$$= 44.6935$$

In knowledge of the probability distribution, any statistical characteristic can be calculated, e.g. relative structural entropy S_r=3.4415, scale-free floral diversity (entropy) *S* = 2.20429, scale-free associatum *A* = 0, information gain relative to the Poisson distribution in plain S_p = 0.61737.

Fig. 1 shows the probability distribution of occurrence at different distances for *Carex rostrata*, namely that calculated from the model and likewise that measured on the point map. By the computerized sampling process the distances from 3000 random points to

their nearest shoots were measured with resolution 1 cm, which approximately corresponds to the measurement precision estimated in field. So, the first scale point on the horizontal axis means that the shoot occurred first at distances $0 \le r_1 < 1$ cm, the second scale point corresponds to the interval $1 \le r_1 < 2$, etc.

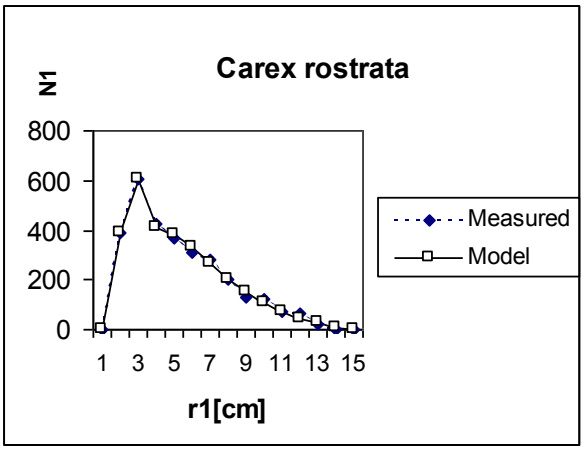

Figure 1

Nearest shoot distribution of Carex rostrata

Similarly, the nearest shoot distribution of *Equisetum fluviatile* is shown by Figure 2. The scale-dependent floral diversity as a function of the radius of sampling circles is given by Figure 3.

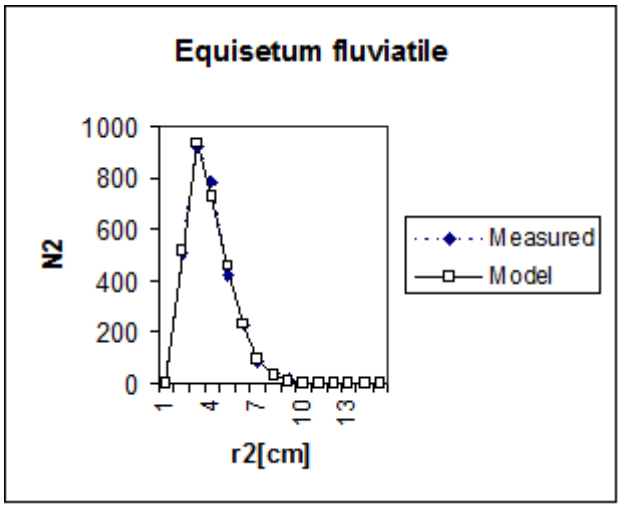

Figure 2

Nearest shoot distribution of Equisetum fluviatile

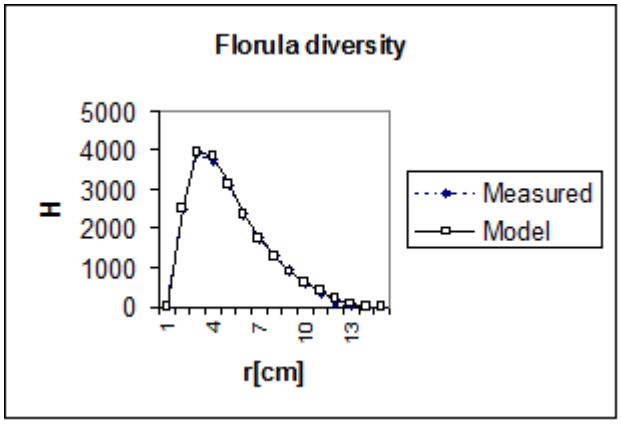

Figure 3

Scale-dependent floral diversity in Equiseto limosi-Caricetum rostratae

DISCUSSION

For *Carex rostrata*, we have obtained that the shoots (except for the domain of very small distances) take place on a fractal. Therefore we also touch briefly upon our ideas about the emergence of these complex formations. Because the above ground shoots of both species arise sympodially from creeping (generally quite intricate) rhizomes below ground, it seems to be obvious to suppose that this rhizome system composes the fractal. Both species are dominant competitors trying to exploit the available resources (oxygen, nutrients, etc.). Their roots grow from the rhizomes. Therefore they develop their below ground shoot system up to a critical point, beyond which the arising deficiency symptoms would cause mass decay of rhizomes. But because the environmental conditions are never constant, from time to time changes (growth and decay) of different size and direction take place in the below ground shoot system, and this results in the complex structure mentioned.

Analogous phenomenon is experienced e.g. by order-disorder phase transitions, where at the transition point various domains (with size distribution characterized by power function) of ordered phase occur. The main difference is that the theory outlined above is non-equilibrium. The supposed critical state rises not by fine tuning of some external parameter (e.g. temperature), but spontaneously, in the course of the system's self-development. This state was recognized first by computer modelling of sand piles, and is customary to mark with the attribute 'self-organized critical' [1]

The method was also applied to a Slender Sedge stand (*Caricetum elato-lasiocarpae*). Some preliminary

results are presented in [11], and will be published later in detail. The rules of spatial arrangement of *Carex lasiocarpa* seem to be analogous to that of *Carex rostrata*, but its interaction with *Carex elata* causes some distortion in the realized structure, accounted for by the model.

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ENVIRONMENTAL MANAGEMENT SYSTEM IMPLEMENTATION INTO THE UNIVERSITY ORGANISATION

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Received: November 2016

Abstract

Traditionally EMSs are implemented across all operations at a facility simultaneously. This way of implementation works well for industry and smaller businesses and offices where operations are easily delineated and there is a simple chain of command structure in place. The University is too enabling to implement the EMS strategy similarly. Environmental Management System is an integrated organized set of policies and procedures under which the University can remain compliant with applicable environmental regulations, and in addition, manage and lessen our impacts on the environment, thereby improving the University's overall environmental performance. The University's EMS will require continual evaluation of the University's activities to ensure the University is doing as much as possible to reduce its impact on the environment and to remain environmentally compliant. This paper describes present situation and approach of universities to implementation of EMSs in Slovakia and into universitie management in abroad. The main principles and key requirements of the organisation management in accordance with the sustainable development are not only safety and quality managing of all activities in organisation in both manufacturing and services (education) but also environmental appropriate access.

INTRODUCTION

The University is made up of a variety of under-graduate, graduate, and professional schools, each comprised of many departments with unique specialities.

In addition to academics, the University maintains a large laboratories, a large educational and research departments, lecture halls and facilities maintenance staff that maintain the infrastructure of the University, such as utilities and building [7]. With so many diverse operations, University-wide implementation is exceedingly difficult. To more effectively communicate the tasks and goals of the environmental management system (EMS) to all the faculty, staff, and students, as well as getting the required support of the EMS from all departments, the EMS is being implemented incrementally on a much smaller scale [2].

ENVIRONMENTAL MANAGEMENT AS TOOL FOR SUSTAINABLE DEVELOPMENT

The main principles and key requirements of the organisation management are not only safety and quality managing of all activities in organisation in both manufacturing and services (i.e. education) but also environmental appropriate access in accordance with the sustainable development [5].

Modern pro-environmental oriented management approaches (as BS 8555 standard, EMS, EMAS etc.) emphasizes the principle of continuous improvement, based on the Deming Cycle, Figure 1.

Implementation of environmental management system influences the growing interest of the public, pressure from customers and business partners, and especially aware of own responsibility for the state of the environment. This system is implemented voluntarily and the enterprise can actively monitor and manage the impact of its activities on the environment, enterprise can gradually reduce all its negative environmental impacts.

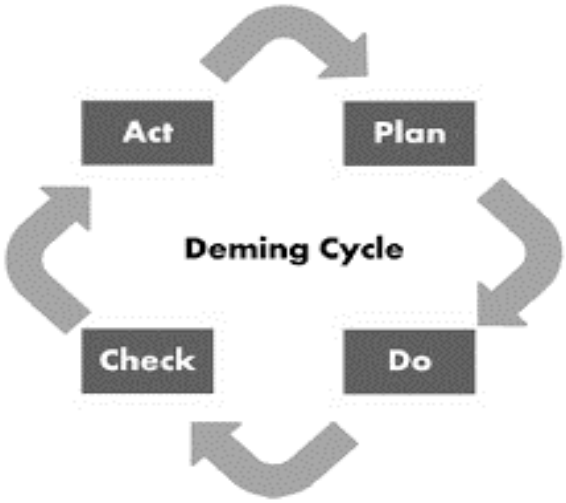

Figure 1

Deming cycle

The most commonly used framework for an EMS is ISO 14001 standard. An integral part of the EMS is the detailed systematic control of all documents including policies, procedures, training records, reports, permits, and all other relevant environmental information, Figure 2.

Figure 2
Continual Improvement model [9]

APPLICABLE OF ENVIRONMENTAL MANAGEMENT SYSTEM INTO UNIVERSITY ORGANISATION

Environmental management system is an integrated organized set of policies and procedures under which the University can remain compliant with applicable environmental regulations, and in addition, manage and lessen our impacts on the environment, thereby improving the University's overall environmental performance. This may sound complicated, but the concept is relatively simple. As coordinated teams, Environmental Health & Safety (EHS) and each department at the University systematically and regularly evaluate the department's operations for environmental regulatory compliance and environmental impacts. Operations are modified as necessary to meet the requirements of the regulations. Identified environmental impacts are ranked and investigated to find ways to prevent, lessen, or eliminate these impacts.

POLICY AND STRATEGY

An EMS enables an organisation to manage its environmental performance in a comprehensive, systematic and documented manner. It serves as a tool to reduce the impact, both immediate and long-term, of an organisation's operations on the environment. It encourages the allocation of resources, assignment of responsibility, and ongoing evaluation of practices, procedures and processes with a view to continual improvement of the system [4].

For universities, the introduction of EMS mean improving the image of the public and may also be proof of its quality and social responsibility. It can reform the education of the students to a better and also open up new opportunities for obtaining research grants and supporting cooperation between faculties [2].

ECOCAMPUS

One of the schemes, which enables to colleges and universities to be recognised for addressing key issues of environmental sustainability is EcoCampus [1]. EcoCampus is a scheme which offers a flexible phased approach to implementing an environmental management system for the higher and further education sector. EcoCampus provides a modular, phased, incremental approach to developing an EMS in line with both BS8555 & ISO 14001. Participants gain recognition at each stage of the process through a series of awards from bronze through silver, gold and platinum. The platinum award conforms to the requirements of the international environmental management standard ISO 14001 (see Figure 3).

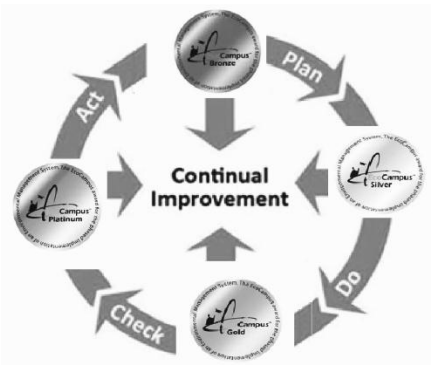

Figure 3
Stage of the process EcoCampus

The scheme enables colleges and universities to be recognised for addressing key issues of environmental sustainability [6]. EcoCampus provides awards relating to 4 levels of achievement, linked to each stage of EMS development:

Phase 1: Planning (Bronze)
- Senior management commitment
- Environmental awareness training
- Baseline environmental review
- Draft environmental policy

Phase 2: Implementing (Silver)
- Legal & other requirements
- Significant environmental aspects
- Objectives, targets & programmes
- Environmental policy

Phase 3: Operating (Gold)
- Resources, roles, responsibility & authority
- Competence, training & awareness
- Communication
- Documentation
- Control of documents
- Operational control
- Emergency preparedness and response

Phase 4: Checking & Correcting (Platinum)
- Monitoring & measurement
- Evaluation of compliance
- Nonconformity, corrective action & preventative action
- Control of records
- Internal audit
- Management review

BS 8555

EcoCampus is closely aligned to ISO 14001, the international environmental management standard, and BS 8555, the British guidance standard. The British Standard BS8555 (full title: Guide to the phased implementation of an environmental management system including the use of environmental performance evaluation, Figure 4) describes how to implement a generic EMS and can be used as a route towards ISO14001 and EMAS.

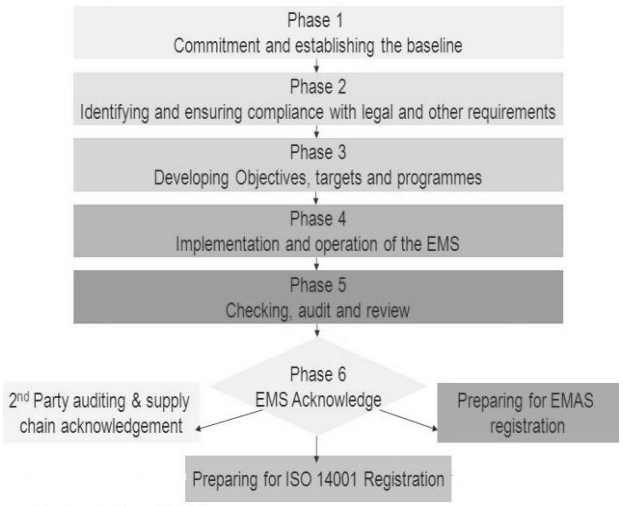

Figure 4
BS8555 Model

FOREIGN UNIVERSITY ENVIRONMENTAL MANAGEMENT SYSTEM

An example of the existing EMS in foreign universities is presented Manchester Metropolitan University (MMU). This University has implemented an Environmental Management System that is certified by ISO14 001 and awarded EcoCampus Platinum as one of only 28% of EcoCampus-registered Universities that have EcoCampus Platinum. The Environmental Management System is implemented by using the phased approach of the EcoCampus scheme, which provides a structured approach to work towards the ISO14001:2015 standard. In 2016, MMU was the first University to achieve the new and more challenging ISO14001:2015 standard. EMS incorporates all of the University's business activities, including estates and operations, leadership and governance, learning, teaching and research and engagement activities. Environmental Sustainability Strategy 2014–2020 sets out the actions MMU needs to take to achieve our aims and become a Sustainable University [8]:

- Placing environmental sustainability alongside graduate employability
- Use of sustainable modes of transport that minimise environmental impact
- Embed sustainable design principle
- Grow sustainability-themed research activity by 2020
- Ambitious targets to reduce carbon emissions by 50% by 2020
- Prevent, reduce, reuse and recycle
- Reuse and recycle 85% of waste by 2020
- Protect and enhance biodiversity across the university
- Offer opportunities to develop skills and knowledge to live and work sustainability

- Zero waste to landfill policy commitment
- Use alternative water sources and reduce water consumption by 25% by 2020.

MMU is an example for other universities which illustrates as to implement and realize the environmental policies and plans into university concept. It's vital that staff, students, trade union representatives should be have the enthusiasm and interest to engage in the development of environmental policies, strategies and management plans of their university.

CONCUTION

Currently, there is no university in Slovakia, which would have introduced a certified environmental management according ISO 14001. According scheme EMAS II, while efforts to introduce environmental education into university teaching process, especially in terms of sustainable development and the establishment of EMS in the next step. This scheme was planning to introduce the issue of sustainable development in relevant study program as well as the introduction of at least one subject on that topic at all levels of higher education.

The next phase is a scheme EMAS III, which is already build under the step of introducing of environmental management system and schemes Green University of Slovakia and also for higher education institutions [3]. The aim for the future is to certify the EMS in the Slovak universities the same as universities abroad that they have been successfully practiced with positive results already in the process of system integration.

ACKNOWLEDGMENT

The research in this paper was supported by a grants: VEGA No 1/0537/2015 (50%) - Research of influence of chosen parameters of working environment on working power and productivity and KEGA 048TUKE-4/2015 (50%) -Transfer of knowledge from scientific-research activities into multimedial education process in the subject “Environment and manufacturing”, supported by Slovak Research and Development Agency.

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THE ASSESSMENT OF SOIL SPATIAL VARIABILITY USING AUTOCORRELATION COEFFICIENT ALONG A TRANSECT IN AN EXPERIMENTAL FIELD AT THE UNIVERSITY OF FERHAT-ABBAS, SÉTIF-1 (EAST OF ALGERIA)

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Received: November 2016

Abstract

Nowadays, there is an interest in the assessment of the spatio-temporal changes of the quality of soil resources in order to manage these resources in a sustainable and a conservative manner. So the aim of this study is to assess the spatial variability of some soil physical (Bulk density, Porosity) and chemical (pHH2O, Total carbonates) soil properties along a transect of 80 m of the experimental field station of Sétif-1 university. 16 Soil samples had been taken from soil surface horizon every 5 m along a 80 m E-O transect, and analyzed in laboratory for Bulk density determination (Core method), pHh2o and total carbonates (%). The main results show that concerning the soil physical properties, the Bulk density vary from 1.008 g/cm3 (E1) to 1.34 g/cm3 (E6), on the other hand, the estimated porosity vary from 50% (E6) to 62.45% (E1). The coefficient of variation of these two physical properties is 8.22 % and 5.99% respectively. Concerning the chemical properties, the results show that pH of the soil sample is alkaline with moderate total carbonate content. With values range for the pH from 8.07 (E2 and E5) and 7.51 (E6); and for total carbonate the value range is from 12, 11% (E16) to 24.08 % (E7). The coefficient of variation of the pH and total carbonates along the studied transect is 2.20 % et 20.20 % respectively. the spatial analysis of the soil properties along the transect studied by computing the autocorrelation coefficient with lag distance of 5 m (h) show that the bulk density and total carbonates had a spatial correlation with a coefficient r(h) of -0.34 and 0.54 respectively. On the other hand, the pH and the estimated porosity had no spatial correlation along the transect of 80 m.

Key words: *Soil spatial variability, autocorrelation coefficient, Transect, Lag distance.*

INTRODUCTION

Conservation Agriculture refers to a series of land management practices that minimize land degradation and increase soil, water and air conservation. Direct drilling (no tillage), crop residues retention, cover crops, appropriate cropping system rotation, integrated pest management are examples of Conservation Agriculture practices. Because of the complexity associated with natural and agricultural ecosystems, a land management practice found to be sustainable at one site might not be equally sustainable at another site [1].

Agricultural production systems are inherently variable due to spatial variation in soil properties, topography, and climate. To achieve the ultimate goal of sustainable cropping systems, variability must be considered both in space and time because the factors influencing crop yield have different spatial and temporal behavior [2]. The spatial variability of the soil is due two both systematic and random processes. Systematic variability is defined as gradual or marked changes in soil proprieties that can be explained by landform, geomorphic element, soil forming factor or human activities. Random patterns of soil variability cannot be related to known cause, although usually viewed as "random", the lack of an observable, systematic pattern is more likely due to a lack of detailed soil information [3]. Soil characteristics generally show spatial dependence. Samples close to

each other have similar properties than those from each other [4], [5]. Different sampling approaches have been used to quantify the spatial variability of soil properties, either using a grid sampling of some meter or several meter in dimension [6], [7] or using a sampling along a transect with a lag distance [8]. Whatever the type of sampling used, the aim is to assess the within-field spatial variability of soil properties, which does not appear in soil maps. this is on this perspective that the present research is undertaken with the aim of the assessment of soil spatial variability of some soil proprieties (pH, $CaCO_3$, Bulk Density, Total Porosity) along a transect of 80 m at the experimental field of the University of Ferhat-Abbas Sétif -1 (East of Algeria).

MATERIALS AND METHODS

General Description of the Study Area

The experimental field of the university of Ferhat Abbas -Sétif is part of the high-plain of Sétif at east of Algeria, which is located between 36°11'49.59"N and 5°21'57.97''E with a mean elevation of 1021 m. In terms of the climate, the high-plain of Sétif is characterized by a semi-arid climate, with mean annual precipitation of 450 mm. the soil of the field experimental is developed on ancient alluvial sediment with the high presence of calcium carbonate.

Methodology

Soil Sampling and Characterization

The sampling of the soil is done along a transect North-South of 80 m with a lag-distance of 5 m at a plot in the experimental field of the University of Ferhat-Abbas-Sétif (Figure 1).

Figure 1
Sampling along a 80 m transect at a lag distance of 5 m.

Overall, 16 soil surface samples has been characterized by determining the Soil bulk density (Cylinder method) and an estimation of total porosity, the soil reaction (pH water on 1:5 soil/water extract), and the total soil carbonate content (volumetric method using a calcimeter). Three repetitions for each soil proprieties had been done.

For the bulk density (cylinder method) each measurement has been replicated three times at each point on the transect. The estimation of total porosity has been done using this formula:

$$\text{Total Porosity (\%)} = (1 - BD/PD) \times 100$$

Where: BD: Bulk density (cylinder method) (Mg/m^3) and PD: particle density which we assume is equal to 2.65 Mg/m^3.

Descriptive Statistics and Spatial Analysis

The Soil data obtained has been analyzed statistically by computing the descriptive statistics such as the mean, the variance, the standard deviation, the variation coefficient). And then, for the spatial analysis, we compute the autocorrelation coefficient r(h) as follow:

The autocorrelation function is a special expression of auto-covariance. The latter describes the average product of differences of two observations, Ai (xi), Ai (xi+h), respectively, from the means of the series A, while the two observations are separated by a distance, the so-called lag h (Wendroth et al., 2011)

$$\text{Cov [Ai(x), Ai(x + h)]} = \frac{1}{N}\sum_{i=1}^{N-h} [\text{Ai (xi)} - \bar{A}] [\text{Ai (xi + h)} - \bar{A}]$$

Normalizing the auto-covariance function yields the autocorrelation function

$$r(h) = \frac{\text{cov [Ai(x), Ai (x + h)]}}{\sqrt{var[\text{Ai(x)}]}\ \sqrt{var[\text{Ai (x + h)}]}}$$

Where: the two variance terms in the denominator describe the variance of both arrays of data Ai (xi) and Ai (Xi+h). The autocorrelation coefficient can take a range of value comprised between -1 and +1 (Wendroth et al, 2011).

RESULTTS AND DISCUSSION

Soil physical and chemical characterization

The results obtained are summarized in the Table 1 with descriptive statistics for each soil proprieties (mean, variance, standard deviation, variation coefficient).

The results obtained show that the bulk density along the transect vary between 1, 0008 Mg/m^3 (S1) to 1.34 Mg/m^3 (S6). Regarding the total porosity, the values obtained are between 50% (S6) and 62.5% (S1). The

variation coefficients for these 2 physical properties of soil are respectively 8.22 % and 5.99%.

TABLE I
ANALYTICAL RESULTS OF SOIL PHYSICAL (BULK DENSITY & TOTAL POROSITY) AND CHEMICAL (pH_{H2O} and $CACO_3$ CONTENT)

Soil samples	Physical properties		Chemical properiies	
	Bulk density (Mg/m^3)	Total porosity (%)	$CaCO_3$ (%)	pH_{water} (1:5)
S1	1,008	62,5	23,33	7,98
S 2	1,065	60	19,69	8,07
S 3	1,29	51,66	15,45	7,89
S 4	1,203	55	14,39	7,983
S 5	1,12	58	16,20	8,07
S 6	1,34	50	16,96	7,51
S 7	1,05	61	24,08	7,67
S 8	1,03	61,66	14,99	7,73
S 9	1,146	57,33	16,51	7,82
S 10	1,106	58,33	23,33	8,05
S 11	1,1	59	18,33	7,74
S 12	1,156	57	15,45	7,80
S 13	1,073	60	19,23	7,75
S 14	1,163	56,66	20,45	7,66
S 15	1,123	58	14,24	7,72
S 16	1,023	61,66	12,11	7,62
The mean	1,124	57,98	17,7	7,81
The variance	0,008	12,10	12,93	0,02
Standard deviation	0,092	3,47	3,59	0,17
The variation coefficient (%)	8,22	5,99	20,20	2,20

Concerning the soil chemical proprieties, the results showed the pH_{water} of these samples is alkaline with moderate total soil carbonate content. The highest pH water value obtained is 8.07 (S2) and the lowest is 7.51 (S5). The highest $CaCO_3$ content is 24.08% (S7) and the lowest is 12.11 % (S16). The variation coefficient of the pH and Total soil carbonate content is 2.20 % and 20.20 % respectively.

Spatial Analysis of the physical and chemical soil proprieties along the 80 m transect (lag distance of 5 m).

The assessment of the soil spatial variability of soil proprieties along the 80 m transect has been done by computing the autocorrelation coefficient r(h).

The Results of the spatial variability of the bulk density and total porosity are depicted in the Figures 2 and 3.

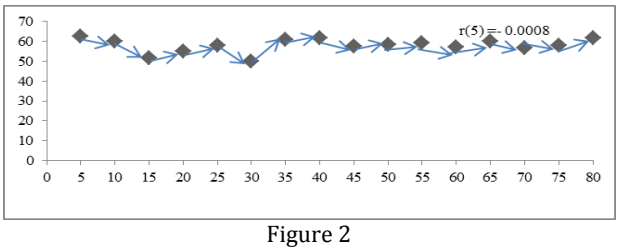

Figure 2
Spatial variability of the total porosity along the transect (80 m).

The Figure 3 shows that the autocorrelation coefficient r(h) for the total porosity values is -0.0008. This results imply that the total porosity has no spatial variability along the transect of 80m. Figure 4 shows the bulk density values along the transect of 80 m has some spatial variability because the autocorrelation coefficient r(h) yielded a value of -0.34.

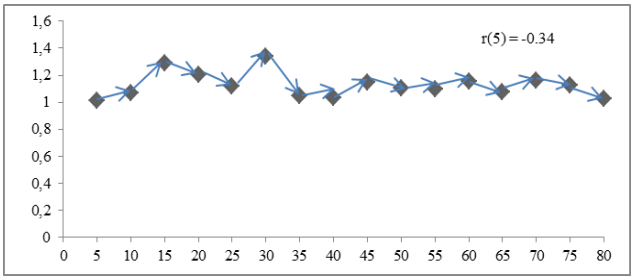

Figure 3
Spatial variability of the Bulk density along the transect of 80 m.

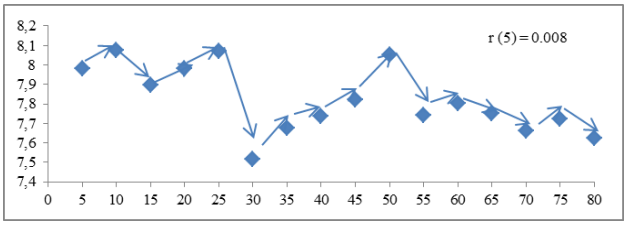

Figure4
Spatial variability of the pH water along the transect of 80 m.

Soil spatial variability for pH water and $CaCO_3$ (%)

The results of the spatial analysis for the pH water and the total calcium carbonate content are depicted in Figures 3 and 4.

It was found (Figure 5) that the autocorrelation coefficient of the pH water values obtained along the transect of 80 m is 0.008, which imply that the pH values are not spatially variable.

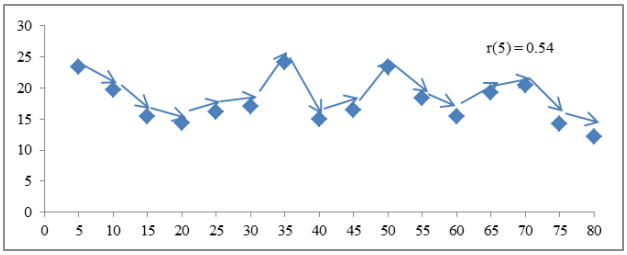

Figure 5
Spatial variability of the $CaCO_3$ along the transect of 80 m.

Figure 6 shows that autocorrelation of the total calcium carbonate content is 0.54. This result suggest a spatial variability of the total $CaCO_3$ content along the transect of 80 m.

The Bulk Density of the soil is an indirect estimator the aggregation of the soil. Aggregation of the soil and its porosity regulate the air and water flow [9]. Our results shows that the bulk density are very low which can be explained by two facts that our plot has never been cultivated, which created a high biological activity. Barbault et al. [10] had shown that some soil

earthworm lower the bulk density of the soil by creating large biopores. Regarding the chemical proprieties (pH_{water} and $CaCO_3$), the results had shown that most of the soil samples had an alkaline pH and a moderate total calcium carbonate content (more than 5%). this can be explained by the fact that the more calcium carbonate content increase, the more the pH become slightly alkaline to alkaline [11].

In general, the soil proprieties are classified in term of their variation coefficient as follow low variability when CV is between 0-15, moderate variability (CV : 16-36) and high variability (CV : >36) [12]. Our result shows the general variability is moderate for the $CaCO_3$ (20.99%) and a low variability to the bulk density (8.5 %), total porosity (5.5%) and pH (2.8%).

Warrick et al. [13] had shown that soil data with structured variation (spatial dependency), the coefficient of autocorrelation decreases with the increase of the lag distance h between the soil sample, but the soil data with no structured variation, the autocorrelation is nul for all lag distance. Our results had shown that the spatial variability of the pH and total porosity is nul because the autocorrelation coefficient yielded a nul value at a lag distance of 5 m. The autocorrelation coefficient of total soil carbonate and the bulk density at a lag distance of 5 is 0.54 and 0.34 respectively. This result imply that there a structured variation of these two soil proprieties.

CONCLUSION

The Assessment of the spatial variability of some soil proprieties (BD, Total porosity, pH, $CaCO_3$) along a transect of 80 m at a lag distance of 5 m at a plot in the experimental field of the University of ferhat abbas 1 using autocorrelation coefficient yielded a structured variation of the soil bulk density and total calcium carbonate content. In order to take to confirm this spatial variability of these soil properties, we must perform another sampling along other transect in this plot and to compare the results obtained and also use other spatial analysis techniques (variogram) and compare it with the autocorrelation coefficient methods. The importance of knowing the soil spatial variability in an experimental field is pre-requisite to site-specific management practices at the field scale that will allow us to manage our soil in sustainable manner and to optimize our crop production.

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ENVIRONMENTAL EDUCATION: MONITORING OF TEACHING CHEMISTRY FOR STUDENTS OF ENVIRONMENTAL SPECIALTIES

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Received: November 2016

Abstract

Authors analysed the teaching load, which is given to chemical disciplines in Ukraine and Slovakia universities; made their quantitative and qualitative comparison of the 5-year period. Also, the analysed student's success in some chemical disciplines, types of tasks and student's methodological support. Based on collected empirical material we have prepared the recommendations and conclusions.

INTRODUCTION

One the main goals of Environmental Education is the formation of ecological culture of individuals and society as a whole, the formation of thought and consciousness, based on respect for nature as universal, unique value. In turn, the environmental education in higher education should be as differentiated, diversified and cover all levels of professional training of future specialists-environmentalists. In respect to this, certainly, importantly is the acquisition of good-quality skills and abilities of the main basic disciplines, key among which is chemical subjects. Chemistry has especially significant role in mastering of such professionally oriented subjects as "Environmental Security", "Environment Monitoring", "Rationing anthropogenic stress", "Normalization of human impact on the environment", "Eco-toxicology", "Techno-Ecology", and so on. That is why, the monitoring of teaching chemistry for students environmental specialties is important.

RESULTS AND DISCUSSION

The specifics of chemistry teaching for students of ecological disciplines are that in today's realities theoretical foundations of chemistry are taught incomplete. Regarding Ukraine, it is primarily due to the fact that in the process of entering the national higher education into the European educational space, that is, in fact, after the signing of Ukraine in 2005 Bologna Declaration [1] the reforms and changes in main aspects of Concept of improving the educational process in higher education are almost continuously held in high school [2-4]. Confirming of key-standards for ecological education also promotes this above mentioned reforms and changes. Unfortunately, it should be noted that in addition to the classic areas of implementation of the Bologna process [3] (introduction of modular technologies; cluster system of organization by students of selection process of disciplines; strengthening of professional orientation training, etc.) – the reducing auditory hours of basic chemical disciplines for students of environmental professions is constantly took place, and in some cases the association of auditory hours from different chemical disciplines also placed (Table 1), which is generally unacceptable in terms of professional, but quite acceptable for a "deeply erudite" official worker and bureaucrats.

TABLE I
PEDAGOGICAL LOADING FROM BASIC CHEMICAL DISCIPLINES AT 2011-2016.

Uzhhorod national university			
Subject	Credits 2011/2016	Theory 2011/2016	Practice 2011/2016
General and Inorganic Chemistry	12/11	64/60	116/104
Analytical Chemistry	11/9[a]	44/32[a]	112/94 [a]
Organic Chemistry	11/8.5	68/52	100/76
Physical Chemistry	11/9	66/52	96/78
Lviv National Agrarian University			
General and Inorganic Chemistry	4/3	36/28	36/28
Analytical Chemistry	1.5/0[a]	18/0[a]	18/0[a]
Organic Chemistry	4/3	36/32	36/32
Physical Chemistry	4/3	36/28	36/28

Uzhhorod national university			
Subject	Credits 2011/2016	Theory 2011/2016	Practice 2011/2016
University of Prešov			
General and Inorganic Chemistry	5/5	13/26	26/26
Analytical Chemistry	5/0[b]	13/0[b]	26/0[b]
Organic Chemistry	5/2	13/13	26/26
Environmental Chemistry	4/4	13/13	13/13

[a] Analytical Chemistry was united with General and Inorganic Chemistry in 2015 year.
[b] Analytical Chemistry was translated to Magister education level in 2015 year.

Thus, over the last 5 years the number of lecture hours was reduced from 68 to 52 and hours of laboratory practical cycle – from 100 to 76 hours on the subject "Organic Chemistry" for students in environmental specialties in Uzhhorod national university (Table 1). In addition, currently we can observe such "know-how" as pegging of the number of hours with student's amount in group. For example, the planned 36 hours of lectures and 88 hours of laboratory on the subject "Analytical Chemistry" for students of environmental specialties were "transformed" in teaching load into 32 hours of lectures and 84 hours of laboratory when student's group contains 7 people.

The elaboration of training programs (Syllabus) which are auditory concentrated precisely on topics that are used to explain the phenomena applied in environmental disciplines, can became an effective method of preserving the quality of education in these conditions of the reducing of auditory hours. That is, a student-environmentalist from one side must get simplified theoretical concepts, but on the other – this knowledge must be deeply enough to understand the main chemical processes in the environment. In this perspective, the considerable increasing in the role of student's individual work is observed [5]. It should be noted that the good conditions to ensure the implementation of student's individual work can partially reverse the negative from reducing of auditory hours (lectures, seminars, practical work).

Kozubovskayi [6] has proved that monitoring of the quality of education is not only a means to improve the educational process, but it is also extremely effective controlling tool of results of educational program reforming. Therefore, we monitored the quality of education in Organic Chemistry, Analytical Chemistry at various universities a 5 year period.

On the analysis of student achievement on some basic chemical disciplines there is a clear downward trend in the overall quality of training (excellent and good level) while reducing auditory pedagogical load, especially in the reduction of hours for laboratory and practical classes. This trend is observed for all analysed disciplines (Figures 1, 2, 3 and 4).

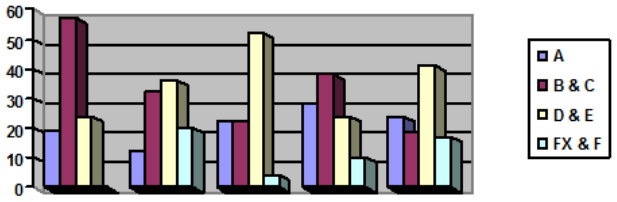

Figure 1.
Uzhhorod national university: student's success in Analytical Chemistry during 2011-2016.

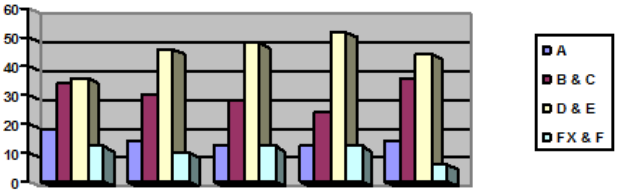

Figure 2
Uzhhorod national university: student's success in Organic Chemistry during 2011-2016.

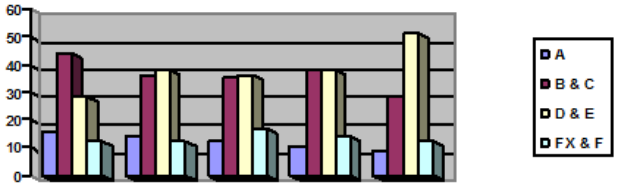

Figure 3
Lviv National Agrarian University: student's success in Inorganic Chemistry during 2011-2016.

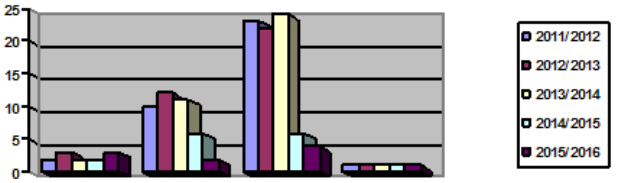

Figure 4
University of Prešov: student's success in Analytical Chemistry during 2011-2016 (columns: A, B+C, D+E and FX+F).

At the same time, diagrams of student achievement describing the growth of assimilation satisfactory and almost minimal changes in the number of negative results. Thus, preliminary conclusions indicate that the reduction in Syllabus of chemical disciplines auditory pedagogical load, especially hours of laboratory and practical cycle, generally leads to a decrease in the quality of education, that is, in these circumstances, it is difficult for students to learn material of basic chemical disciplines at a high level. Especially sharply these trends are observed in the case of such non-chemical universities, which prepare specialists in environmental branches.

According to recommendation of Ministry of Education of Ukraine the association of basic courses of chemical disciplines (Analytical chemistry, General chemistry and Inorganic chemistry) was done. For example, the

level of quality of education has fallen almost in half in Lviv National Agrarian University (Figure 3). The experimental results indicate the fact that the individual work of students, even in ideal conditions of the educational process, unable to replace practical and laboratory classes in preparing professional of high level. It is also interesting to observe the general trend of low level assimilation of physical chemistry by students of ecological direction in Ukrainian universities.

The specificity of the subject is to combine large theoretical material with complex mathematical calculations. That is why, when teaching physical chemistry it is important to increase the practical part of presentation on the background of simplifying supply theoretical issues. At the same time, traditional universities of Ukraine do not read to students-environmentalists the "Green chemistry" or "Environmental chemistry" as a basic chemical discipline! But the methods of "Green chemistry" and "Environmental chemistry" are increasingly being used in the industry, in chemical laboratories and so on.

The opposite situation can be observed in Presov University – against the background of a lack of physical chemistry curriculum, students-environmentalists teach the course "Environmental Chemistry" as a basic chemical discipline. The authors are aware that presented in this investigation analysis of chemistry teaching for students of environmental specialties will have no direct influence on government decisions regarding the proportion of chemical disciplines in the curriculum for training specialists in the field of ecology. Therefore, we also have analysed a possible ways to improve the quality of teaching of chemical sciences by students of ecological specialties in auditory hour's reducing stress. The obvious first step is to improve self-learning system [7]. The most common form of self-learning is providing a list of information sources that describe the theoretical part of the course in combining with consulting sessions. In some cases, the lectures are given to student's free use (in paper or electronic form). For example, teaching of Organic chemistry in Uzhhorod National University was providing in condition of pedagogical experiment for improving of student's individual work (only for students of ecological specialties).

So we give in free usage for students a lecture course on Organic chemistry and recipes to laboratory and practical works. Copyright on these scientific and educational products have been protected through the use of e-learning system, which works at Uzhhorod national university [8]. Electronic system of distance education provides for the creation of an electronic page for each discipline, which is password protected and has a group of users (usually students), which prescribes password by the lecturer of this discipline [9]. For a more effective organization of individual work of students the special unit which contains examples of practical tasks (50 examples for each topic) was included in recipes to laboratory work (these tasks were made in accordance with the requirements of program material of theoretical topics). It should be noted that lecturer weekly put 5-10 examples of practical task's solution on web-page of discipline during the performing of laboratory classes. Separately the full database of MSQ tests (without answers!) was outlined on web-page of discipline. MCQ is a must in the module tasks preparation. Similar on-line scheme started at Lviv National Agrarian University this year.

The results of the above teaching experiment clearly visible on the results of student's achievement in Organic chemistry (Figure 2) – against the background of decreasing quality of education while reducing auditory pedagogical load in the 2015/2016 academic year, there was a marked increase of education quality (good and excellent level) with a further reduction of the pedagogical load of lectures and practical works compared with the previous year. Instead satisfactory level and negative results is reduced. Especially clearly above experiment results are observed when comparing data diagrams with success in Organic Chemistry in Uzhgorod National University and the Lviv National Agrarian University, where the e-learning system was not early put into effect (started only this year).

EXPERIMENTAL DATA

In the experimental part the official empirical data of educational process are shown; they are base for the analysis, conclusions and recommendations.

SUMMARY

Based on collected empirical material we can make the following recommendations and conclusions:

1. The success of students in chemical disciplines is at the average level – it can be explained by the small number of specific laboratory and practical classes, which would allow bettering, master the theoretical material.
2. We recommend focusing on the practical significance of the different sections of chemistry and less – on theoretical issues in the teaching of chemical sciences for students of environmental specialties. In addition, it is advisable to introduce the "Green Chemistry" to environmental academic disciplines.
3. We recommend developing an expanded base of practical tests and MCQ in basic chemical disciplines for effective self-training students, which is an important component of the training of future professionals in the field of ecology. We recommended providing the possibility of free access for students to

the database of these tasks within the web-page of university or of corresponding discipline.

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NEW APPROACHES IN CREATION OF 1,2,4-TRIAZOLE-CONTAINING BIO-ACTIVE COMPOUNDS FOR ENVIRONMENTAL TECHNOLOGIES

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Received: November 2016

Abstract

Triazoles are important structural motifs in material science, medicinal chemistry, and are useful building blocks in organic synthesis. Herein we report a new approaches in creation of 1,2,4-triazole-containing bio-active compounds for environmental technologies.

INTRODUCTION

One of the objectives of "clean industry" is: to develop of energetically no-costs technologies, to remove of toxic and harmful substances that are involved in the production process or formed during the manufacturing process [1]. Modern environmental technologies now are widely used in industry, particularly, in the production of medicines and external disinfecting and antifungal agents. Current trends in organoselenium & organotellurium chemistry are going forward the introduction of these reagents into the field of green chemistry, organocatalysis, as well as into the preparation of biomimetic materials [2-8].

The aim of our study was to develop for environmental technologies the procedure of the creation of new bio-active condensed and functional 1,2,4-triazole's derivatives, which contain such elements as Selenium and Tellurium. Development Se, Te-containing bioactive compound is an actual task, because these minerals are essential to the human body with one hand, and on the other hand all know about high toxicity of Selenium and Tellurium compounds [9-14]. Now a day majority of Se-containing drugs includes Selenium (IV) oxide or its "alkaline form" Na_2SeO_3. This remedies are high water soluble (SeO_2 in alkaline medium) that is why it is necessary considerably their amount for reaching sufficient concentration in cell – it causes the accumulation of Selenium in human body, that is leads to intoxication. We reasoned to introduce Se, Te-moiety in organic molecule for increasing of lipophility of target products. As a model object for binding Selenium and Tellurium in organic form we have chose the 1,2,4-triazole system, because this heterocycle has small toxicity (Table I); functional and fused derivatives of symmetric triazoles have possess essential bio-activity [15-23] and they can be synthesized from available reagents and with using of such safe-environmental solvent as water and ethanol [24-26].

EXPERIMENTAL SECTION

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker DPX-400 instruments; ^{77}Se NMR spectrum was recorded on Bruker DPX-400 instrument for the compound **6b**. The chemical shift values (δ) are given in parts per million (ppm) downfield from TMS as internal standard and are referred to the residual peak of the deuterated solvent used ($CDCl_3$, $(CD_3)_2SO$). Microanalyses were performed by the microanalytical unit of the Institute of Organic Chemistry of the National Academy of Sciences (Kyiv, Ukraine). MS analyses were carried out using an Agilent 1100 LCMSD SL instrument for the compound.

TABLE I

TOXICITY OF INORGANIC Se AND, Te CONTAINING COMPOUNDS AND COMPOUNDS 3-6

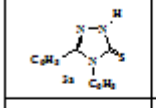
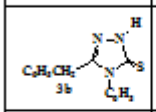
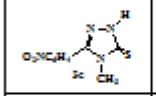
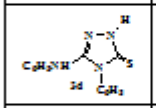
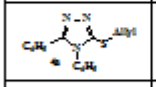
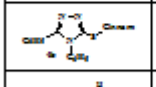
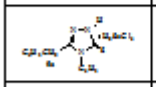
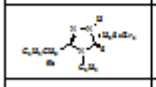
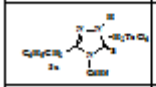
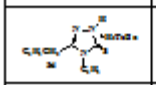
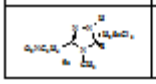
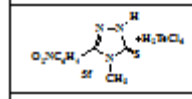
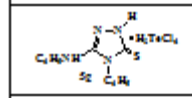
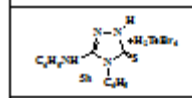
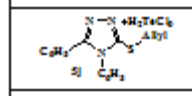
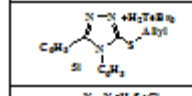
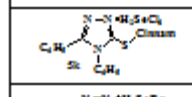
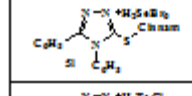
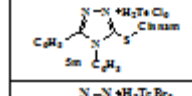
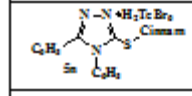
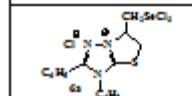
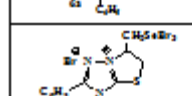
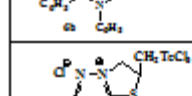
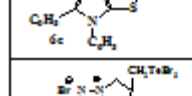
Compound	Rat IP LD_{50} (mg/kg)	Rat IV LD_{50} (mg/kg)	Rat Oral LD_{50} (mg/kg)	Classification
SeO_2	62.0	53.5	30.8	2
TeO_2	246.3	145.3	405.1	4
Na_2SeO_3	172.9	172.9	172.9	3
Na_2TeO_3	221.6	221.6	221.6	3
H_2SeCl_6	116.7	96.1	57.5	3
H_2SeBr_6	261.8	169.2	100.7	3
H_2TeCl_6	164.1	110.7	63.4	3
H_2TeBr_6	274.7	171.0	105.6	3
	752.4	128.9	962.8	5
	776.1	134.4	970.6	5
	558.4	176.4	1720.5	5
	486.8	89.9	1788.0	4
	682.6	202.2	1862.2	5
	477.5	184.1	1794.0	4+
	559.0	559.0	559.0	5+
	825.7	825.7	825.7	Non Toxic
	607.7	607.7	607.7	5+
	874.4	874.4	874.4	Non Toxic
	576.6	576.6	576.6	5+

TABLE I (Cnotinue)

Compound	Rat IP LD50 (mg/kg)	Rat IV LD50 (mg/kg)	Rat Oral LD50 (mg/kg)	Classification
	546.6	546.6	546.6	5+
	608.7	608.7	608.7	5+
	875.4	875.4	875.4	Non Toxic
	633.7	633.7	633.7	5+
	900.4	900.4	900.4	Non Toxic
	661.2	661.2	661.2	5+
	927.9	927.9	927.9	Non Toxic
	709.8	709.8	709.8	Non Toxic
	976.5	976.5	976.5	Non Toxic
	424.8	213.8	637.1	4
	695.6	266.9	653.8	5
	428.3	214.6	770.6	4
	525.8	261.0	1136.0	5

The melting points were determined on a Koefler block instrument and were not corrected.

All compounds give satisfactory elemental analyses within 0.4% of the theoretical values. All reagents and initial compounds **1a-c** were obtained from commercial suppliers and used without any further purification. Dry solvents were prepared according to the standard methods.

*Geneal procedure for the preparation of 2H-1,2,4-triazol-3-thiones **3***

Hydrazines **1a-c** (10.0 mmol) were dissolved in ethanol (20 mL). The phenylisothiocyanate (12.0 mmol) in ethanol (5 mL) were added to the solution of hydrazines **1a-c**.

The mixture heated for 1 hour at 60-70°C. After cooling the precipitated product **2a-c** was filtered, washed by ethanol and next treated by 10 mL of concentrated (40%) water solution of Potassium hydroxide at room temperature* during 24 h. Yielded triazoles **3a-c** were obtained after addition of 5 mL 10% water solution of acetic acid to final solution at room temperature.

Same results were achieved when thiosemicarbazides **2a-c was heated with 8% water solution of Sodium hydroxide at 80 ^{0}C during 2 h.*

4,5-Diphenyl-2*H*-1,2,4-triazol-3-thione (**3a**). This compound was obtained from **1a**; yield 94% (colorless

crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 7.28, 7.86 (2m, 10H, $2C_6H_5$), 13.72 (bs, 1H, NH). A triazole **3a**: mp 223 °C.

5-Benzyl-4-Phenyl-2*H*-1,2,4-triazol-3-thione (**3b**). This compound was obtained from **1b**; yield 82% (colorless crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 4.14 (s, 2H, CH_2), 7.08-7.72 (m, 10H, $2C_6H_5$), 13.54 (bs, 1H, NH). A triazole **3b**: mp 209 °C.

5-(4-Nitrophenyl)-4-methyl-2*H*-1,2,4-triazol-3-thione (**3c**). This compound was obtained from **1d**; yield 89% (colorless crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 4.02 (s, 3H, CH_3), 8.04, 8.42 (2d, 4H, C_6H_4, 9.0), 13.78 (bs, 1H, NH). A triazole **3c**: mp 252 °C.

5-Aminophenyl-4-phenyl-2*H*-1,2,4-triazol-3-thione (**3d**). This compound was obtained from **1c**; yield 78% (colorless crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 6.89 (s, 1H, NH), 7.35, 7.54 (2m, 10H, $2C_6H_5$), 12.92 (bs, 1H, NH). A triazole **3c**: mp 179 °C. ; [24]: 207 °C.

General procedure for the preparation of 3-S-alkylthio-2H-1,2,4-triazoles 4

1,2,4-Triazole-3-thione **3a** (10.0 mmol) and Potassium hydroxide (11.0 mmol) were dissolved in water ethanol (20 mL, 1:3 v/v) with heating. The alkenyl halogenides (12.0 mmol) in ethanol (5 mL) were added to the cooled solution of triazole **1a**. The mixture heated for 1 hour at 50^{0}C. After cooling the precipitated product was filtered, washed with ether, dried.

3-Allylthio-4,5-Diphenyl-2*H*-1,2,4-triazole (**4a**). This compound was obtained from **3a**; yield 84% (colorless crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 3.66 (d, 2H, CH_2, 6.9), δ 5.04 (d, 1H, $=CH_2$, 9.9), δ 5.19 (d, 1H, $=CH_2$, 17.1), δ 5.86 (m, 1H, =CH), 7.66, 7.89 (2m, 10H, $2C_6H_5$). A thioether **4a**: mp 144 °C.

3-Cinnamylthio-4,5-Diphenyl-2*H*-1,2,4-triazole (**4b**). This compound was obtained from **3a**; yield 72% (colorless crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 3.97 (d, 2H, CH_2, 4.2), 6.36 (m, 1H, =CH), 6.58 (d, 1H, =CH, 9.3), 7.23 – 7.52 (m, 15H, $3C_6H_5$). A thioether **4b**: mp 152 °C. ; [28]: 152-154 °C.

General procedure for the preparation of molecular complexes 5

The solution of tetrahalogenides of Selenium or Tellurium (10.0 mmol) in water acetic acid (10 mL, 1:5) was dropwise added to the solution of triazoles **3, 4** (10.0 mmol) in water acetic acid (20 mL, 1:5) with constant stirring at room temperature during 0.5 h. The product was filtered, washed with acetic acid, dried.

Complex of 5-Benzyl-4-phenyl-2*H*-1,2,4-triazol-3-thione and Hexachloroselenide acid **5a**. This compound was obtained from **3b**; yield 72 % (colorless powder); ^{1}H NMR (400 MHz, DMSO-d6): δ 4.16 (s, 2H, CH_2), 7.28-7.74 (m, 10H, $2C_6H_5$). A complex **5a**: mp 202 °C (decomp).

Complex of 5-Benzyl-4-phenyl-2*H*-1,2,4-triazol-3-thione and Hexabromoselenide acid **5b**. This compound was obtained from **3b**; yield 88 (colorless powder); ^{1}H NMR (400 MHz, DMSO-d6): δ 4.12(s, 2H, CH_2), 7.32-7.70 (m, 10H, $2C_6H_5$). A complex **5b**: mp 194°C (decomp).

Complex of 5-Benzyl-4-phenyl-2*H*-1,2,4-triazol-3-thione and Hexachlorotelluride acid **5c**. This compound was obtained from **3b**; yield 72 % (colorless powder); ^{1}H NMR (400 MHz, DMSO-d6): δ 4.14 (s, 2H, CH_2), 7.30-7.71 (m, 10H, $2C_6H_5$). A complex **5c**: mp 210 °C (decomp).

Complex of 5-Benzyl-4-phenyl-2*H*-1,2,4-triazol-3-thione and Hexabromotelluride acid **5d**. This compound was obtained from **3b**; yield 72 % (colorless powder); ^{1}H NMR (400 MHz, DMSO-d6): δ 4.16 (s, 2H, CH_2), 7.32-7.74 (m, 10H, $2C_6H_5$). A complex **5d**: mp 208 °C (decomp).

Complex of 5-(4-nitrophenyl)-4-methyl-2*H*-1,2,4-triazol-3-thione and Hexachloroselenide acid **5e**. This compound was obtained from **3d**; yield 62% (yellow crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 4.14 (s, 3H, CH_3), 8.12, 8.30 (2d, 4H, C_6H_4, 10.2). A complex **5e**: mp 217 °C (decomp).

Complex of 5-(4-nitrophenyl)-4-methyl-2*H*-1,2,4-triazol-3-thione and Hexachlorotelluride acid **5f**. This compound was obtained from **3c**; yield 66% (yellow crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 4.11 (s, 3H, CH_3), 8.16, 8.29 (2d, 4H, C_6H_4, 10.2). A complex **5f**: mp 222 °C (decomp).

Complex of 5-Aminophenyl-4-phenyl-2*H*-1,2,4-triazol-3-thione and Hexachlorotelluride acid **5g**. This compound was obtained from **3c**; yield 57% (yellow crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 6.21 (s, 1H, -HNPh), 6.48-6.87 and 7.11-7.34 (m, 11H, $2C_6H_5$-, triazole). A complex **5e**: mp 135 °C (decomp).

Complex of 5-Aminophenyl-4-phenyl-2*H*-1,2,4-triazol-3-thione and Hexabromotelluride acid **5h**. This compound was obtained from **3c**; yield 70% (colorless crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 6.23 (s, 1H, -HNPh), 6.51-6.88 and 7.09-7.41 (m, 11H, $2C_6H_5$-, triazole).. A complex **5h**: mp 220 °C (decomp).

Complex of 3-Allylthio-4,5-Diphenyl-2*H*-1,2,4-triazole and Hexachlorotelluride acid **5j**. This compound was obtained from **4a**; yield 81% (colorless crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 3.80 (d, 2H, CH_2, 6.9), δ 5.12 (d, 1H, $=CH_2$, 9.9), δ 5.25 (d, 1H, $=CH_2$, 18.6), δ 5.93 (m, 1H, =CH), 7.30, 7.55 (2m, 10H, $2C_6H_5$). A complex **5j**: mp 148 °C (decomp).

Complex of 3-Allylthio-4,5-Diphenyl-2*H*-1,2,4-triazole and Hexabromotelluride acid **5i**. This compound was obtained from **4a**; yield 83% (yellow crystals); ^{1}H NMR (400 MHz, DMSO-d6): δ 3.81 (d, 2H, CH_2, 6.9), δ 5.12 (d, 1H, $=CH_2$, 10.2), δ 5.25 (d, 1H, $=CH_2$, 18.9), δ 5.94 (m, 1H, =CH), 7.31, 7.56 (2m, 10H, $2C_6H_5$). A complex **5i**: mp 156 °C (decomp).

Complex of 3-Cinnamylthio-4,5-Diphenyl-2*H*-1,2,4-triazole and Hexachloroselenide acid **5k**.
Complex of 33-Cinnamylthio-4,5-Diphenyl-2*H*-1,2,4-triazole and Hexabromoselenide acid **5l**.
Complex of 3-Cinnamylthio-4,5-Diphenyl-2*H*-1,2,4-triazole and Hexachlorotelluride acid **5m**.
Complex of 3-Cinnamylthio-4,5-Diphenyl-2*H*-1,2,4-triazole and Hexabromotelluride acid **5n**.
These compounds were obtained from **4b** according to above procedure with same properties as described [28].

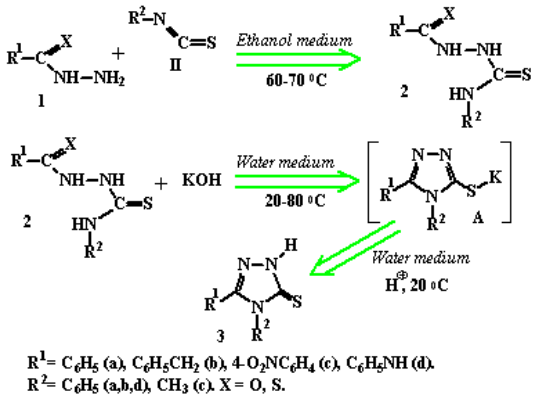
General procedure for the preparation of fused salts 6
The solution of tetrahalogenides of Selenium or Tellurium (10.0 mmol) in water acetic acid (10 mL, 1:5) was dropwise added to the solution of triazole **4a** (10.0 mmol) in water acetic acid (20 mL, 1:5) with constant stirring at room temperature during 24 h. The product was filtered, washed with acetic acid, dried.
5-Trichloroselenomethyl-2,3-diphenyl-5,6-dihydro-3H-[1,3]thiazolo[3,2-b][1,2,4]triazol-7-ium chloride **6a**. This compound was obtained from **4a**; yield 48% (white powder); ^{1}H NMR (400 MHz, DMSO-d6): δ 4.21 (d, 1H, SCH_2, 11.1); 4.54 (d, 1H, SCH_2, 11.1); 4.68 (d, 1H, CH_2SeCl_3, 8.1); 4.86 (d, 1H, CH_2SeCl_3, 8.1); 5.67 (m, 1H, CH); 7.34-7.56 (m, 10H, $2C_6H_5$). ^{13}C NMR (100 MHz, DMSO-d6): 49.82, 55.12, 74.98, 127.44, 128.62, 129.74, 129.98, 131.80, 132.79, 153.92, 155.68. A thiazolotriazole **6a**: mp 218 °C.
5-Tribromoselenomethyl-2,3-diphenyl-5,6-dihydro-3H-[1,3]thiazolo[3,2-b][1,2,4]triazol-7-ium bromide **6b**. This compound was obtained from **4a**; yield 52% (yellow powder); ^{1}H NMR (400 MHz, DMSO-d6): δ 4.33 (d, 1H, SCH_2, 11.1); 4.92 (d, 1H, SCH_2, 11.1); 4.38 (d, 1H, CH_2SeCl_3, 9.1); 4.59 (d, 1H, CH_2SeCl_3, 9.0); 5.59 (m, 1H, CH); 7.22-7.32, 7.33-7.48 (2m, 10H, $2C_6H_5$). ^{13}C NMR (100 MHz, DMSO-d6): 47.76, 54.47, 74.55, 126.78, 128.04, 129.37, 129.80, 131.31, 132.57, 153.45, 155.32. ^{77}Se NMR (DMSO-d6): 660. A thiazolotriazole **6b**: mp 207 °C.
5-Trichlorotelluromethyl-2,3-diphenyl-5,6-dihydro-3H-[1,3]thiazolo[3,2-b][1,2,4]triazol-7-ium chloride **6c**. This compound was obtained from **4a**; yield 93% (yellow powder); ^{1}H NMR (400 MHz, DMSO-d6): δ 3.88 (m, 1H, CH_2TeCl_3); 4.05 (m, 1H, CH); 4.48 (dd, 1H, SCH_2, 12.6, 1.5); 4.92 (m, 1H, CH_2TeCl_3); 5.12 (dd, 1H, SCH_2, 12.6, 1.5); 7.45, 7.61, 7.71 (3m, 10H, $2C_6H_5$). A thiazolotriazole **6c**: mp 175 °C.
5-Tribromotelluromethyl-2,3-diphenyl-5,6-dihydro-3H-[1,3]thiazolo[3,2-b][1,2,4]triazol-7-ium bromide **6d**. This compound was obtained from **4a**; yield 87% (yellow powder); ^{1}H NMR (400 MHz, DMSO-d6): δ 3.87 (m, 1H, CH_2TeCl_3); 4.19 (m, 1H, CH); 4.49 (dd, 1H, SCH_2, 12.6, 1.5); 4.81 (m, 1H, CH_2TeCl_3); 5.13 (dd, 1H, SCH_2, 12.6, 1.5); 7.46, 7.61, 7.71 (3m, 10H, $2C_6H_5$). A thiazolotriazole **6d**: mp 175 °C.

Biological assays
All compounds were dissolved in DMSO at concentrations of 200 μg/ml.
Bacterial strains *Staphylococcus albus, Staphylococcus aureus, Sarcina flava, Bacillus subtilis, Klebsiella oxytoca, Pseudomonas aeruginosa* and *Candida albicans* were obtained from Collection of Microorganisms at Regional Station of Epidemiology and Sanitary, Uzhhorod, Ukraine.
Preliminary antimicrobial activities were tested by Agar disc-diffusion method. Sterile filter paper discs (6 mm diameter) moistened with the test compound solution in DMSO of specific concentration 200 μg/disc were carefully placed on the agar culture plates that had been previously inoculated separately with the microorganisms. The plates were incubated at 37 °C and the diameter of the growth inhibition zones were measured after 24 h in case of bacteria and after 48 h in case of fungi. Cefotaxime was used as a reference antibacterial agent. Ketoconazole was used as a reference antifungal agent.

Computational investigation
Our investigation we started with simulations and comparing of the toxicity of Sodium Selenite and Telurite (that used as carriers of Selenium and Tellurium), other inorganic forms of Se(IV), Te(IV) (their oxides, halogenides) and Se, Te-containing 1,2,4-triazoles, used by us. Also we calculated the toxicity of synthesized Se,Te-containing compouds **5,6**. All calculations were performed with GUSAR program [25]. Results are described in Table 1.

RESULTS AND DISCUSSIONS

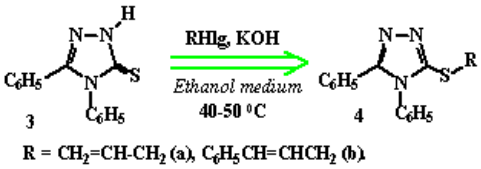
Our investigation deals with the evolution for environmental technologies the procedure of the creation of new bio-active condensed and functional 1,2,4-triazole's derivatives, which contain such elements as Selenium and Tellurium.
Synthesis of model triazoles **3** was carried out due to optimization (according to requires of green procedures) of technique early elaborated by us [26, 27] (Scheme 1).



Scheme 1

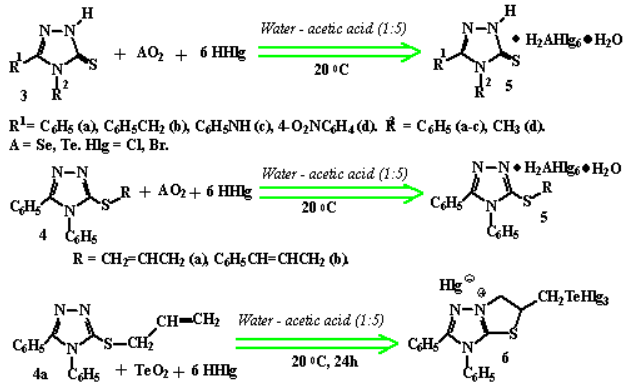
So, hydrazines **1** react with equimolar amount of phenyl-(methyl-)isothiocyanate in ethanol medium at moderate heating. Resulting thiosemicarbazides **2** can be transformed into target triazoles **3** under alkaline action in water medium at room temperature or at light heating without isolation of intermedium potassium salts (**A**). All triazoles **3** were isolated with excellent yields.

The previous investigation of the properties of received triazoles tells about high protonation ability of triazole ring, especially in 5-aminotriazoles [24]. It can be explained by high electrostatic potential of triazole ring and also by thione-thiol tautomerizm in triazol-thiones. That is why we also synthesized some alkylated triazoles **4** for representation of thiol-form too. Alkylation was performed by modification of early described procedures [28, 29] according to green chemistry requires: usage of non-toxic solvents & safe-energy procedures (Scheme 2).



Scheme 2

Introduction of Selenium and Tellurium was made according to elaborated by us technology (Scheme 3) which uses as a medium non-toxic solvents (acetic acid - water) and does not requires significant energy costs (air medium, room temperature) – that is, our technology developed is consistent with the main requirements of environmental engineering.



Scheme 3

It should be noted that selenium (tellurium) tetrahalogenation of triazol-3-thiones **3** leads to formation of molecular complexes **5**. If we used as initial compound thiol-form, the different routes of reaction were observed. So cynnamilmercaptotriazole **4b** reacts with formation of similar complexes **5**. Allyl-triazole **4a** in same condition gives also molecular complex **5**, but after stirring during 24 h – it can be transformed onto the fused thiazolotriazoles **6,** which contained Selenium or Tellurium trihalogenide moiety, were obtained.

We studied in detail the composition and structure of the obtained compounds by elemental analyses & NMR tools. In general we can observe very similar spectral data in molecular complexes **5** and appropriative triazoles **3, 4**. The structure of fused thiazolotriazoles **6** was determined by complex of spectral tools: 1) signals of allyl protons are disappeared in ^{1}H NMR spectra; 2) the absence of signal of ethylene-Carbons in ^{13}C NMR spectra; 3) signal of Se-atom is at 660 ppm (figure 1) ^{77}Se NMR spectrum – in more weak region as described about heterocycles with endocyclic selenium [30].

It must be noted that all received Se,Te-containing triazole derivatives **5,6** have low toxicity (Table I). That is why we calculate some important structural parameters of received compounds for effective estimation of potential biological activity (Table II).

TABLE II

Different calculated parameters for studied compounds

Name	HL	logP$_{o/w}$	Mass g/mol	HOMO eV	LUMO eV	GAP eV	η eV
$SeBr_4^{-2}$	-1.50	-1.63	560.40	-8.76	-0.84	7.92	3.96
$SeCl_4^{-2}$	-2.57	-1.88	293.69	-8.95	0.22	9.17	4.58
$TeBr_4^{-2}$	-0.60	-1.41	609.04	-6.95	-1.50	5.45	2.72
$TeCl_4^{-2}$	-1.40	-1.60	342.33	-7.25	-1.27	5.99	2.99
3c	7.63	2.14	236.25	-9.07	-1.55	7.53	3.76
3c-(H+)	8.05	0.68	237.26	-9.56	-1.91	7.65	3.82
5e*	5.54	0.07	529.94	-8.87	-1.81	7.06	3.53
5d*	6.71	0.36	845.29	-7.20	-1.86	5.33	2.67
3b	11.36	3.62	267.35	-9.07	-0.40	8.66	4.33
3b-(H+)	11.79	1.58	268.36	-9.59	-1.06	8.53	4.27
5a*	10.49	1.27	827.75	-8.78	-1.08	7.70	3.85
5b*	9.45	1.02	561.04	-9.00	-0.63	8.37	4.19
5c*	11.35	1.48	876.39	-7.11	-1.81	5.30	2.65
5d*	10.67	1.31	609.68	-7.52	-1.45	6.07	3.04
3d	10.45	3.26	268.34	-8.72	-0.61	8.12	4.06
3d-(H+)	10.78	1.34	269.34	-6.81	0.18	7.00	3.50
5g*	10.59	1.29	877.38	-7.05	-1.73	5.33	2.66
5h*	9.83	1.11	610.67	-7.548	-1.532	6.02	3.01
4a	12.84	4.20	308.40	-8.726	-0.678	8.05	4.02
4a-(H+)	12.85	1.84	309.41	-9.63	-1.192	8.44	4.22
6a**	11.54	1.52	691.96	-9.47	-1.65	7.82	3.91
6b**	10.81	1.35	514.16	-9.10	-1.17	7.93	3.96
6c**	12.02	1.64	740.60	-8.26	-2.61	5.65	2.82
6d**	11.54	1.52	562.80	-9.05	-1.98	7.08	3.54
5i*	12.42	1.73	902.42	-7.14	-1.82	5.32	2.66
5j*	11.67	1.56	635.72	-7.59	-1.58	6.01	3.01
4b	16.56	5.67	384.50	-8.66	-0.56	8.11	4.05
4b-(H+)	16.62	2.75	385.50	-9.22	-1.27	7.96	3.98
5k*	15.26	2.42	944.90	-8.89	-1.22	7.67	3.84
5l*	14.23	2.17	678.19	-9.05	-0.95	8.09	4.05
5m*	16.15	2.64	993.54	-7.14	-1.82	5.32	2.66
5n*	15.40	2.45	726.83	-7.57	-1.58	6.00	3.00

Intermolecular hydrogen bonding between potential molecule and target receptor can be an important interaction for tight binding. This interaction type can drive selectivity for binding of one target over another. Active compound with optimal binding potency and

selectivity requires a balance of lipophilicity and hydrogen bond forming groups. Lipinski's "rules of five" [31] deals with orally active "drug-like" compounds and defines 4 physicochemical parameter ranges: molar weight ≤ 500, logP ≤ 5, H-bond donors ≤ 5, Hbond acceptors ≤ 10. These physicochemical parameters correspond in oral bioavailability through acceptable range aqueous solubility and intestinal permeability. Good intestinal permeability of small "drug-like" molecules can be reached in the case of molecules with 0< logP< 3 [32].

Experimental determination of logP is relatively problematic and time consumedly which is overcome usually by computation prediction of logP with different software [33]. In our investigation we face with the problem for direct prediction of charged species with Se and Te atoms. So, we used a hydrophilicity/lipohilicity index (HLI) introduced by Dapson [34] which is based on partial charges obtained with semiempirical AM1 quantum method: *HLI = sum (M – Abs C)*, where *M* value was found by trial and error, *Abs C* is absolute value of partial atomic charge on each atom. In this study we used 0.5 as value for *M*. The advantage of this procedure is possibility for using with charged species [35] and all atoms that parameterized in AM1 method [36] can be used. For finding the correlation between obtained HLI and logP we used values of logP calculated for free and protonated triazole species (Table III) with ALOGPS-2.1 online program [37].

Plotting estimated HLI against logP values for the small dataset of studied triazoles yielded good predictability of log P from HLI (R^2 = 0.9936 for neutral molecules and R^2 = 0.7765 in the case of charged species) if suggest that differing ionic states required separate analysis (Figure1).

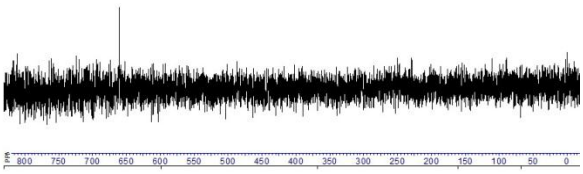


Figure 1
^{77}Se spectrum of compound **6b**

In similar manner we calculate HLI for Se- & Te-containing compounds and found corresponding logP values using the equation for charged species: logP = 0.2415*HLI-1.2638 (Table II).

Stability is also very important characteristic for drug like molecules that can decrease the dosage of the drug as it is more inert upon the action of enzymes. In literature was shown that more stable compounds have higher values of HOMO-LUMO gap and more inert species are harder in terms of HSAB theory [38, 39].

We have performed bio-evolution as anti-tubercular, bactericidal and fungicidal agents for some of them. Compounds **5,6** were tested for in vitro antimicrobial activity against the gram-positive bacteria *Staphylococcus albus*, *Staphylococcus aureus ATCC 25923*, *Sarcina flava*, *Bacillus subtilis ATCC 6633*, the gram-negative bacteria *Klebsiella oxytoca ATCC 13182*, Pseudomonas aeruginosa *ATCC 27853* and fungi *Candida albicans CCM 885*.

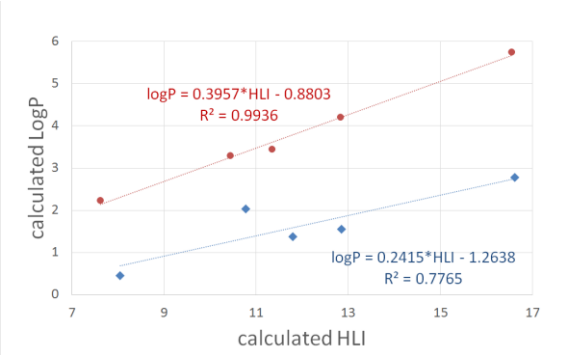


Figure 2
Magnetization as a function of applied field
Note how the caption is centred in the column

The primary screen was carried out by agar disc-diffusion method [40, 41] using nutrient agar medium. Cefotaxime and ketoconazole were used as control drugs. The observed data on the antimicrobial activity of particular compounds and control drugs are given in the Table IV and Table V for anti-tubercular activity.

TABLE IV

ANTIBACTERIAL ACTIVITY OF COMPOUNDS **5,6**

Compound	Concentration (µg/disc)	Zone of inhibition (mm) Gram positive bacteria & Gram negative bacteria						
		Staphylococcus albus	Staphylococcus aureus ATCC 25923	Sarcina flava	Bacillus subtilis ATCC 6633	Candida albicans CCM 885	Klebsiella oxytoca ATCC 13182	Pseudomonas aeruginosa ATCC 27853
3a	200	-	-	-	-	-	-	-
4a	200	-	-	-	-	-	-	-
4b	200	-	-	-	-	-	-	-
5i	200	-	-	20	-	10	14	14
5j	200	-	-	22	12	12	22	15
5k	200	18	-	26	15	8	26	9
5l	200	12	-	16	12	8	18	-
5m	200	-	-	13	-	12	14	10
5n	200	-	-	11	-	10	12	10
6a	200	12	-	17	14	-	22	10
6b	200	11	-	8	9	-	14	8
6c	200	-	-	13		16	14	16
6d	200	-	-	10		12	12	11
Cefotaxime	200	19	22	24	18	-	24	18
Ketoconazol	200	-	-	-	-	14	-	10

The results revealed that all Se,Te-containing compounds **5, 6** exhibited high activity on fungi and gram-negative bacteria. Molecular complexes **5** in general are more active then fused thiazolotriazoles, especially as antifungal. On the other hand, Se, Te-containing compounds **6a,b** exhibit higher activity against gram-negative bacteria than another compounds. Results of the investigation presented in the Table IV revealed that Se, Te-introduction into

organic moiety considerably increases the activity of these compounds towards fungi and gram-negative bacteria and decreases their toxicity in comparing with toxicity of known Se-containing remedies.

TABLE V
ANTI-TUBERCULOSIS ACTIVITY OF **5G, H**

Structure	Activity		
	0.2 mg/ml	1 mg/ml	2 mg/ml
3d	0%	0%	0%
5g	0%	20%	80%
5h	0%	20%	80%

Also anti-tubercular activity was observed for some Te-containing compounds **5d,g,h**. Only 80% of tested tuberculosis species were suppressed and only with relatively high concentration (2mg/ml), which means about relatively weak anti-tubercular activity.

ACKNOWLEDGMENT

This study was partially supported by International Visegrad Fund (App. ID. 51600925). This publication also contains the results of studies conducted by President's of Ukraine grant for competitive projects (F-63/94-2016) of the State Fund for Fundamental Research.

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APPLICATION OF MODERN TOOLS FOR NOISE SOURCES VISUALIZATION AND IDENTIFICATION

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Received: November 2016

Abstract

Noise reduction is important field in the acoustics. Application of modern tools can provide the important data and information about the noise sources. In the recent years were developed tools for noise visualization. The target of these tools is identification and localization of noise sources. These tools are nowadays used in the variety industries. The range of usage is very wide. The results obtained by the noise visualization are useful for the next noise reduction measures. The results of visualizations are acoustic pictures or acoustic movies. The analysis clearly shows which sound sources are active when and where are located. These tools also provide classic sound analysis, third octave band analysis and weight filters. These visualization tools used different principles and techniques. On these base is also their application different and have some advantages in field of application. Nowadays on the market there are available different visualization tools from different producers. The basic differences are in the visualization technique and construction of microphone arrays. The most used visualization technique is beamforming and near field technique. Some of these tools are suitable for noise visualizations from small distances, others are suitable for the long distances, and the important parameter of these tools is frequency range for sound visualization. These parameters are important for the application for measurement of noise sources.

INTRODUCTION

Home appliances used in households for its activities emit noise that is undesirable practices. Currently it focused attention on the possibility of reducing the noise emission of individual types of household appliances.

Household appliances emitting noise are a large number of different kinds and types, which differ by their design, principles, purpose of use as well as characteristics of the noise that can be produced during their activity.

In assessing the noise of household appliances it is a primary step is to perform measurements. Measurements in most cases carried out by conventional sound level meters that allow quantitative and qualitative analysis of the noise source.

The acoustic camera is a tool, which greatly extends the capabilities of conventional sound level meters. Acoustic camera as a tool for visualization of noise in addition to the use of traditional methods of analysis than the one-third octave analysis, narrowband analysis, and application of a weighting filter greatly extends the analysis of noise sources visualization with the noise emitted from the source. After measurements are spectrograms generated for a specific frequency range in a given time. From this selection, it is then possible to create acoustic movie or acoustic images. These outputs it is then possible to precisely determine localization and duration of action of sound source. It is also possible to analyze the moving objects.

The use of acoustic cameras, and the subsequent visualization of the emitted sound is the in the field assessment of noise sources, a new element These visualization tools allows to perform the analysis of the household appliance noise sources, to obtain the data for the subsequent implementation of measures to reduce noise. [1, 3]

ANALYSIS OF SOUND VISUALIZATION METHODS

For visualization of sound sources it is possible to use one of the following visualization methods:

- beamforming,
- spherical beamforming,
- acoustic holography,
- focalization,
- "direct method". [3]

Tools for visualization of noise sources consist of three basic parts:

- array microphones with digital cameras,
- unit to record data,
- laptop with software for data processing.

Currently, there are more manufacturers that are developing devices which can be used for sound visualization. These most relevant companies are Acoustic Camera, Head Acoustics, LMS, Microflown Technologies and Brüel & Kjær.

Beam forming

Beam forming uses a rectangular image plane for precise calculation of the delay of acoustic sound signals emitted from various noise sources to individual microphone. The calculation is carried out, provided that the image plane does not move during measurement. The result of the distribution of imaging plane into rows and columns is a finite number of pixels and the centre of this area is used to calculate. Placement of the microphone array from the source is in the far field. Microphone array microphone shall be located at a distance greater than the size, resp. diameter of the microphone array. The range of the frequency band of the method is from 200 to 10,000 Hz.

The advantages of this method are fast, suitability for high frequency and large objects from a single measurement can be created a whole different maps and different shapes of a microphone array construction.

The main disadvantage is the unsuitability of using this method for the low frequencies. [2, 3]

Acoustic holography

The method uses the measurement of sound pressure microphones arranged in a rectangular array. Microphones are placed horizontally and vertically. The measured sound pressure levels are transformed back to the actual surface of the object. For calculation is used Fourrier transformation. This method is for the near field an area which is not more than one or two wavelengths of the highest frequency. The distance between the microphones determines half the wavelength of maximum frequency and size of the field determines half the wavelength of the minimum frequency. The range of the frequency band of the method is 50-3000 Hz.

The advantages of this method are accuracy, identification of small sound sources, the independence of the frequency resolution, quantification source.

Improved method of acoustic holography in near field is statistical method optimized near-field holography (SONAH). This method is different from classical holography near field that does not use spatial Fourier transform, but the process takes place directly in the spatial domain.

Disadvantages of the method is that the method is not applicable to higher frequencies measured surface must be parallel to the surface of transmitted plane size measurement surface must be the same as the transmitted plane area. [3]

Focalization

The principle of focalization is identical to beam forming method, a difference in the distance field. Beam forming technique is based on near-field measurements. It either reprocesses already acquired NAH data or allows the beam forming array to be moved closer to the sound source. In the near field, the sound waves no longer arrive at the microphone as planar waves but as spherical waves. The original beam forming back-propagation is reformulated to deal with these waves.

Direct method

The method is based on direct measurement of the sound pressure and the acoustic particle velocity. Array microphone is placed close to the measured surface and is made up of acoustic pressure sensors and transducers acoustic particle velocity.

This is a new method, which preferably compared to previous described method is that it is not necessary to obtain information on the previous acoustic field.

Range frequency range of the method is 20 to 20,000 Hz, so it is the widest range compared to previous methods. [3, 5]

NOISE VISUALIZATION OF WASHING MACHINE

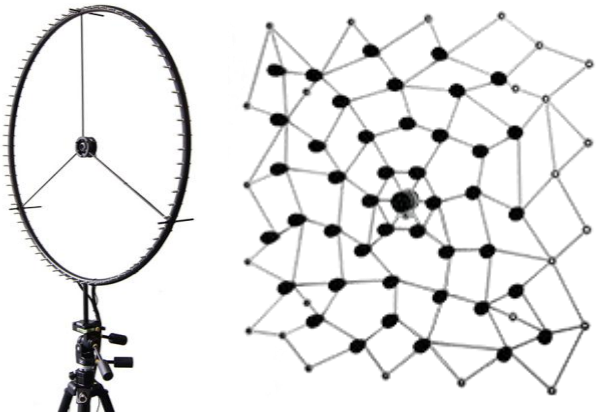
Measurement procedure

Subject to measurement and visualization of noise was a washing machine. The measurements were performed in an anechoic chamber. The measurements were carried out at the spin mode, which produces the highest noise pollution. For the measurements were used three different visualization tools:

- acoustic camera with a circular array microphone,
- noise inspector with the array microphone with "spider" layout,
- combined sensor microflown.

Each of these visualization tools using a different principle of sound visualization. Acoustic camera uses of beam forming, noise inspector works on the principle of acoustic holography in the near field (SONAH) and combined sensor microflown uses the

direct method in the near field. Used visualization devices are shown in Figures 1 and 2. [4, 6]



a) acoustic camera with circular microphone array

b) noise inspector with spider microphone array

Figure 1
Noise visualization tools

Figure 2
Visualization combined sensor - microflown

Figure 3 is shown visualization measurements in anechoic chamber by the se acoustic cameras with a circular array microphone and equipment noise inspector.

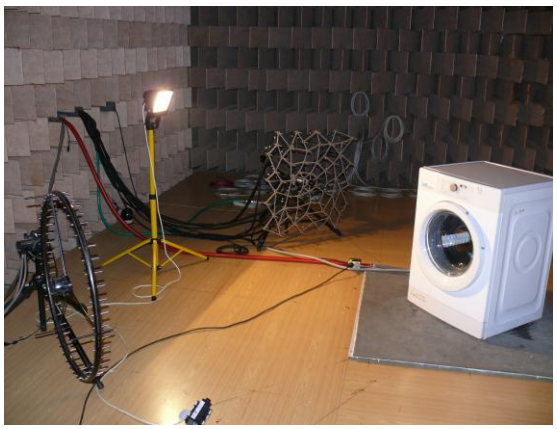


Figure 3
Noise visualization measurements in anechoic chamber by the acoustic camera and noise inspector

Figure 4 shows measurements in anechoic chamber using the combined sensor microflown.

Figure 4
Noise visualization measurement in anechoic chamber by the combined sensor microflown

Measurement results

Acoustic images obtained by various visualization tools was realized in a frequency range from 63 Hz to 2500 Hz. Images below (Figures 5 - 7) presents the results of visualization of noise the washing machine of the four sides for the selected frequencies.

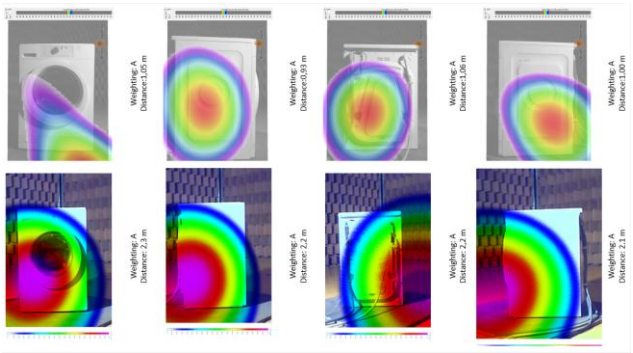


Figure 5
Results of noise visualization in 1/3 octave band in frequency range 63 Hz

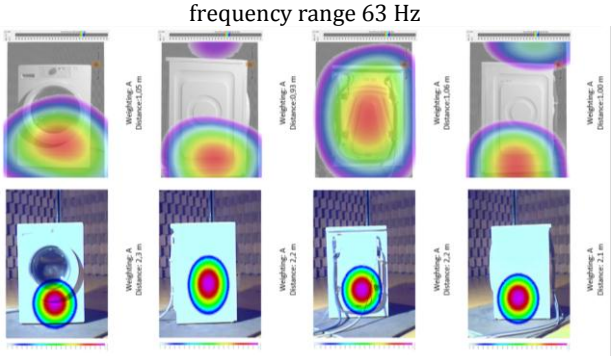


Figure 6
Results of noise visualization in 1/3 octave band in frequency range 315 Hz

In the top row are given acoustic images obtained by device noise inspector and in the bottom row are shown images obtained by the acoustic cameras with a circular array microphone. Acoustic images was created for each frequency in 1/3 octave band. Presented are only selected, most relevant acoustic images.

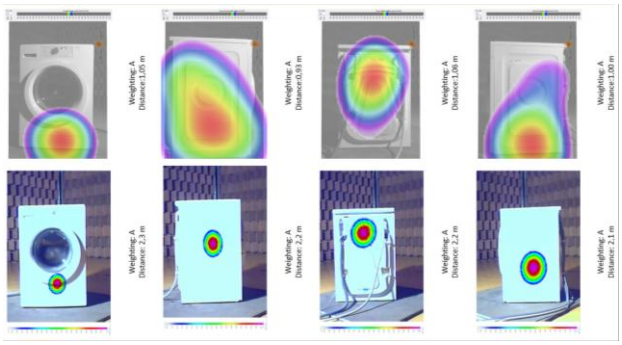


Figure 7
Results of noise visualization in 1/3 octave band in frequency range 355 – 708 Hz

Next Figures show results of noise visualization by the combined sensor microflown for the selected frequencies Measurement by the microflown sensor was realized from distances about 20 mm and was scanned all four sides of washing machine.

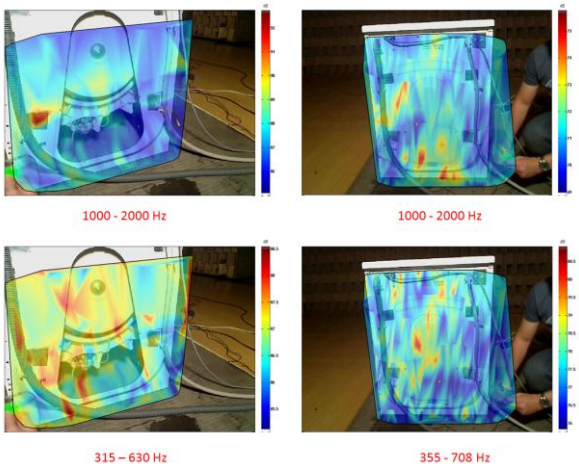


Figure 8
Results of noise visualization by microflown

EVALUATION OF REALIZED MEASUREMENTS

From the above results it is clear visualization of noise, the differences are greatest at low frequencies 63 Hz (Figure 5) and 125 Hz. In other frequency bands are the results of sound visualization by the individual tools almost identical. The differences at low frequencies are caused mainly by beam forming method that is suitable for higher frequencies from about 300 Hz.

Comparison of different acoustic images and obtained frequency spectra, we can conclude:

- Noise emitted in frequency bands 63, 125, 315Hz is generated by side panel and rear cover of the cabinet, and from front view we can also see noise emission generated by front panel and particularly door area with front panel,
- In the frequency band 315 Hz also was identified higher level of noise emission in the upper part of rear cover of the cabinet a bottom part of side walls of the cabinet,
- In frequency band 400 Hz is noise emitted by the centre area of the left side wall of the cabinet and by the washer front bottom parts,
- In the frequency band 500, 630 Hz is noise emitted by the bottom sides of side walls, and also from front bottom parts of the washer,
- In the frequency band 500, 630 Hz is noise emitted also by the rear side of the washer in the top area (between top of the rear cover and table top),
- In the frequency band 1000 Hz is noise emitted by the door frame assembly and bottom parts of the front side and also from the rear side of the cabinet,
- Level of noise emissions in the frequency band 2500 Hz is not the most significant and mostly coming through the bottom edge of the cabinet,

Conclusions of noise visualization with Microflown combined sensor:

- Microflown measurement was used for more detailed visualization and confirmation of the measurements realized by the acoustic camera,
- Realized measurements confirm results obtained by the acoustic camera,
- Low frequencies and low harmonic frequencies of spin speed and affect to plint and generated noise emission in the range of 63 Hz,
- Emission of the noise in the frequency band 500 Hz are emitted by the whole front of the washer (front panel, door assembly),
- In frequency bands over 1000 Hz noise emissions by the front panels rear side of the washer are not significant,
- In the frequency range 315 – 630 Hz measurement without rear cover show that noise is generated by the direct drive motor area, same effect is not visible in the frequency range 1000 – 2000 Hz.

CONCLUSION

Equipment for visualization and identification of noise sources are effective tools in the analysis of noise sources. The outputs of visualization and identification of noise sources serve as the basis for implementing measures to reduce noise. Perhaps the most important parameters of visualization tool are the frequency

range and measuring distance. While devices using beam forming are suitable for distances over 1 m and frequencies above 300 Hz, devices using acoustic holography principles of near field are applicable for a distance of several cm and a frequency of about 50 Hz.

Application equipment for visualization of noise in the home appliance is proving very important data and these methods can detect deficiencies and bottlenecks that increase the overall noise household appliances. Identifying these critical elements is crucial in the subsequent implementation of measures to reduce noise.

For the complex assessment of noise sources is suitable to use for measurement combination of different visualization tools to reach objective results.

Using equipment to visualize noise sources is very wide. They are useful both in the laboratory and in the interiors of various equipment and operations, as well as outdoors.

ACKNOWLEDGMENT

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-15-0327.

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ATTEMPT TO CALCULATE ENVIRONMENTAL DAMAGE DUE TO ILLEGAL AMBER EXTRACTION IN UKRAINE IN 2015

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Received: November 2016

Abstract

The problem of illegal amber extraction is highly acute in *some regions of north-western Ukraine. It was estimated that approximately 120-300 tons of this mineral were extracted in 2015 without official permission, while legal extraction was responsible for only 4 tons. The most common mining technology used by unlawful prospectors is based on eroding the barren rock layer with high pressure jet of water (motor pump) to reach amber-containing layer. Such method is critically harmful for the environment: it results in soil erosion, humic layer depletion, elimination of ground water circulation, etc. Thus, the aims of the paper are to calculate losses inflicted on the state due to illegal amber extraction in Ukraine using different formulas, and analyse the effectiveness of above formulas.*

INTRODUCTION

The problem of illegal amber extraction in Volynska, Zhytomyrska and Rivnenska oblasts of Ukraine (north-western regions, or Polissya) is critical and requires additional research to evaluate its environmental impacts. Annual state losses due to this unlawful activity, including illegal amber sale, unfortunately cannot be fully and precisely estimated without expensive field investigation and usually are believed to reach millions of hryvnas. Only according to official information roughly about 400 ha of land are destroyed because of motor pumps use while extracting amber in three mentioned regions [1]. The consequences are dramatic as can be seen at Figure 1. It is recognized that Ukrainian amber (Klesiv deposit, in particular) has high quality and by number of features exceeds Baltic amber. It has wider range of colouring; higher density and lesser fragility; generally wider variety of fractions and forms, etc. [2].

Figure 1
Consequences of motor pump use in Polissya forests

This determines also high market prices for Ukrainian amber and its popularity in Ukraine and beyond. For better understanding of the issue it should be mentioned also that it has many-sided nature which makes it even harder to address. Thus, it is important to analyse the situation from different perspectives, particularly geographic, socio-economic, ecological and political. Experts believe that among the main causes of the problem are corruption on national and local levels and high unemployment rates in relevant regions which push citizens to engage in unlawful activities that can bring them profit [3]. In support of this idea some statistics can be provided: as to the beginning of 2016, there was 13% of unemployed in Volynska oblast, 13.2% in Zhytomyrska oblast and 11.9% in Rivnenska oblast, while the average rate in Ukraine was 10.3% [4].

All in all, the aim of this paper is to define approximate state losses and analyse acting methodologies assessing environmental damage in Ukraine using different available formulas.

THE SPECIFICS OF USED METHODOLOGY

Some aspects of extraction methods

Some experts distinguish the following methods used in Ukraine for extraction of amber. The first is mechanical and it assumes quarrying an open pit or underground. In this case the productive soil layer is disclosed, then excavation works are carried out, amber layer is transported and panned out. While, the extraction via hydraulic method is accompanied with eroding the barren rock layer with high pressure jet of water to carry amber over the surface [5]. Both methods have highly negative impact on the environment.

Another method developed in National University of Water Industry and Nature Management is absolutely worth mentioning, as it gives a chance to improve extraction practices and move towards more sustainable resource use and management. The proposed hydromechanical method is based on saturation the soil layer with water, stirring it with vibration and subsequent segregation of amber due to buoyancy force. According to the study, the use of the method leads to extraction of 90-95% of amber in deposit and has less negative impact on the environment [6].

While above mentioned methods are used for industrial extraction, majority of unlawful prospectors prefer using compact motor pumps. Motor pumps allow washing over upper soil layer with high pressure water jet. Thus, it can be characterised as hydraulic method. In Polissya the depth of damaged plots sometimes can reach up to 20 m. Such method leads to disastrous consequences for the natural environment.

First of all, geological section is destroyed; the humic layer is washed out or mixed with parts of less rich layers. Moreover, absolute elimination of normal ground water circulation takes place which ultimately results in microclimate change. Illegal extraction often is carried out without advance exploration work, hence, sometimes the damaged plots even do not contain amber layer. Another side of illegal extraction is that damaged areas are not restored and environmental damage, as a rule, is not remediated [7]. Amber tends to occur in forested areas, so the trees are usually either cut or their root system is critically damaged [8]. According to official data provided by the State Forestry Agency, at the beginning of 2016 more than 2000 ha of forest have been damaged in respective regions [7]. Among other ecological consequences are grass cover destruction, amber-contained layer depletion, erosion intensification and damage caused to flora and fauna [8].

Recent studies and asessments

There are a number of studies in Ukraine aimed at calculating environmental damage caused by illegal amber extraction in particular regions of Polissya. Philipovych in her study [9] makes such calculations for the land area between Hrani and Hrytski villages (Rivnenska oblast). She uses officially adopted state methodology for assessing environmental damage and comes to conclusion that: damaged area between respective settlements had widened in two times for less than a year in 2015; the amount of losses for that area in 2015 prices has concluded at least in 345,912 thousand hryvnas. To assess the caused damage she relies on several methods analysing the following: violation of Bowels Laws; removal of humic layer without official permission and unauthorized occupation of agricultural lands. Philipovych recommends using satellite shots to evaluate the size of damaged land area [9].

Nadtochiy also relies on methodology used by the State Ecological Inspection while evaluating damage caused by illegal amber extraction on the territory of Olevskiy and Korostenskiy administrative districts (Rivnenska oblast). The land plot he investigates has the area of 10,86 ha. According to the results, approximate damage due to illegal amber extraction on respective land plot consists of 103.8 thousand hryvnas for one month [10].

As it is seen, mentioned calculations refer to particular limited land areas and estimate rough Figures, as it is physically impossible to rely on precise data which are simply absent.

As provided by the State Ecological Inspection, in 2015 damage due to illegal amber extraction in Volynska oblast corresponded to 147 thousand hryvnas, Zhytomyrska oblast – 10 thousand hryvnas [7]. Hence, the idea of current paper consists in defining rough amount of environmental damage in Polissya in 2015, simultaneously using officially adopted methodology in Ukraine and alternative formula presented in Methodology for calculating environmental damage assessment and relevant compensation by "Association of Environmental Assessors" NGO [11].

Formulas and basic data

Empirical problem of the calculation lies in absence of full official data concerning the amount of extracted amber and real size of the affected areas. For the aims of the research official available (even if it is not full) data used. That leads to extremely rough results which mean that, potentially, actual losses are expected to be higher. The State Ecological Inspection uses the equation (1) to assess losses (3) due to unauthorized use of bowels:

$$З = Pi \cdot N \cdot Дi, \qquad (1)$$

where Pi – basic rate in parts of minimal salary,
N – minimal salary (₴),
Дi – volume of illegally extracted mineral (kg).

Pi is given in Methodology for each particular mineral and equals for amber 1.42 [12]. Information on

minimum salary is taken from the Law on State Budget for 2015 and is ₴ 1 218 [13].

Within current research officially declared data concerning Ді is used. According to those, annually from 120 to 300 tons of amber is extracted illegally in Ukraine [1]. Thus, there is double calculation for both Figures and the results will vary from minimum to maximum. Alternative methodology [11] proposes slightly different formula (2) which, though, seems a bit more logically developed:

$$X = Q \cdot P + Знс, \quad (2)$$

where Q – volume of illegally extracted mineral (kg),
P – market price on mineral,
Знс – remediation measures costs (₴/$).
Q figure corresponds to Ді from (1).

Index P is quite uncertain, as in terms of market economy and depending on quality of amber prices are notably varied. To define an average and most appropriate price of amber for calculation a little comparison was made which is summarised in Table 1.

Table I.
Market Prices for Row Amber in 2015-2016

Fraction	Amber Europe [14] ($/1 kg)	Gdansk Exchange [15] ($/1 kg)	Ukrainian Exchange [16] ($/1 kg)	Ukrainian Black market [17; 15] ($/1 kg)
Up to 2 g	180			
2-5 g	500	350-500		205
5-10 g	1100	600-800		540
10-20 g	2200	1300-1700		1160
20-50 g	4500	2200-3200	3200	1780
50-100 g	5500	3000-4300	5300	1980
100-200 g	6500	4000-5200		2420

Compared available prices the basic market price to be used for calculation was chosen from Gdansk Exchange, i.e. minimal price for fraction 20-50 g (as average fraction) which is $2200 (or according to 2015 rates about ₴ 52 000).

Gdansk price rather corresponds to the one on Ukrainian Exchange, while being slightly higher than on black market, and a bit lower than proposal from large European "Amber Europe" company.

As to figure, corresponding to remediation costs, it can be stated that there are different approaches and methods to evaluate costs needed for remediation [18;19;20;21;22], and most of them embrace indicators which can be defined only through field investigation or provided with thorough monitoring data.

According to official declaration of the Head of Forestry and Hunting Agency in Zhytomyrska oblast A. Kurinskiy, 400 thousand hryvnas required to carry out relevant restoration measures on lands damaged due to amber extraction. If the total damaged area equals 393 ha (total for three respective regions), then:

$$Знс = 400\,000 \cdot 393 = ₴\ 157\,200\,000 \quad (3)$$

MAJOR FINDINGS

First, let us refer to official methodology used by the State Ecological Inspection in Ukraine to assess environmental damage due to illegal extraction of minerals. Taking into account varying data concerning the volume of amber extracted annually, the calculation will have two options (min and max):

$$З_{min} = 1.42 \cdot 1218 \cdot 120\,000 = ₴\ 207\,547\,200, \quad (4)$$

which corresponds to approximately $ 8 794 373 at 2015 rates.

$$З_{max} = 1.42 \cdot 1218 \cdot 300\,000 = ₴\ 518\,868\,000 \text{ (or \$ 21 985 932).} \quad (5)$$

Using the alternative methodology of "Association of Environmental Assessors" the following results were reached:

$$Хзб_{min} = 120\,000 \cdot 52\,000 + 157\,200\,000 = ₴\ 6\,397\,200\,000 \text{ (or \$ 271 067 797).} \quad (6)$$

While maximum losses according to (2) are the following:

$$Хзб_{max} = 300\,000 \cdot 52\,000 + 157\,200\,000 = ₴\ 15\,757\,200\,000 \text{ (or \$ 667 677 966).} \quad (5)$$

It is quite apparent that the results differ depending on the methodology used, though the aim of both is the same. The reason lies in difference of indicators which consist of respective formulas. Market price logic of (2) is opposed to minimum salary logic of (1). Perhaps, it indicates also different approaches to remediation and environment as a whole. Respective methodology officially used in Ukraine by the state actors does not take into account environmental impacts, while costs needed for remediation are responsible for essential part of environmental damage, evaluated via (2), as it can be seen in (5),(6).

CONCLUSIONS AND RECOMMENDATIONS

Mixed methodology and possible solutions

However, there is a set of other official methodologies which can be used in addition to before mentioned, so it would be possible to make more or less comprehensive assessment of caused damage. For example, there is a methodology for evaluation damage due to removal of humic layer without formal permission [23]. It takes into consideration normative assessment of land, depending on regions and soil quality. Not providing specific calculations, such damage in 2015 approximately concluded in ₴ 4 207

686 865.52 (or $ 178 291 816). So, it can be suggested that, if these results add to the amount of losses found via (1), more feasible figures can be reached.

There is a range of different formulas which are used by the State Ecological Inspection to estimate environmental damage due to different impacts and activities, so if all relevant methodologies are involved during the assessment, the final figure can be more indicative. Such approach possibly can help to make more or less systemic assessment of caused damage.

To tie minimum salary to the amount of compensation seems a little inconsistently for Ukraine, where national currency is relatively weak and salaries barely go through indexation. On the other hand, relying on more flexible and reliable market prices helps to evaluate actual state losses due to illegal amber extraction and its subsequent selling.

When it comes to calculation of costs needed for carrying out remediation measures, the methodologies are even more mixed and complicated. Moreover, Ukraine does not have an adequate framework of laws which would define all the aspects and conditions of restoration of damaged environment. Among others, it means that the funding of such activities is undefined or critically limited.

So, developing this methodology would have a specific importance in creating a responsibility and accountability mechanism for identifying an extent of damage imposed or likely to be imposed on the environment through a relevant economic assessment as well as for calculating ecological damage assessment and related compensation.

Ecological compensation is a form of charges to be paid for polluting nature and environment, and destroying lands, plants or animals. According to Methodology for calculating environmental damage assessment and relevant compensation [11] an amount of compensation for the damage caused by mining extraction industry consists of the environmental restoration expenses, fine for polluting or declining natural resources and the expenses on the work for identifying the extent of the environmental damage. As for the regions with the developed mining industry, it is important to pursue a principle to correctly determine the natural reserve, ecological capacity and recoverability, put into consumer circulation the observation, monitoring and management data, and implement technological and financing operations stage by stage [11].

The good news is that in April 2015 The Law on Extraction and Selling of Amber was considered during the first reading in Ukrainian Parliament and now is waiting for approval at the second reading. The major pro of the document is that it determines the legal state of so called “local prospector”, who is a resident of regions with amber deposits and under certain conditions can realize legal extraction of amber. This is believed to eliminate the problem of citizens engagement in unlawful activities.

To sum up, the problem of illegal amber extraction in Ukrainian Polissya is critical and demands efficient and urgent measures for its solving. First of all, the adoption of Law on Extraction and Selling of Amber is needed. Further legislative work with regard to remediation, restoration activities should be continued and have to be more effective. Relevant improvements of methodology on calculating environmental damage and assessing remediation measures cost should be pursued and put into practice.

Possible practical improvements

To solve the problem of illegal amber extraction in Ukraine which is a complex, deep issue, it is important to imply holistic approach and work on the improvements in different dimensions.

Deeper and more effective cooperation between different public services and bodies would be crucial in prevention and elimination (including punishment under law) of illegal activities taking place in respective regions with amber deposits.

Higher fines and penalties can be introduced for those who break Bowels Law. At the same time, legislation should be harmonized and improved to grant local communities conditions for legal participation in amber extraction.

A framework on remediation and restoration measures also has to be made and adopted.One of the major problems occurred during any calculation is the lack of full and precise data. Such banks of data are possible, particularly, due to permanent and efficient monitoring of environmental state. As to amber extraction, for instance, Philipovych [9] suggests using data that can be inquired from the satellite, in support of this idea she did a research which fully relied on satellite data.

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Appraisal of Pedological Functioning of Two Wetland Ecosystems in Sétif (East of Algeria (Sétif)

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Received: November 2016

Abstract

The Algerian wetlands are natural ecosystems which offer a huge faunistic and floristic diversity. The main factor affecting the evolution of these ecosystems is Water. The soil study of these ecosystems is often omitted. So, the aim of this work is to assess the state of the soil in two Algerian wetlands regions (Sebkhas) classified in Ramsar Convention. These sites are located in East of Algeria (Sétif), namely the Bazer-Sakhra Sebkha (BS) and also Sebkha of El-Hamiet (HM). We follow the evolution of some soil properties (pH, EC, $CaCO_3$ and OM, soil particle size distribution) along a six months duration, namely from 10/2014 To 06/2015. The results obtained reveal a predominance of saline and alkaline traits of these soils with association with calcium carbonate in the two wetlands studied. The OM content is more present in Sabkha of El Hamiet (HM). Soil texture is mainly fine with a high content of clay in both regions. Spatio-temporal variability of these properties shows a dynamic linked with climatic conditions (evapotranspiration and rain) and edaphic conditions (water table, texture and vegetation). Finally, the OM, EC and pH can be used as diagnostic tool to understand the dynamic, functioning and the preservation of these two ecosystems.

Keywords: *Sebkha Bazer-Sakra, Sebkha El -Hamiet, spatio-temporal variability, Soil dynamic, Wetland ecosystem.*

INTRODUCTION

Wetland ecosystems are a natural resources of global significance, their high level of plant and animal (especially bird) diversity is perhaps the major reason why wetland protection has become a high priority worldwide, supported by international agreements such as the Ramsar Convention and the International Convention of Biological Diversity [1].

Soil resources are an important part of wetland ecosystems. The functioning of these wetland soils are linked to the presence of permanent or temporary waterlogging [2].

The wetlands of Algeria have been studied in several works like [3], [4], [5], [6] from the perspective of the biodiversity without taking into account the soil resources. To better understand the wetland ecosystems, the soil deserves to be better known because it is an indicator of their history and their evolution. It's an important element for understanding their ecological and biogeochemical functioning. So our aim is in two folds: to characterize the soils of two wetlands in east of Algeria Bazer-Sakhra (BS) and El-Hamiet (HM) sebkha and to follow the spatio-temporal variability of their characteristics.

MATERIALS AND METHODS

General Description of the Study Area

The experimental field of the university of Ferhat Abbas -Sétif is part of the high-plain of Sétif at east of Algeria, which is located between 36°11'49.59"N and 5°21'57.97''E with a mean elevation of 1021 m. In terms of the climate, the high-plain of Sétif is characterized by a semi-arid climate, with mean annual precipitation of 450 mm. the soil of the field experimental is developed on ancient alluvial sediment with the high presence of calcium carbonate.

General Description of the Two Wetlands

Bazer-Sakhra Sabkha is an endoreic saline depression, with a permanent lake throughout the year. It's located at 9 Km south of El-Eulma province (North-east of Algeria). Its geographical coordinates are: 36° 00'et 36°05'N and 5°37'E à 5°45'E (Figure 1).

Figure 1
Geographical Location of BS Wetland

This wetland covers an area of 4379 ha with an average altitude of 915 m above sea-level. The average slope is about 2%. The wetland is supplied with El-Melah River which carries waste water from the province of El-Eulma. In winter, and during high precipitation years, the water table raise to 1.5 m. this wetland is classified in the Ramsar convention according the criteria 2 and 6. Regarding, the soil of nearby the wetland, most of the soil are saline, but we also found calcisoils in the west part of the region [7].
Hamiet Sebkha is located in the south of the Bazer Sakhra Sabkha. This wetland is an endoreic saline depression with an average slope of about 3% and it covers an area of 2509 ha, with an average altitude of 910 m [5]. Its geographical coordinates are: 35°55'N and 5°33'E (Figure 2).

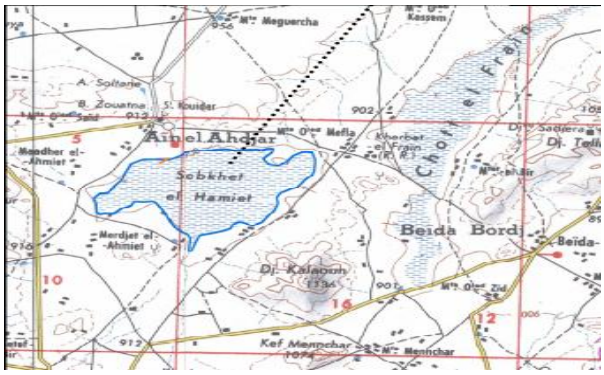

Figure 2
Geographical Location HM Wetland

This wetland is temporary flooded especially in the winter and is dry in the summer. It's classified in Ramsar convention according to the criterion 6. Regarding the soil nearby the wetland, the soils are mainly saline with some calcisoil found in the North-East.

Soil Sampling Methodology and Methods of Characterization

We use two criteria for sampling of the soil, which are the waterlogging of the soil and the presence of halophytic species. The Sampling of the soil was done with a manual auger in 3 soil profiles per wetland according two soil depths (0-20 and 20-40 cm). And also for the assessment of the spatio-temporal variability of some soil properties, we sample the soils of the two wetlands in three periods (October 2014, March 2015 and June 2015).

RESULTTS AND DISCUSSION

Static proprieties of the soil of the two weltands (Soil particle size distribution)

The result obtained show a predominance of the clay texture for the two wetland (Table 1) except for the soil profile 3 which has a silty texture in the two wetlands.

TABLE I
SOIL PARTICLE SIZE DISTRIBUTION OF SOILS IN BAZER SAKHRA AND HAMIET WETLANDS

Soil profiles	Soil depths (cm)	Soil particles fraction (%)					Textural Classes
		Clay	Fine Silt	Coarse Silt	Fine Sand	Coarse Sand	
P1BS	0-20	61,7	17,11	6,34	10,37	4,1	Clayey
	20-40	72,83	17,11	4,27	4,27	1,49	Clayey
P2BS	0-20	27,8	8,55	4,27	42,03	17,32	Sandy clay
	20-40	41,39	17,11	17,11	20,42	3,95	Clayey
P3BS	0-20	26,84	4,27	4,27	46,31	18,28	Sandy Loam
	20-40	20,4	34,78	22,72	13,15	8,66	*Silty*
P1HM	0-20	52,94	8,55	4,25	17,96	16,25	Clayey
	20-40	50,6	17,4	11,8	10,37	8,66	Clayey
P2HM	0-20	47,05	8,55	8,55	20,32	15,5	Clayey
	20-40	50,6	17,4	11,8	10,37	8,66	Clayey
P3HM	0-20	53,5	8,55	4,27	16,25	17	Clayey
	20-40	24,17	8,55	29,94	18,82	18,5	Silty

BS: Bazer Sakra wetland, HM: Hamiet wetland

Spatio-Temporal Variability of Dynamic Soil Proprieties (pH, EC, CaCO3 and O.M) In The Two Wetlands (Table II)

pH

The Soil pH in BS and HM wetland is alkaline. In terms of the temporal variability, we notice a slight increase in pH in our monitoring period between T1 and T3 in the majority of the soil samples for the two Wetlands.

EC

The results obtained for the soil of the two districts show a saline tendency in all the soil samples. In terms of the evolution of the salinity according to three periods of sampling, we notice for BS wetland a slight decrease in P1 from 16.1 to 15.2 $dS.m^{-1}$ for the

soil depth 0-20 cm and a decrease from 15.55 to 14.3 $dS.cm^{-1}$ for the soil depth 20-40 cm during the time period of the study.

TABLE II
SPATIO-TEMPORAL VARIABILITY OF SOME DYNAMIC SOIL PROPERTIES IN BAZER SAKRA WETLAND (BS) AND HAMIET WETLAND (HM)

Soil profile	Soil depth	pH_{water}			EC-25°C ($dS.m^{-1}$)			$CaCO_3$ (%)			O.M (%)		
		T1	T2	T3	T1	T2	T3	T1	T2	T3	T1	T2	T3
P1BS	0-20	7,7	8,41	8,30	16,1	15,7	15.2	27,2	24,5	20,9	2,22	1,16	1,06
	20-40	7,55	8,62	8,60	15,5	15,1	14.3	26,8	22,7	23,6	1,58	2,01	2,22
P2BS	0-20	8,69	8,44	8.7	6,1	5,40	8.40	28,6	27,2	28,61	1,37	1,27	1,45
	20-40	8,25	8,29	8.24	0,35	2,34	3.50	29,1	28,6	27,7	1,58	1,48	1,63
P3BS	0-20	8,03	8,5	8.3	2,0	1,38	2.13	27 ,2	31,0	26,8	1,48	0,95	1,55
	20-40	8,20	8,0	8.1	3,2	2,90	3.17	27,2	20,4	25,4	2,54	0,74	2,71
P1HM	0-20	8,27	8,64	8.32	13,11	9,56	12.42	24,1	28,6	24,5	1,06	1,05	3,28
	20-40	8,15	8,5	8.20	12,3	14,1	11.87	24,5	24,5	29,5	2,43	1,58	3,50
P2HM	0-20	8.20	8,55	8.38	12.57	13,97	14.36	21.2	20,4	29,5	1.36	1,27	3,07
	20-40	7.74	7,95	8.20	10.53	10,41	12.89	21.2	20,0	27,2	2.10	1,90	3,70
P3HM	0-20	8.33	8,45	8.39	11.84	11,66	10.69	14.1	16,8	28,6	0.76	0,21	1.9
	20-40	8.41	8,6	8.48	14.46	15,72	9.47	20.7	21,3	27,7	0.89	1,05	2,75

***BS**: Bazer Sakra wetland; **HM**: Hamiet Wetland; **T1**, **T2**, **T3** stand for respectively: October 2014, March 2015 and June 2015*

For the P2 and P3, we notice a slight increase in the soil salinity in T2 period (April 2015). For the HM wetland, there is no clear tendency in the evolution the soil salinity, except for the P2 where there is a steady increase in salinity during the time period of the study.

$CaCO_3$

The results of this element show a moderate accumulation of these mineral in the two wetlands. In terms of the evolution with time, for BS wetland, there is a small decrease in the $CaCO_3$ Content during the time period of the study, and we notice an increase in its content in the P3 of HM wetland during the time period of the study.

OM

The organic matter content of the soils of these wetland ecosystems is low, the maximum value obtained in BS wetland is 2.54, and the maximum value obtained in HM wetland is 3.70 % during the time period the study. The evolution of organic matter content with time shows a relative accumulation in the two areas but it's more important in all the soil profile of the HM wetland.

COMPARISON OF THE PEDOLOGICAL FUNCTIONING OF THE TWO WETLANDS

Soil Characterization of the two wetlands (BS, HM) has yielded an alkaline saline, moderate carbonate content, and a low organic matter with a clayey textural class. Alkaline pH is always coupled with moderate total carbonate content. This fact has been confirmed in the two weltands. We notice in BS wetland a tendency toward soil salinization with time, especially in the soil Profile 1 located in the north of the BS wetland, and in the upstream of the Waste water treatment plant. In HM wetland, the analytical results show a high degree of soil salinity independent of the time period. We can say that the association of salinity, carbonate content accumulation and alkaline condition in the soil of the two wetlands affect their functioning.

Regarding the organic matter content terms, its status in the 2 Wetland, do not present similar rates. The soils of BS have less organic matter than the soil of HM wetland. Concerning the evolution with time, the tendency is the same. There is a slight increase of the organic matter content at the end of the time period of the study. This can be explained, according to Redyy et *al.* (1986) in Jaffrezic (1997), by the slow degradation of the M.O in waterlogged soils. Moreover, according to Swift and Woomer (1993) in Feller [5], they have found that the stock of soil organic matter in wetlands reflects the balance between the factors that determine its development and those who contribute to its mineralization.

CONCLUSION

Our study has highlight some important soil features in regards to the pedological functioning of two wetlands in north-east of Algeria, Namely salinization, alkalinisation, and relatively low organic matter.

We conclude that in the context of the study, the soil characterization of the two wetlands. In their natural functioning during the autumn 2014, spring 2015 and the beginning of summer 2015, we found spatial and temporal differentiation in their physico-chemical and biological characteristics. These variabilities were observed over a short period. Nevertheless, they reflect the dynamic of these Characteristic in the soils of these two wetlands in East of Algeria.

We should also mention that despite these constraints (high salinity, alkalinisation and low organic matter content), the soils of these sites present a huge potential, and can provide to these wetland ecosystems goods and services as long as we monitor each year the dynamics of their soil proprieties, so that we implement the appropriate set of sustainable soil management practices.

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YARN FLIGHT IN U-SHAPED WEFT PASSAGE

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Received: November 2016

Abstract

Fabric formation generally and weaving in particular are likely as old as human history. A loom is a machine for weaving yarn or thread into textiles. Several types of shuttleless weaving machines (looms) have been developed. These operate at higher speed and reduced noise level. Some of the common shuttleless looms include rapier looms, projectile looms, water jet looms, and air jet looms. In air jet weaving the weft yarn is transported through the weft passage by means of flowing air. The weft yarn ejected with high speed air flow is carried by the drag force caused by friction between the yarn and the air that comes through the nozzles from a high pressure tank. As it is well known, the main disadvantage of air jet weaving machines is their high energy costs compared to projectile and rapier weaving machines, but their advantage is lower noise and vibration levels from the point of view of environmental protection.

The main purpose of this analysis is to determine the distribution of the flow velocity in the weft passage. The air flow velocity at the exit of the accelerating tube and in the U-shaped cross section profile reed determines the motion of the yarn in weft passage. The velocity distribution of the air flow was measured and examined at different tank pressures without weft yarn. The velocity distribution of the air flow which comes from the main and relay nozzles in the weft passage was measured with a Pitot (Pradtl) tube. The main conclusion of this examination is that the air flow field in the weft passage can be divided into two parts. In the first part, where there is only the effect of the main nozzle, it is the initial section, where the characteristics of the axial velocities are similar to the flow of the free air jet. The velocity of the air flow in this range decreases rapidly. For the second part, the relay nozzles take effect, and the flow is nearly periodic. An important goal for the loom designers is to minimize the air consumption on air jet looms in weaving mills.

INTRODUCTION

Weaving is a mixture of science and art. Despite all the technological advances, weaving is still not a positively controlled process. The reason is that hardly possible to control the individual fibers which are the smallest meaningful building blocks in a woven structure. This fact makes weaving an interesting technology [2].

The modern weaving machines stand out as an expensive class compared to conventional machines in terms of capital investment. Intermittent weaving machines have the property that the weft is repeatedly laid into shed and tightened to the selvedge one after the other. This procedure is repeated during the whole weaving. The structure of these weaving machines is designed according to the characteristics of weft insertion. Figure 1 shows classification of weaving machines.

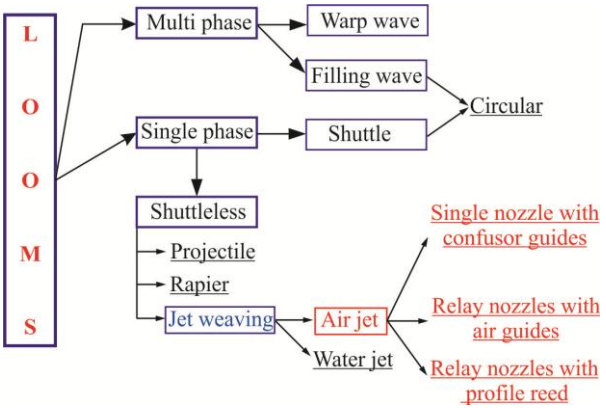

Figure 1
Classification of weaving machines

It is a general characteristic of weaving machines without shuttle that the length of one shoot of yarn is measured by the weft accumulator, position of the weft accumulator can be seen in Fig. 5. Weft accumulators or feeders are used to wind a predetermined weft (thread, yarn) length to make it ready for insertion. Their main purpose is to supply filling weft yarn to the weaving machine smoothly and a constant and proper tension. There are various types of weft accumulators used, for example one of them can be seen in Figure 2.

The typical features of these devices are the following:

- integrated weft break sensor,
- one-step pneumatic threading up,
- stepless weft separation adjustment,

- sealed spool body,
- S/Z rotation shifting,
- floating element yarn store sensors,
- insertion speeds up to 2000 m/min,
- serial communication interface,
- microprocessor controlled speed and motor effect.

The selection of a weft accumulator depends on several factors, such as:

- maximum speed delivered,
- weft yarn count,
- winding direction (S or Z),
- thread reserve control [2].

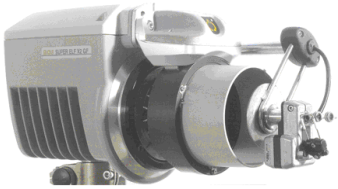

Figure 2
A modern ROJ SUPER ELF X2 GF weft accumulator [10]

The maximum speed depends on the weft yarn count range. On air jet looms can be done electronically by means of photocells. Weft yarn is removed and taken into the open shed by the air flow (Figure 3).

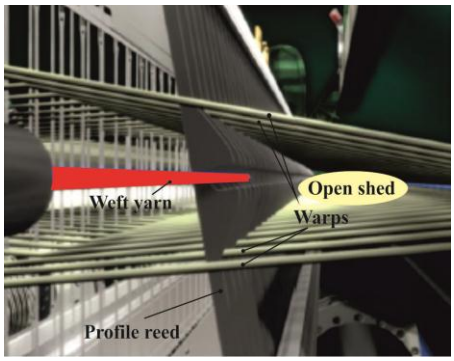

Figure 3
Weft yarn motion is in the open shed

The main nozzle (with acceleration tube) and relay nozzles can be seen in Figure 4.

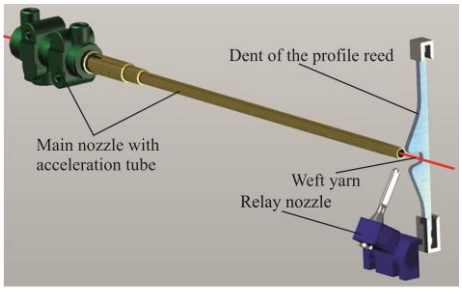

Figure 4
Schematic illustration of the main, and relay nozzles in front of the U-shaped dent

The weft is cut on the side of the main nozzle with each shoot at the selvedge. Most parts of the air jet filling insertion with open profile reed can be seen in Figure 5.

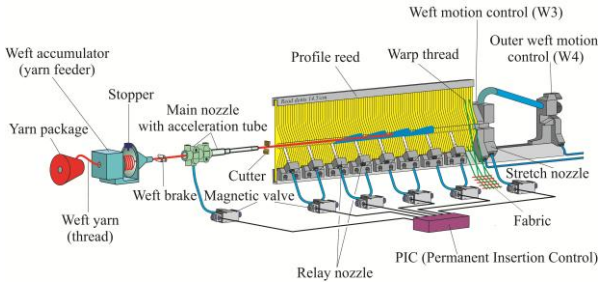

Figure 5
Air jet filling insertion with open profile reed

The first commercial machine was the Maxbo air jet weaving machine which was introduced by Max Paabo and was first exhibited in Sweden, 1951 weaving cotton cloth 80 cm wide with a frequency of 350 picks a minute. In 1969 Te Strake developed the filling insertion system with main nozzle, relay nozzles and U-shaped cross section profile reed.

The air jet weaving machine combines high performance with low manufacturing requirements. It has an extremely high insertion rate. The advantages of air jet looms are [1, 2]:

- high filling insertion rates
- high productivity
- low initial outlay
- simple operation and reduced hazard because of the few moving parts
- reduced space requirements
- low noise and vibration levels
- low spare parts requirement
- reliability and minimum maintenance.

Air jet weaving machines are under constant development. The current research is mainly focused on interaction between air and yarn as well as the guide system to increase the yarn velocity.

YARN FLIGHT IN THE DIFFERENT WEFT PASSAGES

The movement of the inserted yarn in weft passage is a complex motion. It is not a positively controlled process. Three different systems have been used on commercial air jet looms (Figure 1.) [2]:

1. Single nozzle, confusor guides and suction on the other side (Figure 6),
2. Multiple nozzles with guides,
3. Relay nozzles with profile reed (Figure 5.).

In first system a single nozzle is used to insert the yarn with air guide. Confusor drop wires are placed across the entire width to guide the air stream which is injected into the open shed (Figure 6.). Weaving

machines with this configuration are of limited reed width (about to165 cm) [4, 5].

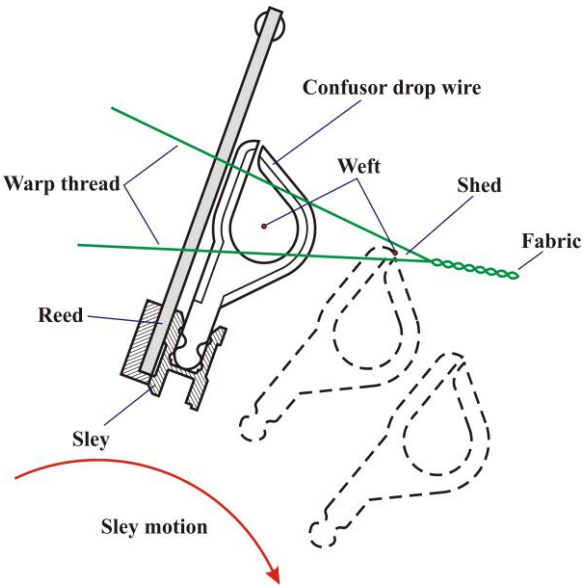

Figure 6
Displacement of confusor drop wire

In second system in addition to the main nozzle relay nozzles are used. They are arranged across the warp width at certain intervals and inject air sequentially and in groups in the direction of yarn movement.
In third system has reed dents built in the reed and relay nozzles (also called subnozzles) across the open warp (Figure 7).

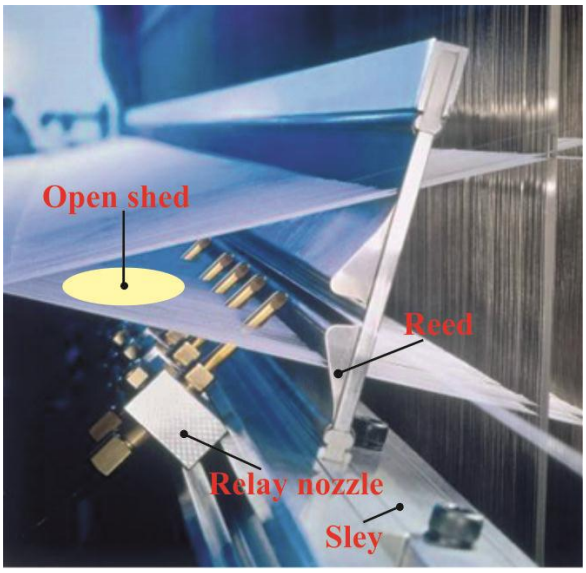

Figure 7
Relay nozzles and profile reed on an open shed

With the profile reed, the restriction on warp density also less severe than in the case of the confusor guide system. Although all the three systems have been used on air jet looms, system 3 relay nozzles with profile reed is the standard in the market today [2].
Relay nozzles are placed along the reed width on the sley (Figures 5. and 14.). A relay nozzle can have either single circle hole or two holes or nine holes or multiple holes (19 of them), as well as single hole of different shapes (rectangle, ellipse or star) (Figure 6).

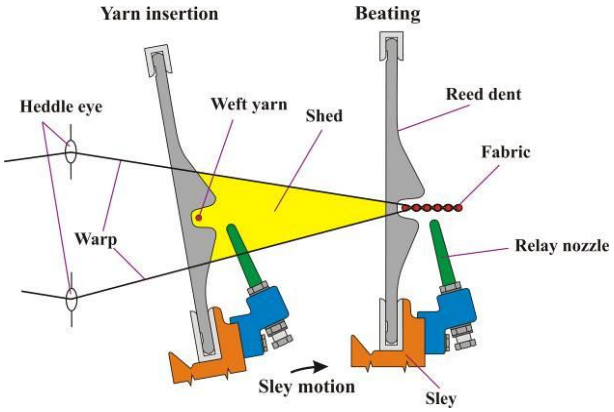

Figure 8
Yarn insertion system with relay nozzles and open profile reed

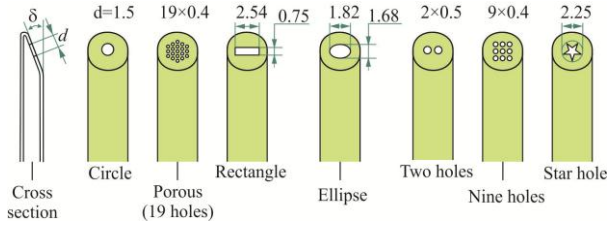

Figure 9
Commercial relay nozzles [8]

DYNAMICS OF YARN INSERTION WITH AIR IN THE WEFT PASSAGE ON PROFILE REED AIR JET LOOMS

In the nozzles the compressed air generates kinetic energy. The air erupting from the circular cross section slot at high speed grabs the weft yarn into the middle of the nozzle and accelerates it to high speed. The transporting substance, the air has a complicated flow. The exact theoretical and mathematical description of the flow is not known.
The propelling force on a weft yarn placed in a stream of air consists of skin friction (equal to the sum of all shear stresses taken over the surface of the yarn). This force is parallel to the undisturbed initial velocity, which is referred to as the friction force F_f as shown in Figure 10.
The propelling force moves the weft yarn in air jet insertion is provided by friction between the air and yarn surface and given by the following form (1):

$$F_f = \frac{\pi}{2}\rho \cdot c_f \cdot D \cdot x \cdot (u - v)^2 \qquad (1)$$

where

ρ - air density; [kg/m³]
c_f - skin friction coefficient; [-],
D - weft yarn diameter; [m],
x - weft yarn length subject to air flow; [m],
u - air velocity; [m/s],
v - weft yarn velocity; [m/s].

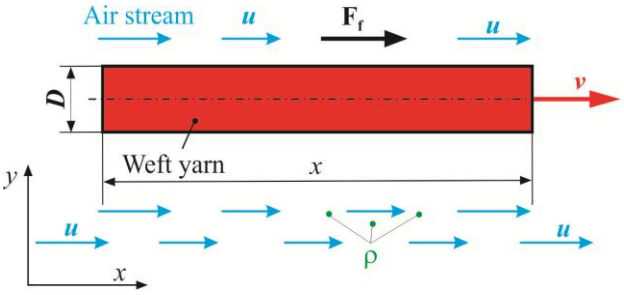

Figure 10
Force acting on a moving weft yarn in air flow

This force is proportional to the square of the relative velocity between the air stream and the yarn. The propelling force increases with the growing of the air velocity and the weft yarn diameter.
The dimensionless coefficient c_f depends on the Reynolds number. The turbulence of the air flow slows down the moving of the weft yarn. This causes deviation of the yarn from the centre of the flow. Therefore the turbulence level should be minimal. However, it is impossible to insert the yarn in laminar flow because the air velocity would be very low [1]. The force acting on the weft in the accelerating tube of the main nozzle can be written by the following (2) formula (Figure 11):

$$F_{mf} = \frac{\pi}{2}\rho \cdot c_f \cdot D \cdot L \cdot (u-v)^2 \quad (2)$$

where:

F_{mf} - air friction force on the yarn by main nozzle in the acceleration tube; [N],
L - weft yarn length subject to air flow; [m],

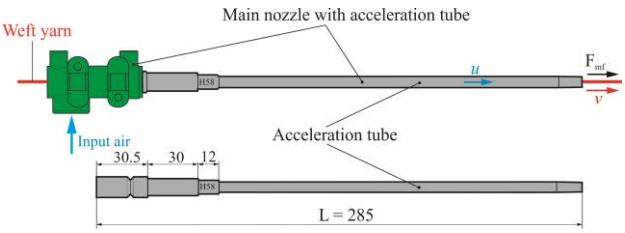

Figure 11
Schematic diagram of the main nozzle

The equation of the motion of the weft in air flow, based on Newton's second law, can be written as (Figure 12) [1]:

$$m \cdot a = m \cdot \frac{d^2 s}{dt^2} = F_{mf} + F_{rf} - F_1 \quad (3)$$

where:
m - total yarn mass involved in the motion; [kg],
a - acceleration of the weft tip; [m / s],
s - length of the inserted weft; [m],
F_{rf} - air friction force on the yarn by relay nozzles; [N].
F_1 - take down force; [N].

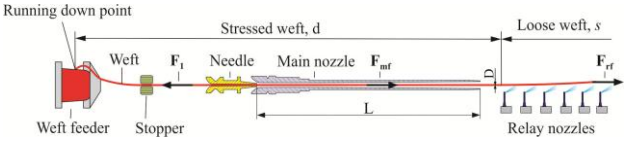

Figure 12
Weft motion in air flow of the main and relay nozzles

According by the weft yarn is stressed or loose in the open shed its mass has to be determined in a different way (Figure 12.). In case of stressed weft yarn:

$$m = d \cdot T_{tex} \cdot 10^{-6} \quad (4)$$

and for the loose weft yarn

$$m = (d+s) \cdot T_{tex} \cdot 10^{-6} \quad (5)$$

where:
d - length of the stressed weft; [m],
s - length of the inserted loose weft; [m],
T_{tex} - linear density of the weft**;** [tex]**.**
The formula of beginning accelerating motion section for the stressed weft yarn in air flow, based on Newton's second law, can be written as follows:

$$a = \frac{dv}{dt} = \frac{\sum F}{m} = \frac{10^6}{d \cdot T_{tex}} \cdot (F_{mf} - F_1) \quad (6)$$

For the loose weft when the speed of the yarn is approximately constant:

$$a = \frac{dv}{dt} = \frac{\sum F}{m} = \frac{10^6}{(d+s) \cdot T_{tex}} \cdot (F_{mf} + F_{rf} - F_1) = 0 \quad (7)$$

ARRANGEMENT OF OPEN PROFILE REED AIR LOOMS, AND MEASURING LAYOUT

In the Textile Workshop of Óbuda University there were examined the flow conditions of air jet weaving machines under laboratory conditions. Fig. 13. shows the layout of the laboratory bench.

Figure 13
Layout of measuring bench

We made the bench by parts used on weaving machines based on the actual dimensions of the weaving machine, which is suitable to measure the velocity distribution developing in the axis of the insertion u=f(x). When designing the bench our aim was that the actual weaving machine conditions should be simulated as large extent as possible. Measuring on operating machines is not possible due to the swaying of the reed.
Figure 14 shows the outline of the main parts of the profile reed air jet weaving machines. The weft yarn is drawn from a filling supply package by the filling feeder insertion by means of a stopper.

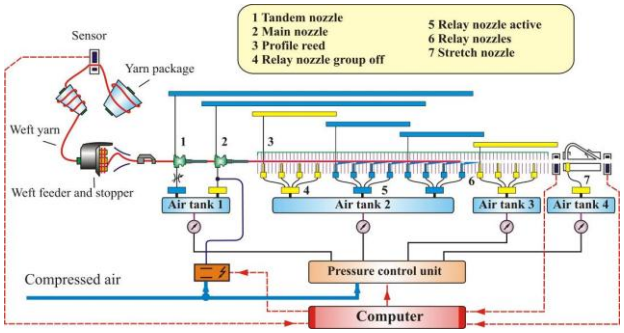

Figure 14
Schematic of air jet insertion with profile reed and air system diagram

The arrangement of the experimental equipment is shown in Figure 15. The experimental equipment included the bench test board with a U-shaped profile reed segment, main nozzle, relay nozzles, a pressure sensor and a stepper motor. The profile reed segment had an overall length of 750 mm, a density of 14.5 dents/cm, profile dents with a thickness of 0.24 mm and a cavity ratio of 65%. The compressed air from the main air tank was led to the main nozzle and to the groups of the four relay nozzle through a pressure regulator and a mass flow meter (Figure 15.).

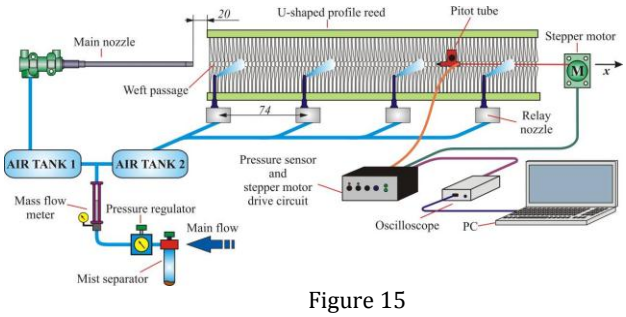

Figure 15
Schematic diagram of the test apparatus

A Pitot tube was used to measure of the air velocity along the axis of the air flow into the profile reed segment (Figure 16).

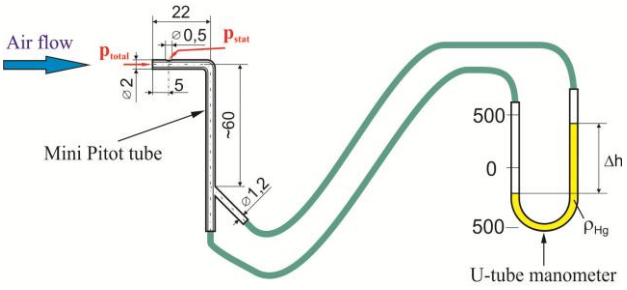

Figure 16
Measurement of the Air flow velocity by Pitot tube

The output change in pressure Δp value from the Pitot tube was proportional to the air velocity. The data Δp measured by an analogue pressure sensor were converted to digital values by a DSO 2090 oscilloscope and a personal computer.
The Pitot tube was driven by a stepper motor and it was moved with constant speed (Figures 15 and 17).

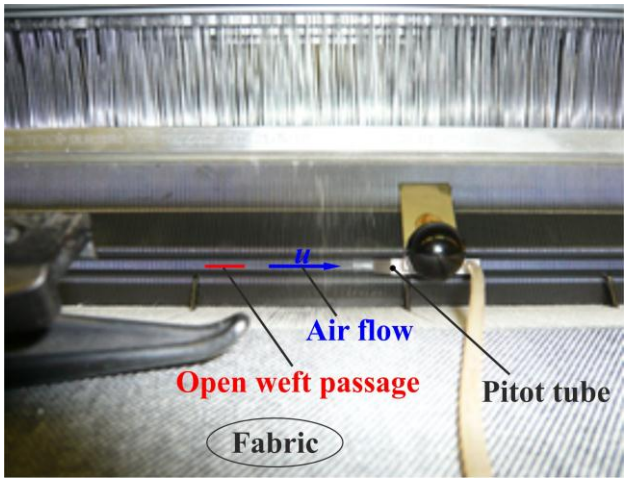

Figure 17
Pitot tube in the weft passage

The direction of the velocity measurement was the *x*-axis. Figure 18 shows the position of the measuring point in the U-shaped weft passage.
The supply compressed air pressure to the main nozzle and the relay ones were set with a pressure regulator to a gauge pressure of 5 bar. The supply mass flow rate $\dot{m}_0$ at this time was 6 g/s under standard conditions of 20˚C and 1 bar.
The velocity distribution along the profile reed cannot be expressed by a closed formula in function of *x*.

MEASURING RESULTS AND DISCUSSION

We measured (determined) and compared air velocities of different air guides (Figure 19).
The examination of the velocity of the air flow in the weft passage has been given the next measuring results.
The values of the air flow velocity distribution along the weft passage depend on two variables:

- the pressure of main tank, and
- the distance in the direction *x*.

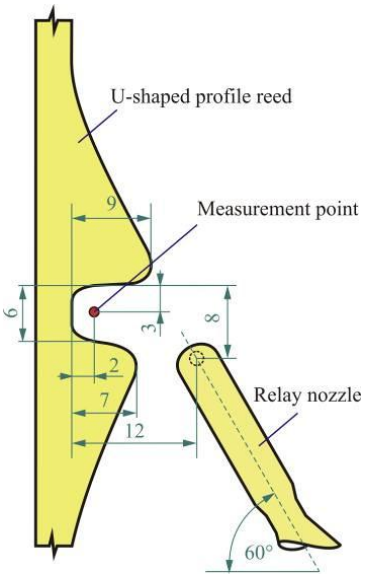

Figure 18
Measurement point of air velocity in the weft passage [7]

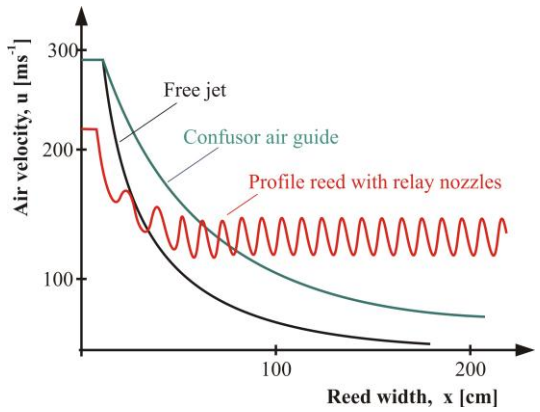

Figure 19
Distribution of the air velocities in the different air canals

The maximum air velocity at the entrance of the profile reed u_0 is 268.9 m/s. Figure 20 shows the velocity distribution at p_t= 5 bar tank pressure. In Excel Visual Basic program has been written to obtain the numerical values of the velocity.

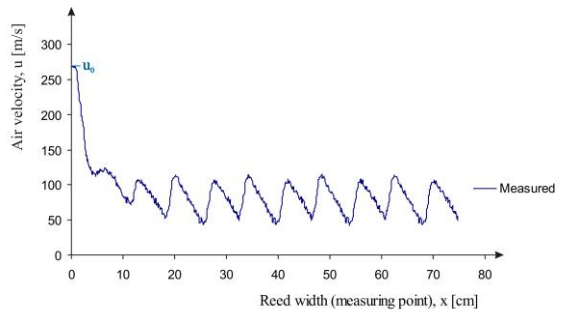

Figure 20
Distribution of the air velocity in the x-axis

The velocity of the air flow in the weft passage decreases rapidly to x=5 cm and at this point the air velocity is 113.23 m/s. Influence of the first relay nozzle stands out in range $5\,\text{cm} \le x \le 12\,\text{cm}$ and subsequently periodical with x=7.4 cm periodicity to 170 cm (was the examined reed width). Figure 21 shows the simulation of the flow from the main nozzle.

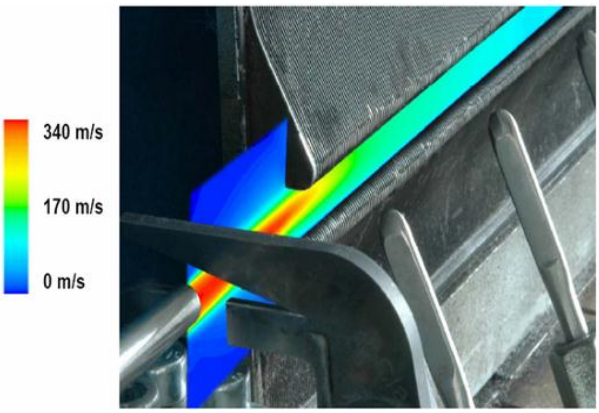

Figure 21
Air flow from the main nozzle [3]

Groups of relay nozzles are located across the whole reed width. Each group jets compressed air in a specific order to feed the filling tip to the right end of the fabric. The compressed air is supplied from the compressor, its pressure is adjusted by the regulators for the main nozzle and the relay nozzles, and it is stored in the proper tank. Figure 22 shows the simulation of the flows from two relay nozzles.

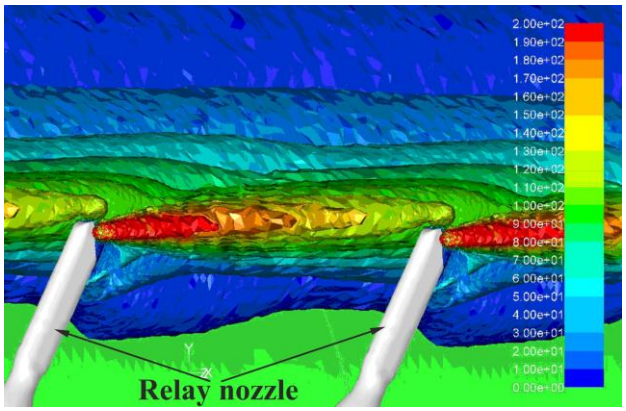

Figure 22
Air flow from relay nozzles [9]

Figure 23 shows the Fourier approximation in undimensioned form obtained by division with the maximum speed u_0 and of the data *x* (measuring position along the *x* axis) with the reed width *w*. The character of dimensionless function does not depend on the main tank pressure, p_t.

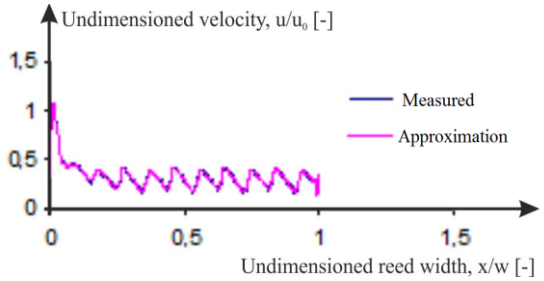

Figure 23
The approximation of the Fourier series with growing number of terms (r=50)

This paper dealt with the U-shaped profile reed air guidance solution. The velocity distribution in the weft passage was investigated. Weft insertion through weft passage by air is a very complicated process.
Main research findings:

- The air flow field in the weft passage may be divided into two parts.
- The first part, the only effect of main nozzle, the initial section, where the characteristics of axial velocities are similar to the flow of free air jet. The velocity of air flow in this range decreases rapidly.
- The second part, effect of relay nozzles, is the nearly periodical part of flow.

In this research we determined the characteristics of the axial velocities in the U-shaped weft passage. The main result are summarized as follows:

1. The ratio of the variation in axial velocities u/u_0 was determined independently of the main tank pressure p_t.
2. The Fourier approximation (DFT) is suitable for the calculation of the approximate axial air velocities in the weft passage if the maximum air velocity u_0 is known at the entry point of the profile reed.

Compressed air is an ideal weaving method of the weft yarn insertion. Air is tender to the different threads and gives high quality weaving of almost each filament yarns. Air jet weaving gives high speed of weaving at low noise level.

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KINETIC MODELLING OF ADSORPTION OF TERASIL RED ON ZSM-5 ZEOLITE

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Received: November 2016

Abstract

Terasil red (TR) is used such as: in colouring paper. Although TR is not strongly hazardous, it can cause some harmful effects (such as heartbeat increase). The best efficient method used for the quickly removal of dyes from the aqueous solution is the adsorption. Activated carbon has been proven to be widely used adsorbent for lowering the concentration of dyes in waste water, but it presents some disadvantages (such as: flammability). Actually, the best alternative to carbon adsorbent is zeolite. There are relatively limited studies done on the TR dyes adsorption by synthesized zeolites. This work aims to understand the potential of ZSM-5 zeolite for removal of TR dye from simulated aqueous solution. Terasil red (TR) was selected from the list of dyes used in Algeria. ZSM-5 zeolite was synthesized, characterized by nitrogen adsorption at 77K and by XRD. Adsorption kinetics of TR onto ZSM-5 was studied in a batch system. The TR concentration was determined at λ_{max} = 417 nm. Kinetic experiments were performed by mixing 200 mL of dye solution (10 mg/L) with 100 mg (0.1 g) of adsorbent during different time. The initial pH for each dye solution was set at 7. TR concentrations in the supernatants were determined and the amount adsorbed of TR was calculated. The BET surface area (S_{BET}) of the ZSM-5 was 349.753 m^2/g. The XRD of the synthesized ZSM-5 zeolite was indicated of the formation of ZSM-5 zeolite. In order to understand the mechanism of the adsorption process, a linear and non-linear Pseudo-first order, Pseudo-second order, Esquivel, Pseudo-third order and Elovich were selected to fit the experimental kinetic data. The optimization procedure has required a defined error function in order to evaluate the fit of equation to the experimental data. The best-fitting equation is determined using the well-known special functions (such as: average relative error deviation) to calculate the error deviation between experimental and predicted data. It seems that the nonlinear pseudo-first order model was the most suitable models to describe satisfactorily the studied adsorption phenomenon.

Key words: *kinetic modelling, adsorption, zeolite.*

INTRODUCTION

The textile industry is one of industrial waste water source. This contaminated water is very toxic for the human and animals [1]. Terasil red (TR) is used in colouring paper, dyeing cottons, wools, silk, leather and coating for paper stock. Although TR is not strongly hazardous, it can cause some harmful effects, such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [2]. The test, application and development of many treatment methods were the essential subjects of many articles such as: physical, chemical, biological [3]. Chemical coagulation–flocculation [4] different type of oxidation processes [5] biological process [6], membrane-based separation processes [7] and adsorption [8] were the treatments used in the purification of waters.

The best efficient method used for the quickly removal of dyes from the aqueous solution is the physical adsorption [9]. In this case, activated carbon has been proven to be widely used adsorbent for lowering the concentration of dyes in waste water, but it presents some disadvantages such as: flammability [10], less regeneralability at low temperature [11-12], weak hydrophobocity [13].

Actually, the best alternative to carbon adsorbent is zeolite [10]. Recently, commercial zeolites have been used to remove the dissolved pollutants in water and/or wastewater [14]. However, there are relatively limited studies done on the TR dyes adsorption by synthesized zeolites.

This work aims to understand the potential of ZSM-5 zeolite for removal of TR dye from simulated aqueous solution in batch mode. The adsorption efficiency of TR was investigated in order to optimize the experimental

parameters, such as contact time and pH at an agitation speed of 300 rpm, initial adsorbent concentration of 10 mg/L and temperature of 25°C. The statistical functions were used to estimate the error deviations between experimental and theoretically predicted adsorption values, including linear and nonlinear method. The optimization procedure required a defined error function in order to evaluate the fit of equation to the experimental data.

MATERIALS AND METHODS

Terasil red (TR) used in the present study was selected from the list of dyes normally used in Algeria. ZSM-5 zeolite was synthesized according to the literature [15]. ZSM-5 zeolite was characterized by nitrogen adsorption at 77K. Nitrogen physisorption data were obtained by N_2 adsorption at 77 K, in a Micromeritics ASAP 2000 instrument. Prior to measurement, the samples were degassed at 393 K for 2 h. The specific surface area was calculated by the BET equation; the total pore volume was determined from N_2 adsorption at a relative pressure of 0.98. The micropore volumes and micropore specific surface of samples were evaluated by the t-plot method. The external Surface Area was the deduction of BET Surface Area and Micropore Area. Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer with Cu Ka radiation. Adsorption Kinetics of TR onto ZSM-5 was studied in a batch system. The effects of pH and equilibrium time were examined. The adsorption parameters were optimized. In each experiment pre weighed amount of adsorbent (100 mg) was added to 200 mL of dye solution (10 mg/l) taken in a 250 mL of conical flask and 0.1 M NaOH or 0.1 M HCl were added to adjust the pH. This solution was agitated at 300 rpm and centrifuged. The TR concentration in solution was determined at λ_{max} = 417 nm by spectrophotometer UV-1700 PHARMA SPEC SHIMADZU. The TR adsorbed amount per mass unit of adsorbent at time t, q (mg/g), (Eq. (1)) was calculated as:

$$q = (C_0 - C)\frac{V}{M} \qquad (1)$$

where C_0 is the initial TR concentration (mg/L), C is the dye concentration at time t, V is the solution volume (in L) and M is the adsorbent mass (g) [16].
Kinetic experiments were performed by mixing 200 mL of dye solution (10 mg/L) with 100 mg (0.1 g) of adsorbent during different time (5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 180, 250, 300 and 350 min).The initial pH for each dye solution was set at 7. The suspensions were kept under agitation during 24 hours. TR concentrations in the supernatants were determined and the amount adsorbed of TR was calculated.

RESULTTS AND DISCUSSION

The BET surface area (S_{BET}) of the ZSM-5, used as adsorbent in the present study, was 349.753 m^2/g. From Figure 1, the XRD of the synthesized ZSM-5 zeolite exhibited some significant peaks of reflections at 2θ of about 7.95, 7.96 and 23.18, which were indicative of the formation of ZSM-5 zeolite [17].
In order to study the effect of every parameter, it is necessary to fix the values of others. The elimination of pollutant from simulated aqueous solution by adsorption is extremely influenced by the medium of the solution which affects the nature of the adsorbent surface charge, the ionization extent, the aqueous adsorbate species speciation and the adsorption rate [18].

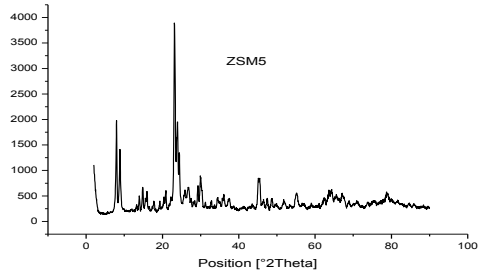

Figure 1
ZSM-5 XRD pattern.

Figure 2 illustrates the effect of contact time on decolourization (dye adsorption) with ZSM-5. The plot (simulated aqueous solution) could be divided in three zones: (i) 0-30 min, which indicated the fast adsorption of TR, suggesting rapid external diffusion and surface adsorption; (ii) 30-60 min, showed a gradual equilibrium, and (iii) 60-350 min, indicated the plateau of the equilibrium state.

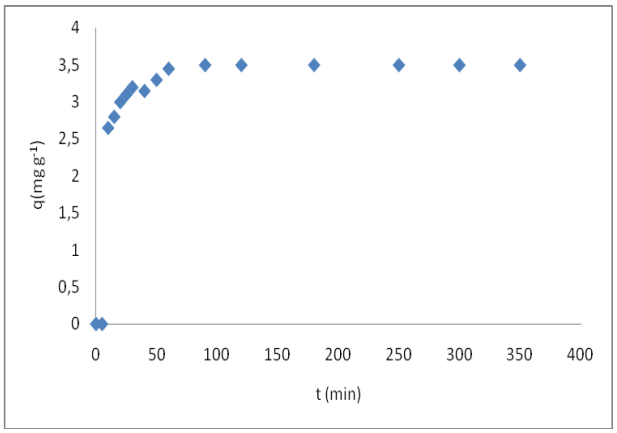

Figure 2
TR adsorption kinetic on ZSM-5

The adsorption was rapid at the initial stage of the contact, but it gradually slowed down until the equilibrium. The fast adsorption at the initial stage can

be attributed to the fact that a large number of surface sites are available for adsorption. After a lapse of time, the remaining surface sites are difficult to be occupied because of the repulsion between the solute molecules of the solid and bulk phases make it took long time to reach equilibrium. Adsorption is a complex process whereby it is influenced by several parameters related to adsorbent and to the physicochemical conditions under which the process is carried out [19].

TABLE I
A LINEAR AND NON-LINEAR PSEUDO-FIRST ORDER, PSEUDO-SECOND ORDER, ESQUIVEL, PSEUDO-THIRD ORDER AND ELOVICH KINETICS ISOTHERMS CONSTANTS RELATED TO THE ADSORPTION OF TR ONTO ZSM-5.

Linear Method	Reference	Non-linear Method	Reference
Pseudo-first order (type 1) $\log(q_e - q) - \log(q_e) = -\frac{k_1 t}{2.303}$ q_e = 3,501 K_1= 0,032 R^2 = 0,507	[20]	Non linear pseudo-first order $q = q_e(1-e^{-k_1 t})$ q_e = 3.483 K_1= 0.086 R^2 = 0.895	[20]
Pseudo-first order (type 2) $\ln(q_e - q) - \ln(q_e) = -k_1 t$ q_e = 3,501 K_1= 0.033 R^2 = 0.507	[21]		
Pseudo-second order (type 1) $\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ q_e = 3,546 K_2= 0,091 R^2 = 0.999	[22]	Non linear pseudo-second order $q = \left[\frac{q_e^2 k_2 t}{1 + k_2 q_e t}\right]$ q_e = 3.778 K_2= 0.033 R^2 = 0.855	[20]
Pseudo-second order (type 2) $\frac{1}{q} = \frac{1}{k_2 q_e^2}\frac{1}{t} + \frac{1}{q_e}$ q_e = 3,571 K_2= 0,076 R^2 = 0,968	[22]		
Pseudo-second order (type 3) $(\frac{1}{q} - \frac{1}{q_e})q_e^2 = \frac{1}{k_2}\frac{1}{t}$ q_e = 3,549 K_2= 0,078 R^2 = 0,968	[22]		
Pseudo-second order (type 4) $q = q_e - \left(\frac{1}{k_2 q_e}\right)\frac{q}{t}$ q_e = 3,566 K_2= 0,076 R^2 = 0,957	[22]		
Pseudo-second order (type 5) $(q - q_e)q_e = -\left(\frac{1}{k_2}\right)\frac{q}{t}$ q_e = 3,100 K_2= 0,594 R^2 = 0.000	[22]		
Pseudo-second order (type 6) $\frac{q}{t} = k_2 q_e^2 - k_2 q\, q_e$ q_e = 3,583 K_2= 0,072 R^2 = 0,957	[22]		
Pseudo-second order (type 7) $\frac{1}{q_e - q} - \frac{1}{q_e} = k_2 t$ q_e = 3,507 K_2= 0,545 R^2 = 0,711	[20]		

In order to understand the mechanism of the adsorption process, a linear and non-linear Pseudo-first order, Pseudo-second order, Esquivel, Pseudo-third order and Elovich were selected to fit the experimental kinetic data. The equations and the constants of all models were given in Table 1.

where k_1 is pseudo-first order rate constant (min^{-1}), k_2 is pseudo-second order rate constant (g/(mg min)), k_3 is pseudo-third order rate constant ($g^2/(mg^2\ min)$), K_E is esquivel rate constant (min), k_4 is elovich rate constant (mg/(g min)), k_5 is extent of surface coverage and activation energy of the process (g/mg), k_6 extent of surface coverage and activation energy of the process (g/mg), k_7 elovich rate constant (mg/(g min)), q_e is amount of adsorption at equilibrium (mg/g), and θ dimensionless parameter (=q/q_e).

A non-linear and linear fitting procedure using Excel and Origin software were used respectively.

The optimization procedure has required a defined error function in order to evaluate the fit of equation to the experimental data. The best-fitting equation is determined using the well-known special functions to calculate the error deviation between experimental and predicted data. The mathematical equations of these error functions were the average relative error deviation (ARED is dimensionless parameter), the percent standard deviation (MPSED Marquardt's is dimensionless parameter) [26], the average relative error (ARE is dimensionless parameter), the sum of absolute error (SAE=EABS is in mg/g), the average relative standard error (ARS is dimensionless parameter), the sum of the squares of the errors (SSE is in $(mg/g)^2$) [27], the percent standard deviation (MPSD Marquardt's is dimensionless parameter) [28], the normalized standard deviation (Δq(%) is in mg/g) [29], and the hybrid fractional error function (HYBRID is dimensionless parameter) [30]. The constants of all error analysis were represented in Table 2.

Adsorption kinetic data are the basic requirements for the design of adsorption systems. In order to optimize the design of a specific sorbate/sorbent system to remove TR from aqueous solution, it is important to

establish the most appropriate correlation for the experimental kinetic data.

TABLE II.
A LINEAR AND NON-LINEAR PSEUDO-FIRST ORDER, PSEUDO-SECOND ORDER, ESQUIVEL, PSEUDO-THIRD ORDER AND ELOVICH KINETICS ISOTHERMS CONSTANTS RELATED TO THE ADSORPTION OF TR ONTO ZSM-5.

Linear Method	Reference	Non-linear Method	Reference
Pseudo-second order (type 8) $\frac{1}{t}=k_2 q_e^2\left(\frac{1}{q}\right)-k_2 q_e$ $q_e = 3,578$ $K_2 = 0,073$ $R^2 = 0,968$	[20]		
Pseudo-second order (type 9) $\frac{q_e}{q_e-q}-1=k_2 t$ $q_e = 3,507$ $K_2 = 1,913$ $R^2 = 0,711$	[22]		
Pseudo-second order (type 10) $\frac{\theta}{1-\theta}=k_2 t$ $q_e = 3,507$ $K_2 = 1,913$ $R^2 = 0,711$	[22]		
Esquivel Model (type 1) $\frac{1}{q}=\left(\frac{K_E}{q_e}\right)\frac{1}{t}+\frac{1}{q_e}$ $q_e = 3,571$ $K_E = 3,675$ $R^2 = 0,968$	[23]	Non linear Esquivel Model $q = q_e\left(\frac{t}{t+K_E}\right)$ $q_e = 3,778$ $K_E = 7,948$ $R^2 = 0,885$	[23]
Esquivel Model (type 2) $(\frac{1}{q}-\frac{1}{q_e})q_e = K_E\frac{1}{t}$ $q_e = 3,549$ $K_E = 3,581$ $R^2 = 0,968$	[23]		
Pseudo-third order (type 1) $\frac{1}{q^2}=\frac{1}{q_e^2}+k_3 t$ $q_e = 3,043$ $K_3 = -0.0001$ $R^2 = 0,406$	[24]		
Pseudo-third order (type 2) $\frac{1}{q^2}-\frac{1}{q_e^2}=k_3 t$ $q_e = 3,020$ $K_3 = -0.0001$ $R^2 = 0,422$	[24]		
Elovich (type1) $q = k_5 \ln(k_5 k_4)+k_5 \ln(t)$ $K_4 = 17,254$ $K_5 = 0,497$ $R^2 = 0,524$	[25]		
Elovich (type 2) $q = (1/k_5)\ln(k_5 k_4)+(1/k_5)\ln(t)$ $K_4 = 4,262$ $K_5 = 2,012$ $R^2 = 0,524$	[21]		

TABLE II
ERROR DEVIATION DATA RELATED TO THE TR ADSORPTION ONTO ZSM-5 USING MOST COMMONLY USED FUNCTIONS.

Error functions	Non Linear Pseudo-first order	Non Linear Pseudo-second order	Linear Esquivel Model (type 1)	Linear Esquivel Model (type 2)	Non Linear Esquivel Model
ARED	3,895	5.940	9.501	8.795	5.841
SAE	2,790	3.992	7.367	7.019	3.959
MPSED	0,080	0.086	0.143	0.137	0.085
SSE	2,058	2.850	13.492	13.139	2.850
HYBRID	0,045	0.069	0.111	0.102	0.068
ARE	0.040	0.059	0.095	0.088	0.058
ARS	0.074	0.080	0.133	0.127	0.078
Δq (%)	7.429	7.999	13.289	12.731	7.863

Applicability of some statistical tools to predict optimum adsorption kinetics of TR onto ZSM-5 after linear regression analysis showed that the highest R^2 value and the lowest ARED, ARE, SAE, ARS, MPSD, Δq, SSE, MSPED, and HYBRID values could be suitable and meaningful tools to predict the best-fitting equation models. The best fitting is determined based on the use of these functions to calculate the error deviation between experimental and predicted equilibrium adsorption kinetic data, after linear analysis. Hence, according to Table 2, it seems that the nonlinear pseudo-first order model was the most suitable models to describe satisfactorily the studied adsorption phenomenon. Therefore, based on these mentioned results, the best useful error estimation statistical tools should point out the nonlinear pseudo-first order followed by nonlinear esquivel, nonlinear pseudo-second order, linear esquivel type 1 and linear esquivel type 2 as the best-fitting models.

CONCLUSIONS

ZSM-5 zeolite was characterized and used for the TR adsorption in simulated aqueous solution. The adsorption–desorption isotherms of N2 indicate that the BET surface area is equal to 349.753 m2 g−1. The XRD image indicates that is ZSM-5 zeolite. ZSM-5 was used for the TR adsorption in simulated aqueous solution. The obtained results revealed the following optimal conditions: pH value of 7 and 250 min of contact time, which lead to 92% TR removal. The adsorption kinetic of TR onto ZSM-5 can be better fitted by nonlinear pseudo-first order as compared to the nonlinear pseudo-second-order, linear pseudo-second-order, linear pseudo first order, linear pseudo third order, nonlinear pseudo third order, linear esquivel, and nonlinear esquivel models. On the whole, the experimental results showed that ZSM-5 is suitable adsorbent for the removal of TR.

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ATMOSPHERIC POLLUTION MONITORING IN SOUTH-EASTEN BALTIC USING AN EPIPHYTIC LICHEN HYPOGYMNIA PHYSODES

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Received: November 2016

Abstract

Epiphytic lichens are known as indicators of an air contamination. The chemical composition of lichens depends on the concentration of pollutants in the environment. Usually the purpose of such researches is a long-term variation of the trace elements or other pollutants in the study area or identification of spatial features air contamination. The aim of this study is the creation of a database of the concentration of trace elements in the samples of the epiphytic lichen Hypogymnia physodes in the Kaliningrad region as a "reference point" for monitoring studies, the identification of spatial trends of iron, manganese, nickel, cadmium, silver, lead, strontium, rubidium and calcium in the Kaliningrad region. The samples of wild lichens were collected on august in 2010 year, on high 1,2 - 1,8 meters from pine and birch in forests of the region according to the regular network. 1-2 years thallus were used for chemical analyzes. Metals such as Ag, Cd, Cu, Pb, Ni, Fe, Mn, Zn were determined by AAS technique (by flame – Mn, Fe; ETA – others) and Sr, Rb, Ca by X-ray fluorescence. Concentration of the metals in the maritime territory (Sambia or Kaliningrad peninsula) in the West is higher than in the central and eastern parts of the region. Features of spatial distribution of the trace elements have been found. Accordingly the prevailing direction of the wind (South-Western), the highest content of trace elements is fixed in the Sambia peninsula, and also in the area adjacent to the coast of the Vistula and the Curonian Lagoon. The big concentration of the trace elements in the samples of the lichen H.physodes in the costal part of the region is associated with higher levels of anthropogenic loading area and as a consequence a significant pollution. It is possible that the chemical composition of the lichens in the Sambia peninsula is formed due to the impact of local pollution sources, such as vehicles, thermal energy facilities, ports, and also under the influence of transboundary transport and sea spray.

Key words: *Epiphytic lichens, monitorin,g pollution*

INTRODUCTION

All living organisms are able to respond to changing environmental quality, lichens are one of them [1-3]. Their sensitivity to an atmospheric pollution is connected with some physiological features. Lichens are the symbiotic association of fungi and algae, and therefore any impact able to change the balance between them and affect the viability. Different kind of lichens can be used to assess the environmental contamination [4-6]. Concentration of contaminants in lichens due to some facts: absorption of atmospheric aerosols and gases by the all surface of thalli, and dehydration of lichens tissues [7-9].

Substrate is not a significant source of metals for the lichens, but this fact has been discussed [10-13]. Sources of heavy metals, mechanisms of heavy metal accumulation and detoxification by lichens and their bioaccumulation capacity are discussed in many papers [14-20].

The biochemical composition, physiological processes, anatomical and morphological characteristics, population structure, species composition and structure of the lichen communities are changed under the influence of pollutants.

The chemical composition changing in lichens depend of spatial and temporal trends of quality their habitat, therefore epiphytic lichens are used as the an indicator in the monitoring of air quality [21-26]. Lichens are used to determine long - term variation of contamination of researching territory, or features of special variability of chemical composition, identification and effects of specific pollutants [27-29].

The purpose of this project is creation of the data base of trace elements concentrations in lichen thallus *Hypogymnia physodes (L.) Nyl*. in the South-Eastern Baltic (Kaliningrad region, Russia) as a «reference point» for monitoring studying and investigation special trends of concentration of trace elements in the Kaliningrad region.

MATERIALS AND METHODS

Sampling Area

Kaliningrad region is the most western region of Russia on the South-Eastern cost of Baltic Sea. The region borders with Poland in the South and Lithuanian in the North and the East. Predominant westerly winds and marine aerosols of the Baltic Sea form the climate of the region and the features of atmospheric transport and deposition of trace elements. It should be noted that there are only 17% of the territory of the region is covered by forests. There are secondary forests; mainly mixed coniferous-broad leafed, very thick. Large forest massifs are mostly located in South-East and South-West of region. There are no large industries, to the exclusion of agriculture. And also there are some mining enterprises. Deposits of amber, peat, oil is developing in region. The West Part of region is very urban. And at the same time the coastal area of the Kaliningrad (Sambia) peninsula is a recreation. The level of anthropogenic load is declining from west to east. The Eastern part is mainly used for agriculture.

Sampling procedure and the method of analysis

The epiphytic lichen *H. physodes* was chosen as a bioindicator of an air contamination in the Kaliningrad region. It is widely distributed and fairly resistant to impurities in the air, therefore it has been used commonly in regional surveys of heavy metal deposition [30-33].

The samples of the lichen *H.physodes* were taken from the plots 50x50 m in the forests, according to the previously developed monitoring network (Figure 1), from birch and pine trunks at a height of 1.20 – 1.80 m in 2010 year. The sampling period was very shot – two weeks. The plot location was fixed by GPS. The distance from the local sources of pollution, roads, housing, cultivated agricultural areas were taken into account [34]. There are sampling rules: 3-5 samples of lichens were taken from one plot (from 3-5 trees); the youngest part (edge) of lichen thallus was cut; the samples of the lichen were packed in the paper bag.

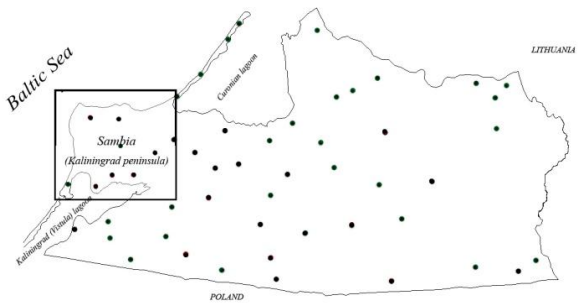

Figure1
The monitoring network.

The unwashed lichen thallus representing 1-2 years of growth were used for analysis after cleaning from foreign materials such as a tree bark, and others. The samples were dried to constant weight for 24 h at 40°C and homogenized.

Wet digestion of a homogeneous sub-sample was applied. About 0.5 g moss samples were transferred to the tubes, and 7 ml of nitric acid was added. The opened tubes were left at a room temperature for 12 h and then the temperature was increased to 135˚C within 15 min and the samples were digested for 15 min at 135°C. After that the solutions were cooled and 2 ml of peroxide of hydrogen was added and the temperature was then increased to 190°C again. After that procedure the volume of acid degreased and the color of solution became light.

The mass was transferred to 25-ml volumetric flasks and was filled till the mark with osmosistreated water. The samples of lichens for detection by X-ray fluorescence were dried and pressed.

Concentration of elements such as Ag, Cd, Cu, Pb, Ni, Fe, Mn, Zn were determined by AAS technique (by flame – Mn, Fe; ETA – others) and Sr, Rb, Ca by X-ray fluorescence.

Quality control

The quality control of AAS and X-ray fluorescence results was ensured by the reference samples (Canadian waterweed CW-1, SSS 8921- 2007 and Birch leaf LB-1, SSS 8921-2007). In addition, the blanks were measured in parallel to the decomposition and the analysis of the samples.

Data processing

Various statistical analysis techniques can be used on spatial distribution and multivariable data to reveal the underlying deterministic behaviors and thus help clarify the cause and the effects of relationships in environmental problems. GIS technology, such as ArcGis and QGISBrighton was used to creature maps of elements distribution in Kaliningrad region.

RESULTTS AND DISCUSSION

The concentration of such elements as iron, manganese, zinc, nickel, strontium, rubidium and calcium were determined in the lichens samples of the whole territory, cadmium, lead, copper and silver - only in the lichens of the Sambia peninsula. The data of descriptive statistic analysis of concentration of heavy meals in the moss samples are shown in Table 1, 2.

TABLE 1
CONCENTRATION OF ELEMENTS IN THE *H. PHYSODES* THALLUS, IN KALININGRAD REGION µg/g DW

	mean	SD	SE	CV,%	mediana	max	min
Fe	446	183	33	41	399	1135	180
Mn	200	135	25	72	187	455	33
Zn	83	47	8	56	78	298	33
Ni	1.30	0,63	0.11	56	1,30	2.43	0.013

Sr	10.1	4.79	0.92	47	8,96	18.6	4.45
Rb	9.74	4.59	0.82	47	10.5	19,9	1.28
Ca	1203	817	140	68	980	2995	219

TABLE 2
CONCENTRATION OF TRACE ELEMENTS IN THE *H. PHYSODES* THALLUS, IN THE SAMBIA PENINSULA, µg/g DW

	mean	SD	SE	CV,%	mediana	max	min
Ag	0.051	0.024	0.009	47	0.040	0.095	0.032
Cd	0.194	0.040	0.016	21	0.185	0.263	0.146
Pb	6.57	2.36	0.96	36	7.15	9.03	3.50
Cu	7.,91	1.21	0.49	15	7.83	9.94	6.69
Mn	313	253	103	81	259	664	74.2
Ni	1.64	0.549	0.225	34	1.611	2.43	0.941
Zn	79.5	22.7	9.26	29	87.7	100	45,6
Sr	15.,0	10.3	4.22	69	10.7	31.5	6.38
Rb	12.,2	5.59	2.28	45.8	10.9	22.6	5.69
Fe	610	279	114	45.7	526	1135	339
Ca	1253	0.855	0.349	68	1118	2684	375

The data of chemical analyses were used to creature maps of elements distribution in the lichens. The prevailing direction of winds (the South - Western) has formed the features of elements distribution in the lichens of the Kaliningrad region. The zones were stretched from the West and the South-West to the North-East. More high concentration of trace elements, such as cadmium, nickel, iron, copper and lead were identified in the Sambia peninsula, and on the cost of Vistula (Kaliningrad) and Curonian lagoons.

Spatial distribution of the elements

Concentration of iron in the thallus of *H. Physodes* varied from 180 to 1135 µg/g DW. The maximum was fixed in the centre of the Sambia peninsula and stretches from the Kaliningrad (Vistula) lagoon cost to the North cost of Baltic Sea. The high level of iron was identified in the south littoral of Curonian lagoon which is lying below sea level. The coefficient of variation is less than 50%, therefore content of iron in the lichens is homogeneously in the entire researching territory. The high concentration of iron is probably related to geological features, there are carstones and iron-manganese nodules. The high level of iron in a soil and water is a great regional problem. Concentration of iron in the lichens decreases from the South-Western to the North-Eastern (Figure 2).

The content of nickel is estimate in hundreds or even thousands of mass units depend on the time of exposure, the distance from the source of emission of the contaminated areas of nickel accumulation [25]. The concentration of nickel in the Kaliningrad region varied from 0.013 to 2.43 µg/g. The coefficient of variation is 56%. The content of nickel in the lichens of the Kaliningrad region has the same feature of distribution as iron. The maximal concentration of nickel in the lichen thallus was determined in the Western and South -Western part of region in the Sambia peninsula and in the coastal area of Vistula (Kaliningrad) and Curonian lagoons (Figure3).

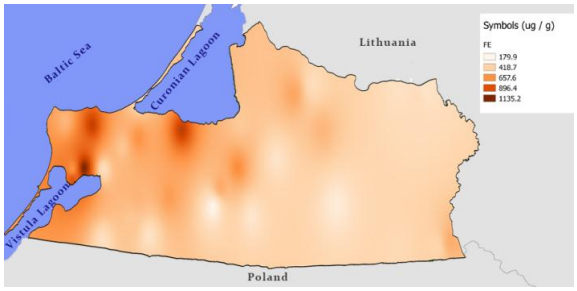

Figure 2
The map of iron distribution in the thallus of the lichen *H. physodes* in the Kaliningrad region, 2010 year

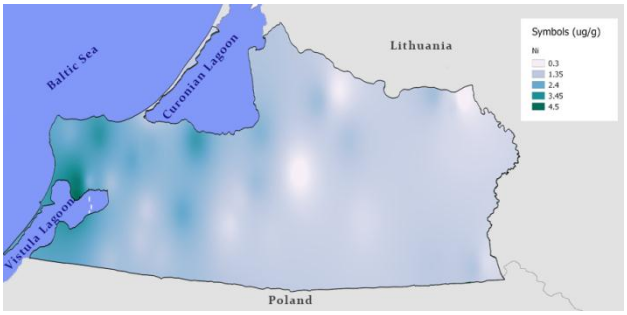

Figure 3
The map of nickel distribution in the thallus of the lichen *H. physodes* in the Kaliningrad region, 2010 year

The average content of manganese in the lichen is slightly above its median value, and the coefficient of variation - 72%, reflecting the heterogeneity of values of manganese in the lichen thallus. The maximum of manganese (more than 450 µg/g was determined in the Sambia peninsula, and in the costal territory of the Curonian lagoon between the rivers Deima and Pregolya, and also in the South-East of the region near the lake Vishtynets (Figure 4).

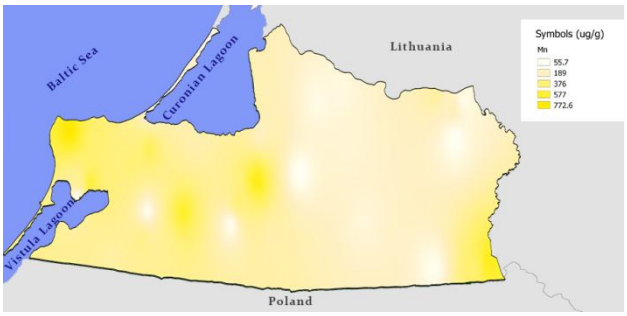

Figure 4
The map of manganese distribution in the thallus of the lichen *H. physodes* in the Kaliningrad region, 2010 year

The concentration of zinc (Figure 5) in the lichens varied in a wide range, from 33 to 298 µg/g, and the coefficient of variation is 56%. The highest content of zinc was fixed in the North part of region in the Neman lowland.

Strontium (Figure 6) goes from an atmospheric air to waters and soils. The coefficient of variation is less than 50%. There is negligible inhomogeneity of strontium content in *H.physodes* in the Kaliningrad region, its concentration varied from 4.45 to 18.6 µg/g. The maximum was determined in the Sambia peninsula and Pregolya lowland.

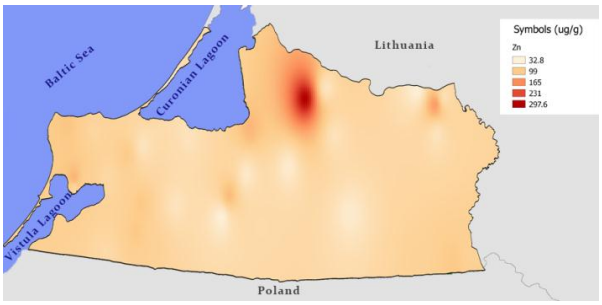

Figure 5
The map of zinc distribution in the thallus of the lichen *H. physodes* in the Kaliningrad region, 2010 year

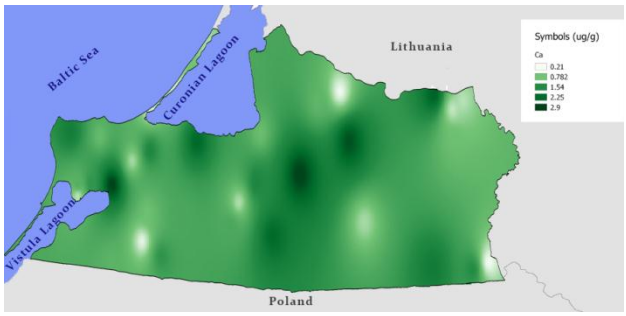

Figure 6
The map of strontium distribution in the thallus of the lichen *H. physodes* in the Kaliningrad region, 2010 year

Biochemical properties of strontium are similar to calcium, and strontium can replace calcium in adversity. The minimal concentration of calcium was 219 and maximal - 2995 µg/g (Figure 6). There are no critical plants levels for strontium and calcium. But elevated levels of strontium can be explained by a technogenic nature (Figure 7).

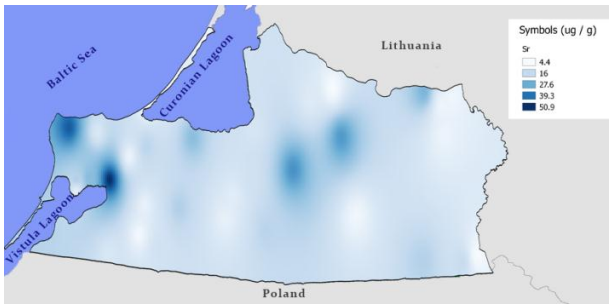

Figure 7
The map of calcium distribution in the thallus of the lichen *H. physodes* in the Kaliningrad region, 2010 year

The coefficient of variation of cadmium content in the lichens in Sambia is 21%, there are the homogeneous samples, and the maximum value 0.263 µg/g was fixed in the north-western part of the Sambia Peninsula (Figure 6).

Rubidium, as other monovalent cations is absorbed by plants. Rubidium can replace potassium in plants cells. The maximal content of rubidium in *H. physodes* was fixed in the west part of the region, the Sambia peninsula and the Northern cost of Kaliningrad lagoon – 19.9 µg/g (Figure 8). The coefficient of variation is 47%, the average values of concentration is the same as the mediana. There is the significant difference of extreme values.

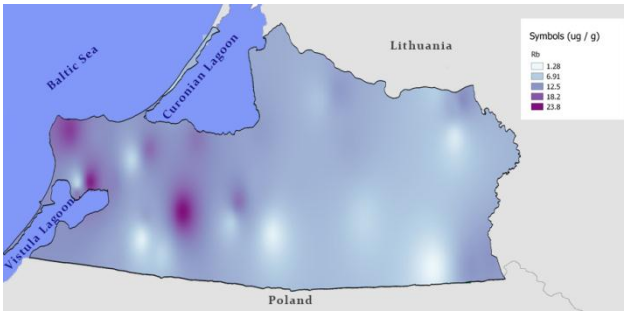

Figure 8
The map of rubidium distribution in the thallus of the lichen *H. physodes* in the Kaliningrad region, 2010 year

The average copper content in the lichen *H. physodes* – 7.91 µg/g, There is the lowest coefficient of variation, and the sampling homogeneity. The maximum value of copper is 9.94 µg/g (Figure 9).

The average value of lead is – 6.57 µg/g. There is the homogeneous sample. The coefficient of variation is 36%. The area with high level of lead in the lichens is situated in the western and central part of the Sambia peninsula (Figure 9).

The average silver content of the lichen is 0.051 mg/g, the coefficient of variation 47% defines a relatively high heterogeneity of silver accumulation of lichens in different parts the Samba Peninsula. There is the maximum silver concentration in the lichen thallus 0.095 µg/g in the north of Kaliningrad was (Figure 9).

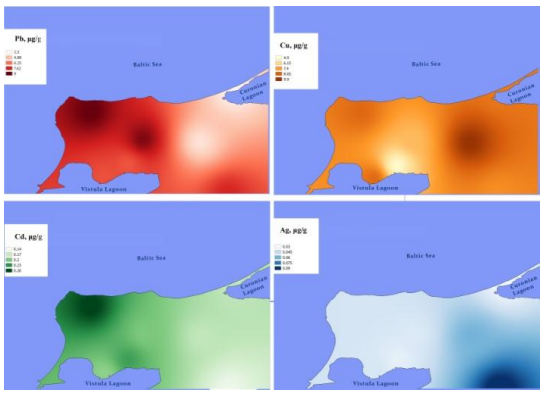

Figure 9
The map of trace element distribution in the thallus of the lichen *H. physodes* in the Sambia peninsula, 2010 year

According to the data of the same researches of accumulation by *H.physodes* in neighboring Poland, in the basic station of complex monitoring varied for iron between 179 and 872 μg/g, for nickel - from 0.33 to 1.06μg/g, for zinc - from 22 to 112 μg/g, for copper - from 1.3 to 3.7 μg/g, for lead - from 1.60 to 18.22 μg/g, for Cadmium - from 0.25 to 0.69 μg/g [35].

The order of the concentration of the elements in the lichens samples was Ca>Fe > Mn > Zn > Sr > Rb > Cu > Pb > Ni > Cd>Ag. Most of elements follow lognormal distribution (P>0.05) that is characteristic for the lithogenic origin of the crustal elements and is reflected in atmospheric deposition from windblown soil dust. But trace element such as Cd, Pb, Ni do not follow the lognormal distribution by indicating that their distribution in lichens samples is influenced by other anthropogenic factors.

For correctly evaluate the degree of contamination in the Kaliningrad region the contamination factor (CF) [21, 36] scales were calculated. The contamination factor is the relationship between of median values of each element of the mosses of the investigated area and the median value of each element of background areas. Arctic (for evaluation of Sr and Rb) and Noth Canada (for other) were chosen as background territory [37.38] (Table 3).

TABLE 3

CONTAMINATION FACTOR IN THE AREA OF KALININGRAD REGION

metal	Sambia peninsula		Kaliningrad region	
	CF	classification	CF	classification
Pb	22	C5		
Cd	3,1	C3	-	-
Cu	2,1	C3	-	-
Ni	2,0	C3	1,6	C2
Zn	2,2	C3	1,9	C2
Fe	9,7	C5	7,4	C4
Ca	1,5	C2	1,2	C2
Mn	2,0	C3	1,4	C2
Sr	2,3	C3	1,9	C2
Rb	2,7	C3	2,6	C3

For interpretation of results would consist of various categories according to the CF values CF, 1 no contamination (C1); 1–2 suspected (C2); 2–3.5 slight (C3); 3.5–8 moderate (C4); 8–27 severe (C5), and 27 extreme (C6) [39].

So the level of air trace elements pollution in the Kaliningrad region may be assess as C2 - suspected, with the exception of Fe and Rb, but there is the western part of territory the Sambia peninsula, where the contamination factors are higher than in other parts - C3 slight. And also the concentration of lead and iron notably exceeds background values.

Principle component factor analysis

To distinguish the origin of the elements in the lichens samples, the matrix intercorrelation was complied. There are slight correlation <0.3-0,4; high correlation – 0.5-0.,75 and significant >0.75.

There are the high and significant positive correlation between Ca-Sr, Fe-Rb, Mn -Ni, Fe-Mn and Cd-Pb. That may be connected with a common source of contamination.

TABLE 4

MATRIX OF INTERCORRELATION

	Mn	Ni	Zn	Sr	Rb	Fe	Ca	Ag	Cd	Pb
Mn	1,00									
Ni	**0,67**	1,00								
Zn	**-0,38**	-0,20	1,00							
Sr	0,13	0,19	**-0,43**	1,00						
Rb	0,28	0,10	-0,12	**0,42**	1,00					
Fe	**0,65**	**0,46**	-0,10	**0,49**	**0,82**	1,00				
Ca	0,17	0,12	**-0,62**	**0,91**	0,16	**0,30**	1,00			
Ag	**-0,47**	-0,01	0,19	-0,08	-0,24	-0,21	0,01	1,00		
Cd	**0,42**	-0,10	0,04	0,25	-0,05	0,23	0,30	**-0,64**	1,00	
Pb	**0,33**	-0,22	0,29	-0,17	0,07	0,34	-0,05	-0,02	**0,56**	1,00
Cu	-0,13	0,24	**0,45**	**-0,64**	**-0,75**	**-0,59**	**-0,60**	0,09	-0,12	-0,22

There are the four significant sources of the trace elements, which are connected with geographic and climatic features of region: atmospheric transport from the marine environment (marine factor); windblound dust, from local soil (soil factor), transport of soluble compounds from atmospheric precipitation and root uptake in vascular plants from soil and subsequent transfer to lichens (vegetative factor).

For a better interpretation of the results, factor analysis was used. Four main factors were extracted from the results of factor analysis and were interpreted as source categories contributing to element concentrations at the sampling sites in the region. The identification of source categories was undertaken by examination of the profiles of the factors, i.e., loadings of the elements and other variables on the varimax rotation. The main criteria in selecting the number of optimal factors and models of major source identification is that eigen values are larger than 1.

TABLE 5

THE MATRIX OF CORRELATION FOR ELEMENTS

	Компонента			
	1	2	3	4
Mn	0.091	0.266	0.518	0.766
Ni	0.077	0.058	-0.107	0.946
Zn	-0.791	0.039	0.010	-0.271
Sr	0.833	0.379	0.046	0.012
Rb	0.126	0.917	-0.041	0.115
Fe	0.115	0.867	0.221	0.407
Ca	0.920	0.173	0.131	-0.044
Ag	-0.119	0.011	-0.695	-0.238
Cd	0.141	-0.001	0.962	-0.063
Pb	-0.358	0.373	0.640	-0.223
Cu	-0.539	-0.755	-0.084	0.276

The results of factor analysis and loading values of each element, the association of the elements with the factors [40] are analyzed as follows (Table 5):

The factor 1 is the strongest factor representing 36.2% of the total variance. It is influenced by high

positive loadings of strontium, calcium, and negative - zinc and copper. Strontium is the satellite of calcium in geochemical processes. It may be connect with marine aerosols.

Factor 2 is the second strongest factor, with 19.4% of the total variance. It is mainly influenced by loads of rubidium, iron, strontium, and negative copper. Most likely the origin of these metals is associated with a natural factor such as uptake by the trees root system and leaching from the pants by lichens subsequently.

Factor 3 with 15.6% of the total variance. This factor contains elements, such as cadmium and lead, normally associated with air pollution. In the same time factor 3 reduces the silver content in the lichens.

Factor 4 with 13,5% of the total variance is connected with positive loads of Mn, Ni, Fe. This factor has a typical crustal composition and is probably significantly influenced by soil particles adhered to the lichens samples.

SUMMARY

In summary, the average content of metals in the epiphytic lichens *H. physodes,* in the South-Western of Baltic in the Kalinіningrad region correspond to the trace elements in the background areas. However, the lichens of the Sambia peninsula accumulate trace elements more intensively. This fact is associated with higher levels of anthropogenic loading of copper, lead, cadmium, nickel and iron in the peninsula. It is possible that the trace element composition of the lichens in the Sambia is formed not only due to the impact of local pollution sources, such as vehicles, thermal energy facilities, ports, and by the influence of transboundary transport and sea spray. The present study is the first step of monitoring air contamination with lichens in the Kaliningrad region, there is a kind of "benchmark" for the future research. It is planned to further study the trace elements concentration of the lichen *H.physodes* and establish not only spatial features, but also the temporal dynamics of air pollution in the Kaliningrad region.

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PRELIMINARY ASSESSMENT OF THE NOX EMISSION RATES ORIGINATING FROM TRAFFIC IN MEDIUM – SIZE URBAN CITY (NOVI SAD, SERBIA)

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Received: November 2016

Abstract

This paper presents a preliminary assessment of the emission rates originating from traffic at a busy intersection in a medium-sized city in Serbia. The study included calculation of the emission rate using available data on number and type of vehicle and its evaluation through a comparative analysis of modelled NOx concentration obtained by ADMS Roads and measured NOx concentrations. Since this study represents the first stage of the research which ultimate goal is to establish a model for the prediction of NOx at the intersection, results obtained within this study are quite suitable for further research.

Keywords: *NOx, emission rates, traffic, city in Serbia*

INTRODUCTION

Traffic has become one of the dominant sources of air pollution which affect life quality in urban areas [18, 13, 28, 14, 8]. Given the fact that the combustion processes in internal combustion engines produce a wide range of pollutants, nitrogen oxides (NOx), carbon monoxide (CO), particulates, benzene as well as various organic compounds, and short-term or long-term exposure to increased concentrations of pollutants can significantly increase health risks [Zhang, 2013]. Concentration levels of air pollutants in urban areas originating in traffic depend on emission rate, meteorological conditions, as well as the microenvironment (e.g. canyon streets). In real conditions, calculating emission rate deriving from traffic is a complex process, taking into account that traffic is a dynamic phenomenon which varies in time and space. Emission factors, data on types and categories of vehicles, fuel, engine type, vehicle speed and other, are used to calculate traffic pollution [Filice, 2007; Harris, 2001; Kittelson, 1998]. On the other hand, in addition to measuring, different dispersion models [Holmes, 2006, 20] are used for determination the contribution of traffic emission (that are subject of complex processes of transport and distribution in the microclimate conditions of urban environment) or for predicting episodic pollution. Modelling of the concentration levels of pollutants at intersection is combined with measurements carried out at the site, provides a reliable way to determine the impact of the traffic to the overall pollution in urban areas, especially when it is not possible to provide sufficient data by measuring or when concentration levels are

below the lower assessment thresholds [21, 35, 16, 34].

Although there are various types of traffic pollutants, NOx originating from traffic with a share of 40%of Europe's NOx emissions, has been identified as one of the most important pollutants [14]. Having in mind the potential impacts of traffic on air quality, as well as the fact that the highest concentrations of NOx are expected at intersections due to unforeseen emission caused by low speeds, a relatively long retention times and different driving modes (queuing, accelerating, decelerating) [10, 23]. This paper shows results of preliminary assessment of NOx concentrations originating from traffic at one of the busiest intersections in the medium-sized urban city in Serbia. The significance of the results presented in this work is reflected in the fact that similar researches have not yet been carried out in the narrow region.

METHODOLOGY

Domain definition

Novi Sad is the third largest city in Serbia and the administrative centre of the province in northern Serbia (Vojvodina) (Fig. 1).

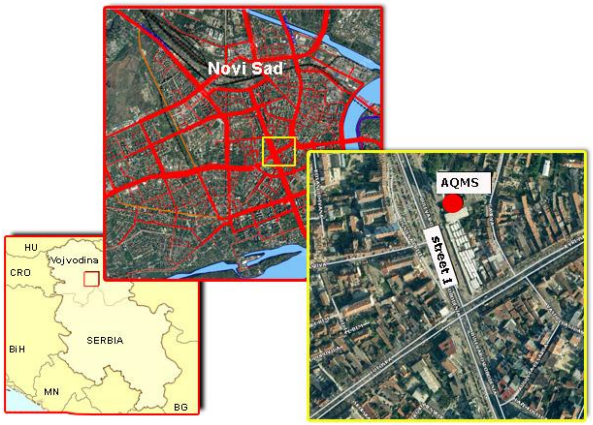

Figure 1
Study domain

During the last 15 years the city has had an expansion in the number of inhabitants (approximately 2x) [5, 6]. As in other cities, the number of people during working days considerably increases. The highest frequency of transportation is through the central boulevard that connects, on one side the railway and bus station across an intersection which connects the main road with the highly-populated city parts and suburbs. For the past 10 years, transport infrastructure has improved by construction of peripheral routes and transit which led to lower traffic volume and exclusion of heavy-duty vehicles through the central part of the city. However, this spot is precisely the one with the highest traffic volume (passenger cars and buses).

ADMS Roads

ADMS Roads is an advanced Gaussian dispersion model developed by Cambridge Environmental Research Consultants, which can simulate air pollution dispersion due to small networks of roads that may be in combination with industrial sites**,** for instance small towns or rural road networks .To define the boundary layer structure, the model uses the Monin - Obukhov length and boundary layer height [CERC, 2010]. Besides defining the type of pollution sources (road, point, linear) and pollution intensity (in this case emission rate), for approaching the real conditions, a series of additional parameters which include information for defining the areas for modelling (modelling domain definition) (surface roughness, road geometry, elevation and width) are needed for simulations, a minimum Monin – Obukhov length of 30 m (Cities and large towns), a surface roughness of 0.5 m (typical for cities) were used.

Meteorology and NOx concetration

To obtain the most approximate data on the concentration levels of NOx and meteorological conditions (cloud cover, surface temperature, wind speed and direction, as well as relative humidity) on the examined intersection, for comparison and research, this study uses the available data in 2012 from a nearby AQMS [30] which is located approximately 10 m from the Street 1 (Fig. 1).

RESULTS AND DISCUSSION

Analysis of the data

NOx concentration

For comparison with modelled data, information on concentration levels of NOx were used (non-heating season: May-September, 2012.). Authors have chosen this approach to avoid impact of additional NOx sources, especially emission from municipality house heating system. Statistical data on concentration levels of NOx measured during non-heating season (2012) show that the average daily NOx values during summer months ranged from 6.54 μg/m^3 to 99, 56 μg/m^3 and that by two days an overrun of 85 μg/m^3 was noted. Average monthly NOx concentration are relatively equal (from 33 μg/m^3 to 37 μg/m^3) with a slight decline in concentration (26 μg/m^3 and 27 μg/m^3) during July and August, which is to be expected, given the fact that during these months most of the population goes out of the town which leads to the fact that traffic flow is reduced.

Meteorology

Before modelling, pre-processing of meteorological data was carried out, which among other things included comparison with statistical data on the national meteorological services for 2012 and 2013, where it has been concluded that there are no

significant deviations in values (t, Rh, WS, WD), so ADMS meteorological data with 1 hour value could be used for simulation.

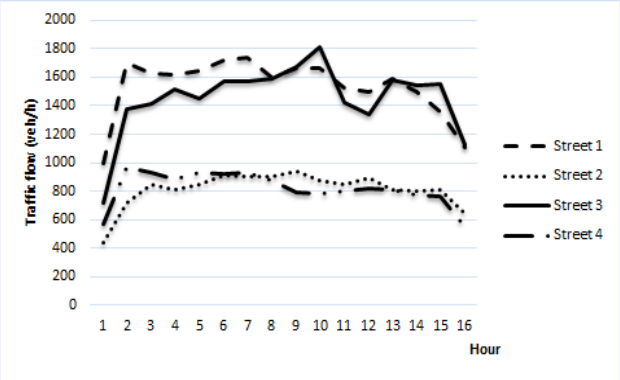

Figure 2
The diurnal traffic flow variations on the busiest intersection in Novi Sad [19]

Traffic

The average number of vehicles per hour that pass through intersection is 4621 (both passenger cars and light duty vehicles, for all directions/both ways), of which 94% are passenger cars, and only 6% are buses and light-duty vehicles. Traffic flow during the day is shown in the Fig. 2 [19].

The incompleteness of information for the calculation of rate emissions by COPERT was found in [33] where it was noted that it is essential to improve data collection system, as well as the quality of information, the structure of the vehicle fleet, records of fuel usage, distance travelled structure, average speed and distance. On the other hand [3] defines the composition of vehicle fleet, number of vehicles and fuel consumption for 2012. in the Republic of Serbia.

The data used to calculate emission rate included information about the share of certain types of vehicles by manufacturing date (passenger cars, light-duty vehicles up to 3.5t) according to the EU classification (E 5-6, E4, E3, E1 -2, ECE 15.05 and 15.0 before ECE), fuel type (diesel, gasoline, LPG) and engine capacity (> 0.8l; 1.4-2l, and > 2l). The fleet composition of the Republic of Serbia is shown in the Fig. 3, where it can be seen that passenger vehicles manufactured 16 to 25 years ago and buses manufactured 6 to 10 years ago are predominant. In the group of passenger vehicles the most represented ones are petrol vehicles with a share of approximately 48%, following diesel fuel vehicles with a share of 32% while the smallest share represents passenger LPG cars (Fig. 5). Buses age is shown in the Fig. 4. Buses predominantly (99%) use diesel fuel. By capacity, vehicles of category 1.4-2l are predominant (81%) while vehicles with a capacity exceeding 2l hold a share of only 13%. > 2l [9, 3].

By analyzing and comparing mentioned data with information-UK Government Department for Transport it has been identified that the United Kingdom has approximately the same percentage of vehicles with same fuel type and capacity as the Republic of Serbia. However, a significant difference in the prevalence of vehicles by manufacturing year is reflected in the higher share of newer vehicles in the UK, even 45,1% of vehicles manufactured 6-13 years ago, which was one of the main assumptions for making a decision to calculate own emission rates.

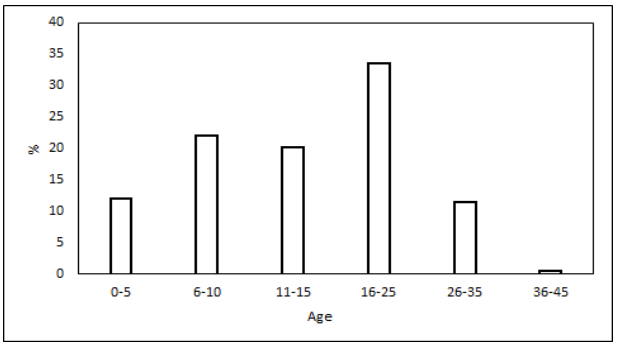

Figure 3
Presence of passenger cars by age

Emission rate estimation

Although emission rates from vehicles can be calculated using available software such as the Emission Factor Toolkit, Version 6 [11], which offers different levels of estimation depending on the available data or by air quality modelling system ADMS Roads.

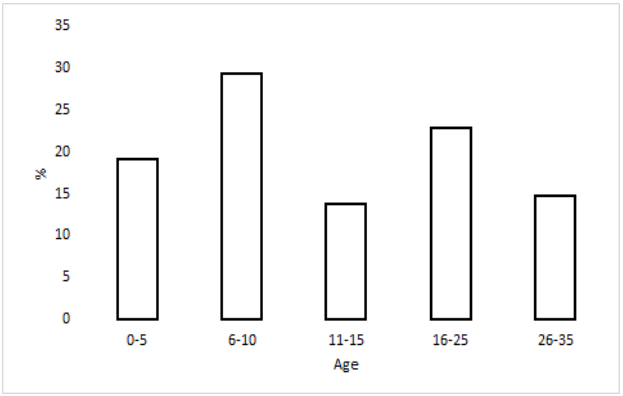

Figure 4
Presence of passenger buses by age

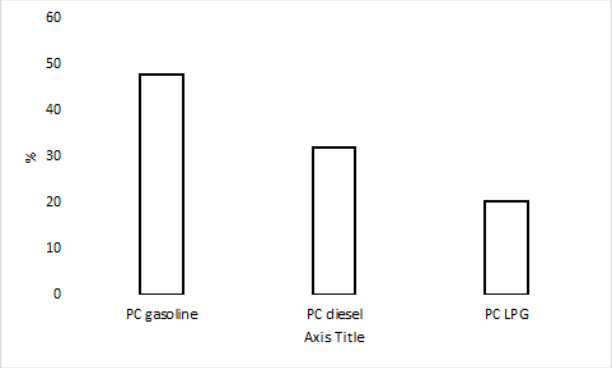

Figure 5
Presence of passenger buses by fuel type

In order to approach the real conditions prevailing on a given territory, authors have decided to estimate emission rates according to the data on traffic fleet in Serbia. As another reason for making this decision, it can be specified the fact that due to the population standard of the countries with the transition economy, as is the case with Serbia, the structure of the vehicle fleet may differ from developed countries, so some deviations in emission rates are possible.
Emission factors (g/km) which are defined in the EMEP / EEA emission inventory guidebook [15] (Tier 2) were used for calculation of emission rate (g/km/s) as well as data on the number of vehicles and the composition of the vehicle fleet in the Republic of Serbia for 2012.

Evaluation of estimated emission rates
In order to evaluate the accuracy of the estimated emission rate, as well as the assessment of concentration levels of NOx originating from the traffic, modelling of average hourly NOx concentrations during the non-heating season was carried out for Street 1 (width: 30m; length: 400m) since it was identified as the street with the highest traffic volume.

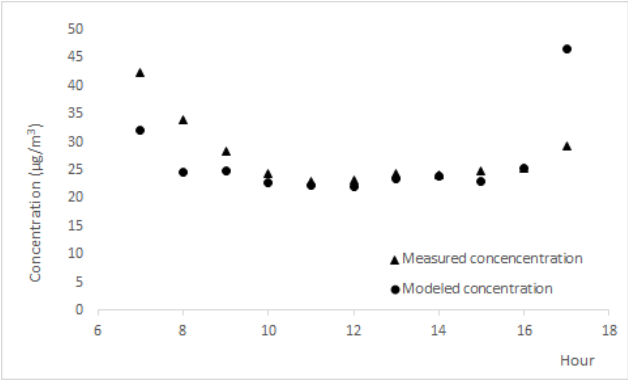

Figure 6
Hourly modelled and measured Nox concentrations –Test 1

The second reason for choosing this modelling domain is because of the position of ADMS which provided meteorological data and concentration levels of NOx for evaluation of the performances of established model (Fig. 1).

TABLE I
Statistical analysis of measured and modelled hourly NOx concentration – Test 1

Hour	Observed concentrations	Modelled concentration	MAPE1	MBE1
7	42.29	32.06	24.19	-10.23
8	33.90	24.74	27.02	-9.16
9	28.44	24.85	12.61	-3.6
10	24.35	22.67	6.82	-1.66
11	22.95	22.36	2.58	-0.60
12	23.31	22.01	5.58	-1.30
13	24.37	23.43	3.84	-0.94
14	24.10	23.98	0.49	-0.12
15	24.77	22.88	7.60	-1.88
16	25.41	25.29	0.46	-0.12
17	29.34	46.69	7.94	17.35

Modelling resulted in two sets of data: NOx concentrations obtained by estimated emission rates (Test 1) and NOx concentrations emission rates obtained by using Toolkit (Test 2)
The results of first running tests with the estimated emission rates (Table 1) revealed that almost all modelled concentration levels were underestimated (negative MBE value) except from hourly average concentrations modelled at 17 h, which is considerably above the measured concentrations of NOx (MBE = 17.34). Modelled hourly concentrations follow, in relatively good way, the trend of the measured concentration levels throughout the day (Fig. 6). The best performance of the modelled NOx concentrations were noted during the rush hours (11-15 h), for which the quality indicators show a large degree of agreement: IA from 0.75 to 0.98, as well as a small percentage of deviations from the measured values (MAPE: 0, 49 to7.5%.0).
One of the following levels of verification of accuracy of established model included the modelling of NOx concentration levels by using emission rates calculated by Emission Factor Toolkit, Version 6. The evaluation of the second set of NOx concentration data included statistical analysis and comparison with measured NOx concentrations. It was noted that deviations of modelled concentrations are significantly less in the morning (7 and 8 a.m.) while the deviation of the modelled values of NOx concentration at 17 p.m. is significantly higher in comparison to the first set of modelled data (Test 1) (Figure 7, Table 2)

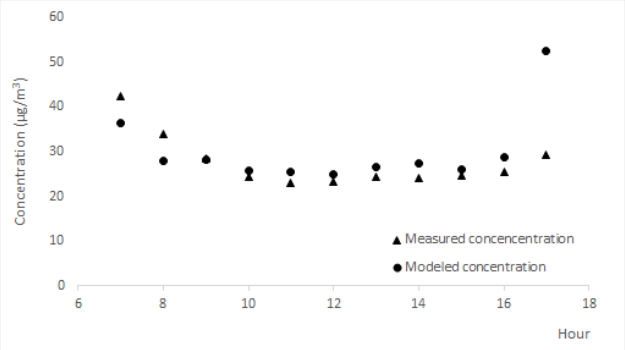

Figure 7
Hourly modelled and measured NOx concentrations –Test 2

Since the both tests has shown relatively good performance, analysis of the overall performances of measured and modelled concentration was carried out, using additional quality indicators (FB, IA, NMSE, and RMS) (Table 3).

Modelled NOx concentrations in Test 1 are slightly underestimated (negative MBE), while the MBE values in Test 2 are positive which indicates that the modelled values are slightly above measured ones. However, the MBE values are relatively low in each case. In the same manner, MAPE shows slightly better performance of the Test 1. Both fractional bias (FB) which represents a measure of agreement between the mean modelled and measured concentrations, and NSME indicates better agreement with the measured concentrations in the case of the Test 1. Since RMSE shows deviations of modelled values from the measured ones in units of variable, as well as that the value of RMSE tends to be minimal, better agreement is also identified in the Test 1.

TABLE II
Statistical analysis of measured and modelled hourly NOx concentration – Test 2 (Toolkit emission rates)

Hour	Observed concentrations	Modelled concentration	MAPE2	MBE2
7	42.29	30.42	14.24851	-6.02606
8	33.90	23.75	17.23215	-5.84064
9	28.44	24.22	0.840343	-0.23899
10	24.35	21.47	-5.87884	1.431321
11	22.95	21.16	-10.7007	2.455748
12	23.31	20.81	-7.31359	1.70467
13	24.37	22.26	-9.26427	2.257541
14	24.10	23.52	-13.0818	3.152796
15	24.77	21.63	-4.95153	1.226401
16	25.41	24.38	-12.8452	3.26361
17	29.34	45.02	7.94125	23.27213

TABLE III
Overall Statistical analysis of the performance of measured and modelled concentration

Indicator	Modelled concentration TEST 1	Modelled concentration TEST 2
IA	0.62	0.57
FB (ideal)	-0.041	0.084
MAPE	13.66	15.97
MBE	-1.11	2.42
NMSE	0.053	0.060
RMSE	6.8	7.68
Mean	26.45	29.98
Measured mean	27.56	

Although the period of non-heating season was taken into account for evaluation of traffic emission rate in order to avoid the impact of additional NOx sources, measured NOx concentrations show higher values compared to model in Test 1, which may be the cause of unidentified sources of NOx in the vicinity of the ADMS. One of the possible reasons for underestimating NOx concentrations may be the fact that there are ongoing harmonization processes in the Republic of Serbia, so that, by 31st of December 2015 it could be possible to put medium fuel oil and heavy fuel oil on the market, whose characteristics are not in accordance with requirements of Directive 1999/32 [26], which possibly led to certain errors in calculating the emission rate.

However, analyzing the data of other authors who deal with similar issues, we have found that NMSE values vary from 0.21 to 1.33 [32, 1], IA from 0.44 to 0.68 [1, 35], RMSE 0d 6.4 to 24.9 [38, 39], it can be determined that the detected deviations of modelled concentration are acceptable for next phase of research.

CONCLUSION

Considering the fact that the aim of the study was a preliminary evaluation of NOx emissions originating from traffic on a busy intersection in the medium-sized city in Serbia, NOx emission rates were established based on the number and composition of the vehicle fleet (type, capacity and age of the vehicle). In order to evaluate emission rate, modelling of concentration levels of NOx for non-heating season (May-September) was carried out in two iterations: with calculated emission levels (Test 1) and with the emission levels obtained by using Emission Factor Toolkit, Version 6 (Test 2). After data processing, two sets of modelled NOx concentrations were obtained and then compared with measured NOx concentrations whereby the statistical analysis (IA FB, MBE, MAPS, NSME, RMSE) were carried out.

Results have shown that the NOx concentrations obtained in Test 1 (with calculated emission rates) indicate better agreement with the measured concentrations, especially in rush hours (11-15h)

when compared to Test 2. Also, the modelled concentrations in Test 1 have lower values than measured NOx concentrations, which could potentially be a result of the influence of unidentified sources that are close to the measuring station. Overall statistical analysis and comparison of NOx concentration levels obtained in both iterations of modelling (Test 1 and Test 2) point out that all selected quality indicators show slightly better agreement in the case of modelled concentrations of NOx in Test 1.

Since the results in this study represent the first phase of research which ultimate goal is to establish a model for the assessment of concentration levels in the wider territory including other types of pollution sources, it can be concluded that results obtained within this study are quite suitable for further research. Following steps which are necessary for establishing better performances and accuracy of the model could be defined. More comprehensive and precise measurement of the number (during the weekday, weekend, seasons) and the type of vehicles that are present at the intersection should be carried out. Also, larger number of sites for NOx measurement should established in order to give more precise estimation for wider area and to identify all potential NOx sources in the testing area and beyond.

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REVIEW ON THE EFFECTIVENESS OF ADSORBENT MATERIALS IN OIL SPILLS CLEAN UP

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Received: November 2016

Abstract

During the last decade of the 20th Century, oil spill pollution has become an essential area of concern on account of its serious environmental impacts and to such an extent of the pollution that it poses a universal threat, therefore, surface water spill or subsurface leakage of petroleum products has been of concern to many industries and governments and NGOs. Exploration, production and transportation of petroleum products, unprofessional discarding of petroleum wastes and stranded oil spills from pipelines, oil wells, underground storage tanks, are the foremost causes of surface and groundwater contamination.

This review aims at to highlight the importance of the oil removal from contaminated sites by adsorption method and to present several adsorbents, such as natural organic sorbents, inorganic sorbents and synthetic sorbents, which are applied to treat the oil-contaminated water, their effectiveness as well as constraints and to set one's sight on the recent development of different adsorbents such as Nano carbon tube (CNT's) adsorbents, hence a lot of attention is given to this new type of adsorbent due to their exceptionally high adsorption capacity for oil–water separation and to their high hydrophobicity properties..

In this review discussion is presented on several different areas such as: (i) adsorption capacity; (ii) kinetic modeling and perspectives of the use of each adsorbent, Investigation for series of adsorbent with its characteristics.

Keywords: *effectiveness, adsorbent materials, oil spills, clean up*

INTRODUCTION

Spillage of crude oil in lands and in seas has triggered an interest in devising environment friendly and economic methods to clean up these pollutions and contaminations since the treatment of an oil spill remains a challenge to environmental scientists due to several hydrocarbon components which are toxic and exhibit a danger on the marine life, ecology and on the human beings. Therefore, the removal of hydrocarbon from soil and from water surface is an essential practice to prevent contamination of water [1].

Crude oil spilled to land or marine environment is instantly subject to a verity of physical, chemical and biological changes. At sea, crude oil, which is usually lighter than water, will spread over the water surface area. Subsequently, oil film layer with about 1 mm thickness forms on the water surface [1]. The rapidity of propagation of the oil on water surface is subject to the type of oil, water temperature, and weathering processes such as; atmospheric temperature, wind and flow Lighter components of the oil tend to evaporate to the atmosphere. The degree of evaporation and the speed at which it occurs depend upon the volatility of the oil [2].

HISTORY OF OIL SPILLS

Accidents of oil spills have attracted researches all over the world to find an immediate, novel clean up techniques since the spilled oil seriously affects the ecological and environmental system. Table 1 includes the oil spill cases which had been registered as vast disaster.

REMEDIATION TECHNOLOGY

There are different techniques that are widely used in spill response. Nevertheless, the effectiveness of each technique is influenced by several aspects, just as the properties and the amount of spilled oil, location and time of the year. Several researches and projects have investigated a large number of experiments to assess the efficiency of different cleanup techniques.

Adsorption is one of the most vital remedies in oil spill response. The removal of the hydrocarbons from soil

and from surface water is an essential practice to prevent groundwater contamination and to prevent the environmental damages in the ecology. Any remained portion of crude oil in the ground acts as a permanent source of contamination.

TABLE 1
THE 13 LARGEST OIL SPILLS IN HISTORY [3].

Case	Date	location	Amount (million gallons)
The Torrey Canyon	1967	Scilly Isles, U.K.	25-36
The Sea Star	1972	Gulf of Oman	35.3
Amoco Cadiz	1978	Portsall, France	69
Atlantic Empress	1979	Trinidad and Tobago	90
Ixtoc 1 Oil	1979	Mexico	140
Castillo de Bellve	1983	Saldanha Bay	79
Nowruz Oil Field	1983	Persian Gulf, Iran	80
Kolva River	1983	Russia	84
Odyssey	1988	Nova Scotia, Canada	40.7
Exxon Valdez	1989	Alaska	53.1
M/T Haven Tanker	1991	Genoa, Italy	45
Arabian Gulf	1991	Kuwait	380-520

As there is no general method which can be commonly applied to completely remove the oil from contaminated sites, the proficiency of each remediation technique requires information about the (i) composition of the crude oil/petroleum products and weather conditions, leakage quantity, sensitivity of the location and the toxicity of the chemicals.

However, the cleanup of heavy crude oil is very difficult. The weathering or evaporation of volatiles may produce solid or tarry oil. The average or medium crude oil is more toxic than the heavy crude oil and has the tendency to infiltrate into porous media. The light crude oil (volatile oil) spreads rapidly on solid or water surface and penetrates porous surface [4].

On a broader basis, oil spill removal methods are divided into three main categories; (i**) Mechanical recovery**, where oil is contained in an area using boom or natural barriers and are removed using skimmers, gravity separation [5], flotation methods (dissolved air, column flotation, electro and induced air), ultra and micro filtration, reverse osmosis, filtration (ultra and micro), various flotation methods (dissolved air, column flotation [6], activated sludge treatment, membrane bioreactors, various materials such as skimmers , solidifiers dispersants are used; (ii) **Non-mechanical recovery** where chemical countermeasures, basically dispersals, burning, or bioremediation are used to degrade or disperse the oil layer, sorption, biological treatment, chemical coagulation, electro-coagulation and coalescence and adsorption [7] [8]; and (iii) **The manual recovery** where oil is removed using simple hand tools and techniques such as pails, shovels or nets [9]. An environmentally preferred and cost effective spill response may require a combination of clean-up methods [10]. Different technologies for oil spill cleanup methods are illustrated in Table 2. [11] [12] [13].

Adsorption is a promising process and cost-effective method to reduce the environmental problems of oil spills and cleanup these types of pollution [14].

This review will focus on the adsorption techniques using several adsorbents with the goal to achieve high sorption capacity. Adsorption is a widely-used technique due to its simplicity and high proficiency. The choice of the adsorbents/absorbents depends on several factors such as availability, cost, and safe use of the adsorbent materials.

TABLE 2
OIL SPILL CLEANUP METHODS

Method¤	Example¤
Physical¤	Skimming·and·Booming¤ Wiping·with·adsorbent·Material¤ Mechanical·removal¤ Low·pressure·flushing¤ washing¤ Stripping¤
Chemical¤	Dispersants¤ Demulsifies¤ Gelling·agents·Solidifiers¤ Surface·film·chemicals·¤ In·situe·burning¤ ¤
Natural¤	Natural·attenuation¤
Biological¤	Bioremediation¤ Phytoremediation¤

ADSORPTION

It has been reported [15] that the sorption is a popular technique for cleanup of oil spills. Adsorption is a simple, relatively inexpensive tool for performing oil spill removal. This section reviews of some main previous research papers of the synthesis and the absorbing properties of the wide variety of porous sorbent materials that have been studied for application in the removal of organics, particularly in the area of oil spill cleanup. The areas for further development of some of these materials are identified also.

In order for a material to be used as sorbent, it should attract the oil preferentially to water, i.e. it should be both oleophilic and hydrophobic. Sorbent materials can act either by adsorption or, less commonly, by absorption. In adsorption, the oil is preferentially attracted to the surface of the material whereas absorbents incorporate the oil, or other liquid to be recovered, into the body of the material. The majority of products available for oil spill response are

adsorbents; few are true absorbents. Sorption can take place in two ways, namely by absorption and adsorption. Absorbents allow oil to penetrate into pore spaces in the material they are made of, whereas adsorbents attract oil onto their surfaces but do not allow it to penetrate into the material [16, 17].

Many parameters governed by the structure of adsorbents play a vital role in separation process, such as hydrophobicity, porosity, suitable pore sizes and surface area. Surface area of the adsorbent is important feature and leads to efficient oil removal from water, in addition, high carbon or oxygen content is also essential since this aspect leads to good oil recovery from water. Nonetheless, limited numbers of materials meet all the requirements for selectivity, sorption capacity, sorption rate and recyclability.

In general, the main characteristics of both adsorbents and oil types must be considered when choosing adsorbents for cleaning up oil spills:

(i) **Rate of absorption:** The absorption of oil is faster with lighter oil products. Once absorbed the oil cannot be re-released. Effective with light hydrocarbons (e.g., gasoline, diesel fuel, benzene).

(ii) **Adsorption capacity** (mass of pollutant adsorbed onto adsorbent per adsorbent's mass).

(iii) **Rate of adsorption**: The thicker oils adhere to the surface of the adsorbent more effectively.

(iv) **Oil retention**: The weight of recovered oil can cause a sorbent structure to sag and deform, and when it is lifted out of the water, it can release oil trapped in its pores. Lighter, less viscous oil is lost through the pores more easily than are heavier, more viscous oils during recovery of adsorbent materials causing secondary contamination.

(v) **Ease of application**: Sorbents may be applied to spills manually or mechanically, using blowers or fans. Many natural organic sorbents that exist as loose materials, such as clay and vermiculite, are dusty, difficult to apply under windy conditions, and potentially hazardous if inhaled.

(vi) **Kinetic model / equation** is used for the description of adsorption procedure which is a very serious factor, regarding the ultimate target to scale up the batch experimental data to fixed-bed column calculations for designing/optimizing the commercial processes.

Added to aforementioned points that it must be an attempt to adjust some crucial techno-economic data of adsorption process in order to carry out scale-up experiments (from lab to industry) with possible economic analysis and perspectives of the use of green adsorbents [18].

To date, the synthesis of adsorbents with superior oil sorption performance remains a great challenge.

CLASSIFICATION OF ADSORBENTS

Currently, about two hundred of various sorbent materials are produced and used [19]. Sorbents can be classified into some basic categories (i) organic and agro-based products [20] (ii) synthetic materials and (iii) inorganic [21].

Table 3 illustrates the most widely used materials with their advantages and their drawbacks. A practical review of the performance of organic and inorganic adsorbents for the treatment of contaminated waters is presented in the following section.

TABLE 3
ADSORBENTS TYPES AND ITS PROPERTIES

Adsorbent Type	Advantages	Drawbacks
(i) Natural fiber materials, and organic Adsorbent (Green Adsorbents)		
Agricultural sources and residues as lignin; Activated carbons after pyrolysis of agricultural sources), Natural fiber materials such as cotton fibers [22] corn stalk [23], bagasse pith [24] and nonwoven wool [25]	• Absolutely environmentally -friendly (from abundant natural sources, • Biodegradable, non-toxic.etc) 2.low-cost materials [18]	• Low sorption capacities and are mostly hydrophilic [26] • Cost-potential makes them competitive • One of the disadvantages of the plant origin sorbent is its high-water absorption, which resulted in loss of the sorbent buoyancy
(ii) Synthetic Adsorbent		
Synthetic polymers such as polyethylene and butyl rubber [26]; polyurethane [27]; polypropylene [28].	• The synthetic polymers are widely used due to their hydrophobic and oileophilic characteristics.	• The synthetic polymers have very slow degradability, which makes them an environmental concern. • They are not naturally occurring as mineral products [29],[30].
(iii) Inorganic minerals (The most widely used)		
Perlite, graphite, vermiculites, sorbent clay and diatomite [26,31] vermiculite [32] exfoliated graphite [30], sepiolite [33] and zeolites [33]	High adsorption capacity of 3.5–4.0 g petroleum/g sorbent Can be regenerated.	• Having porous structure for these materials can actively absorb water that can be considered as its disadvantage, sensitivity to fouling and susceptibility to ageing processes
(iv) Recent Advances in Adsorption Processes Nanotubes and Nanoparticles		
CNTs [34] copolymer consisting of modified multi walled carbon nanotube (MWCNT) [35]), granulated NaA zeolite nanoparticles modified with hexadecyltrimethylammonium bromide [36] and magnetic carbon nanotube sponges (Me-CNT sponge) [37]	• Exceptional one-dimensional structure and large specific surface area [38],[34]. • Their oileophilic and hydrophobic nature [38]	• Poor solubility and process ability restrict their applications. • Also, because of very fine particle size, working with this material is too difficult so that it is limited to laboratory-based studies [35]

(i) Natural fiber materials, and organic adsorbent (green adsorbents)

Several studies had been carried out and special attention was paid onto the natural fiber materials,

straw, grain crops hull, flax processing wastes, sawdust, and peat that have been used as sorbents. Cellulose as one of the important structural component of the plant materials is of special consideration.

A biomass carbon-based, material which derived from plants or animals and mostly found in the form of agriculture waste refers to those organic adsorbents. Globally, 5 billion metric tons of agricultural biomass waste is produced annually, the thermal equivalent of approximately 1.2 billion tons of oil or 25 percent of current global production [39]. The conversion of lignocellulosic material to valuable products requires an efficient fractionation method of the major components: hemicelluloses (10-25%), cellulose (40-50%), and lignin (25-40%) [40]. Bio-adsorbents are based on renewable sources, non- toxic, non-corrosive, fully active upon recycling and low cost are expected. the utilization of biomass resources, and its contribute to the prevention of global warming, the agriculture wastes have a high potential to be utilized in oil spill clean up for complete sustainability and renewability rather than the irreplaceable materials.

Reference [41] studied oil adsorption processes using natural adsorbents of plant origin – a peat moss grown in Russia, as well as nature Corby and spill-sorb, manufactured in Canada. Oil uptake capacity (OC) of the sorbents, buoyancy, solubility of hydrocarbons in water, as indicators are used to compare the sorption efficiencies for the individual adsorbent.

Reference [14] compared the oil sorption capacity of phragmites australis, sugarcane leaves straw, and sugarcane bagasse in the dry system and sugarcane bagasse was then used in different particle sizes to remove a crude oil layer dispersed over artificial seawater. The results indicated that sugarcane bagasse had a higher oil sorption capacity compared to others. Therefore, sugarcane bagasse was selected as the preferred sorbent and the effects of sorbent contact time and its particle size on oil adsorption capacity were evaluated for the systems of dry and crude oil layer on water.

(ii) Synthetic Adsorbents

Synthetic adsorbents are adsorbents prepared from agricultural products and wastes, household wastes, industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used include fruit wastes, coconut shell, scrap tyres, bark and other tannin-rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes, blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil.

Synthetic materials, such as polypropylene and polyurethanes, are the most commonly used commercial sorbents due to their oleophilic and hydrophobic properties [15]. Fig. 1 and 2 show the polypropylene sorbents, which is used during the final stages of shoreline, clean up.

On the other hand, these materials are not biodegradable, which is a major disadvantage. Landfill disposal is environmentally undesirable (as indicated in Fig.1b), and the incineration is expensive [42] and environmentally not friendly

Therefore, there is a renewed interest in natural sorbents and a wide variety of organic vegetable products, such as rice straw, peat moss, wood, and cotton, which have been employed as sorbents in oil spill clean-up. The main drawbacks of these plant-derived sorbents that those exhibit relatively low oil sorption capacity, low hydrophobicity and poor buoyancy compared to synthetic sorbents.

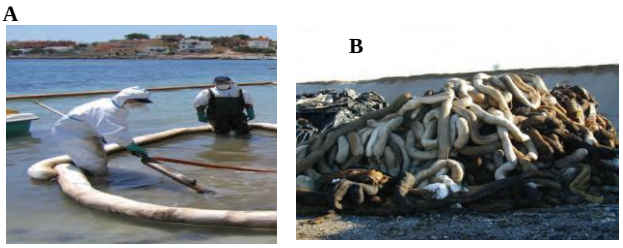

Figure 1
(A) Polypropylene sorbent boom used to collect oil released during flushing operations, (B) Used sorbent piled in a temporary storage site. Compression will cause recovered oil to be squeezed from the boom and care is needed to avoid secondary contamination (ITOPF report).

(iii) Inorganic Adsorbent

It has been particularly interesting to develop an adsorbent demonstrating a high adsorption capacity and low cost for removing various pollutants from contaminated waters. Thus, natural adsorbents including charcoal, clays, clay minerals, and zeolites adsorbents have been studied extensively, targeting to provide an alternative to the activated carbon in the treatment of surface and ground water and industrial effluents [43].

These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities [44]. Nowadays, studies on zeolites as adsorbent are becoming more frequent. Research on synthetic zeolites has confirmed their superior efficiency compared to the adsorbents currently used on a large scale to remove oil from water surfaces [45], owing to their low cost and the capability of ion- exchange and adsorption. Zeolites have gained a wide application in environmental remediation in terms of removal of contaminants from water [43].

Reference [46] prepared mesoporous silica materials and used it for adsorption of organic pollutants in water. Mesoporous silica materials are utilized with using self-assembling micellar aggregates of two surfactants: cetylpyridinium bromide (CPB) and cetyltrimethylammonium bromide (CTAB). The retention properties have been studied over two kinds of mesoporous silicas towards environmental pollutants (mono-, di-, tri-chloroacetic acid, toluene, naphthalene and methyl orange). The effect of the composition (presence and absence of surfactants, different kinds of surfactants) on the sorption performance has been considered. It was concluded that these materials show an excellent retention performance toward chloroacetic acids, toluene, naphthalene and methyl orange. The materials without surfactants does not show, if any, affinity for ionic and non-ionic analytes.

(vi) Nanotubes and Nanoparticles Adsorbent

In the field of oil adsorbent materials, the interest in carbon nanotubes (CNTs) lies in their light weight, excellent hydrophobic properties and the flexibility of surface modifications and functionalization (Fig.4 and 5).

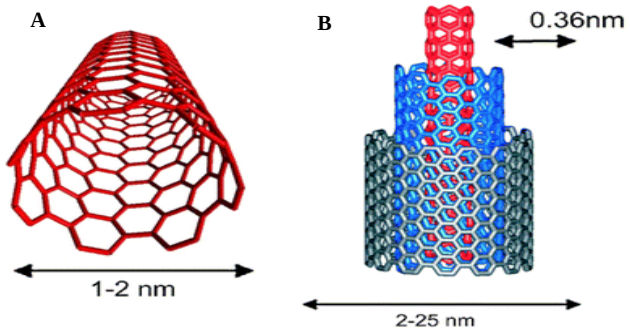

Figure 2
(a) Schematics of a single walled carbon nanotube SWCNTs and (b) Multi walled carbon nanotube MWCNTs

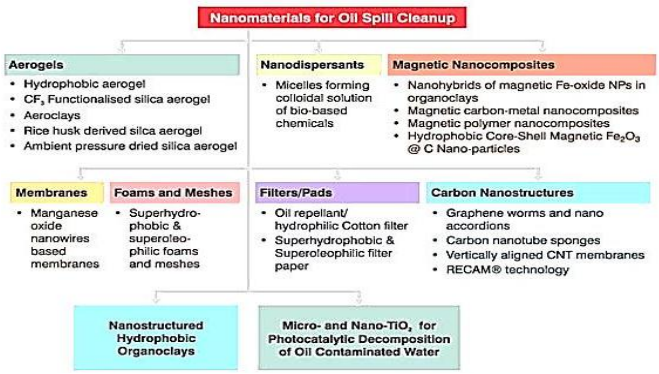

Figure 3
Various approach used for oil spill cleanup using different Nano material [47].

Figure 4 shows the modes of CNT functionalization. Notes: (A) noncovalent functionalization on the CNT surface are commonly achieved through hydrophobic and π-stacking interactions. (B) Covalent functionalization are commonly performed using 1,3-dipolar cycloaddition and oxidation by acids.

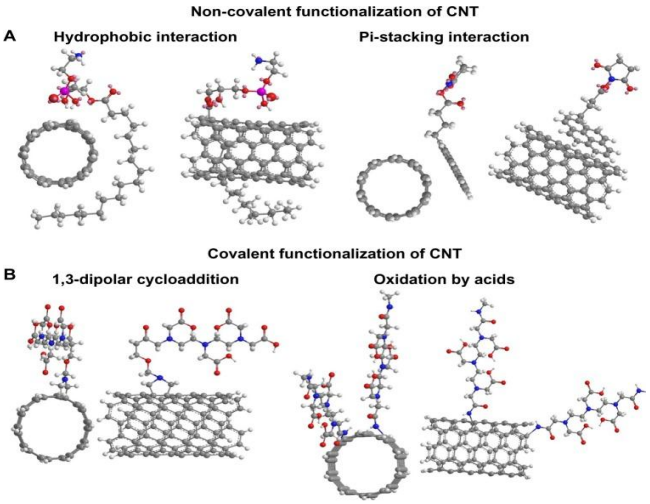

Figure 4
Modes of CNT functionalization [48]

Carbon nanotubes CNTs and multiwall carbon nanotube MWCNTs have generated a lot of attention as a new type of adsorbent due to their exceptionally high adsorption capacity for oil–water separation. The high hydrophobicity of CNTs makes them good candidates to enhance the de-oiling process from waters [36]. Furthermore, CNTs characteristically have hydrophobic properties and thus the adsorption technique is a relatively simple and cheap procedure.

Oil-water purification and treatment using CNTs as adsorbents have been reported by researchers and is considered to be a new field of research. The reported studies for oil-water separation have been dealing with mainly on cleanup of oil spills from the surface of waters [7].

Reference [49] reported that a team of US researchers developed a sponge made of pure CNTs with a dash of boron that shows a remarkable ability to absorb oil from water. The oil can be stored in the sponge for later retrieval or burned off so the sponge can be reused. If they succeed in producing bulky sheets or find a way to attach the sheets together, the sponge material can be practiced in large scale removing oil spills.

Super hydrophobicity is a property which is primarily found on hydrophobic surfaces with enhanced surface roughness since it minimize the area of contact between the surface and water by trapped air [50],[51]. Consequently, multiwalled carbon nanotubes have been extensively used for the synthesis of super hydrophobic surfaces for their large aspect ratio, chemical inertness, and hydrophobicity [52]. Reference [38] stated that the carbon materials have shown potential application in the field of oil spill cleanup due to their outstanding

absorption capabilities, high selectivity, chemical inertness and excellent recyclability.
Coated CNT sponges have been widely studied [53-55] used three-dimensional porous polymer material (as shown in Fig. 5a.) The CNTs as reusable oil sorbent scaffold in water, this adsorbent showed high oil absorption capacity and good reusability. CNTs on sponge have an interesting fact that it can alter its nature to only absorb oil while repel water completely, as shown in Figure 5b.

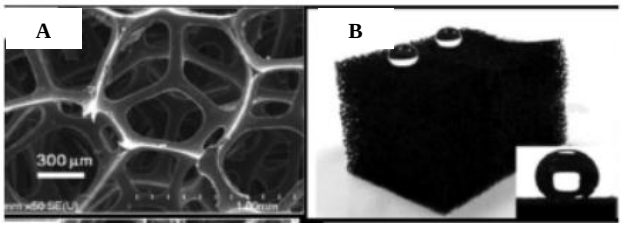

Figure 4
(a) SEM image of PU sponge, (b) an optical image of the CNT/PDMS-coated PU sponge. Inset showing the superhydrophobic nature of the as-prepared sponge.

Reference [34] used in his work two types of CNTs namely, P-CNTs and C-CNTs, (Produced CNTs from the IV-CVD reactor and commercial CNTs) for oil removal from water. It was found that PCNT can take oil up to 17 times their weight. P-CNT showed higher efficiency with almost 97% removal compared to 87% removal using C-CNTs.
Table 4 in Appendix "A" show different results for different types of CNT used for oil spill removal.
In this regard, carbon-based absorbents have been considered to be the best candidate as they possess high surface area, low density, excellent mechanical properties, good chemical stability, environmental friendliness and large pore volume. Carbon aerogels, graphene or carbon nanotubes (CNTs) coated sponges, carbon nanotube forests, graphene foams or sponges, carbon coatings, activated carbon, porous carbon nanoparticles and carbon fibers have been widely investigated for water filtration, water/oil separation, oil-spill cleanup, wastewater treatment, gas separation and purification.

CONCLUSIONS

Different adsorbents have been developed as reliable adsorbents for oil removal from water surface. This review focused on several studies and compared different sorbents and applicability of these materials in oil spill removal. An appropriate adsorbent material must show up high hydrophobicity and oleophilicity, low water uptake capacity (high oil/water selectivity), high buoyancy, high oil sorption capacity, low cost and easily availability. In another contest, the review showed that the CNTs have been proved to have high potential application in the fields of oil-water separation, with a number of advantages, including strong mechanical properties, rapid sorption rates, high sorbent capacity and engineered surface chemistry.

RECOMMENDATION

Any new proposed adsorbent system should be more environmentally friendly, economically feasible and technically applicable with a minimum level of complexity in terms of preparation and use, with attention to reduce inappropriate and excessive use that can present major logistical complications affiliated with secondary contamination, recovery, storage and disposal

ACKNOWLEDGEMENT

This work was supported by **GINOP-2.3.2-15-2016-00016** project: Excellence of strategic R+D workshops: Development of modular, mobile water treatment systems and waste water treatment technologies based on University of Pannonia to enhance growing dynamic export of Hungary

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APPENDIX A

Table 4
Different results for different types of CNT used for oil spill removal.

Description	Sorption Capacity	Method of Preparation	Kinetic Model
Hydrophobic corncobs/based Plant [56]	0.0768 mg sorbent/g oil	Acetylation	The Langmuir and Freundlich models.
Sugarcane bagasse Phragmites australis [14]	6.6 -8 g/g crude 4.5 g oil / gram phragmites	Carbonization Process	-
Activated Carbon Tablets from Corncobs[57]	Percentage adsorption of 22.82% of oil	The optimum condition which give a percentage adsorption of 22.82% of oil	Langmuir isotherm was the best fit isotherm for adsorption of ACT
Raw luffa[58]	12 g oil (Diesel)/g sorbent	Raw Material	Pore diffusion and the first order kinetic models
Hydrophobic Silica Aerogel[59]	Oil removal of 96 and 90 %	Co-precursor method	-
Polypropylene[15]	4.5 g/g sorbent	-	-
Ferric oxide nanoparticles doped carbon nanotubes adsorbents[34]	7 g/g,	wet impregnation method	Equilibrium data were correlated by the Langmuir and Freundlich isotherms, while the sorption energy was calculated using the Temkin model
Vertically-aligned CNT on stainless steel [60]	Good ability to dewater water–oil emulsion	Thermal chemical vapor deposition with a diffusion barrier of Al_2O_3 film	-
p-phenylenediamine modified carbon nanotubes (P-CNTs) [61]	3 to 12 times their own weight	Diazotization reaction.	-
Super-hydrophobic carbon nanotubes[34]	7 g/g.	Injected Vertical Chemical Vapor Deposition (IV-CVD) Reactor	Freundlich Isotherm
Carbon nanotube CNT foam [62]	650 Kg m^{-3}	Low temperature chemical fusion	-
Carbon nanofibers/carbon foam composite [63]	15-28 g/g	template synthesis of carbon foam and CCVD treatment	-
Carbon nanotube (CNT) sponge [64]	92.30 g/g	The CNT sponges were synthesized by chemical vapor deposition (CVD)	Pseudo-second order kinetic model
A three-dimensional carbon nanotube network B [65]	Can adsorb to 150 times its initial weight	Sulfur-addition strategy during an ambient-pressure chemical vapor deposition process	-

ASSESSING THE COMBINED EFFECT OF RISK FACTORS IN A SELECTED WORK ENVIRONMENT

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Received: November 2016

Abstract

The research aimed at assessing the combined effects of risk factors on human health. The research is based on theoretical and practical knowledge acquired during the research stay at the workplace. The experimental proposal of the assessment focuses on the workplace featuring metalworking machinery and technological equipment. The authors paid a significant attention to the risk assessment process and synergistic effects of factors. Moreover, the authors proposed a detailed time frame for particular positions as well as a comprehensive questionnaire for assessing the combined effects of harmful factors present in the given work environment. The article mentions only the most important parts of the analysis.

INTRODUCTION

The huge development of science and technology has brought with itself new technologies, new business processes, possibility to explore the unknown, introduce newer and more modern machinery and technologies, automated processes, and also new job opportunities. With these advances and the introduction of new technologies a new and **yet-unknown risks began to emerge**. The work process now entails more work factors which are becoming **increasingly difficult to identify, objectify or assess.** The qualitative-quantitative assessment requires new modern measuring equipment, best laboratories and competent personnel for its implementation. In order to eliminate or reduce harmful factors of work and work environment to the lowest level possible **it is necessary to adopt** a variety of **technological, technical, organizational and other measures**. Despite the adoption of these measures, the workplaces feature physical, chemical, biological and other factors in excess of permissible limits, and **their effects can adversely affect health of employees.**

In order to prevent potential damage to health, it is important to know all the adverse factors that occur in the workplace, **i.e. identify them, objectify them, ensure their quality-quantitative assessment, draw up reports on risk categorization and take measures to reduce them.**

For the assessment of any harmful agents present in the work environment it is important to know the adverse effects of each one of the present factors and the ways they enter the body, which parts of the body they can damage, what difficulties they may cause, signs they entail, and many others.

Given the fact that the assessment of the combined effects of risk factors is not strictly outlined by our legislative framework, the analysis relies on literature, expert studies and articles on the assessment of the combined effects of the risk factors in the work environment.

METALWORKING WORKSHOP

Metalworking workshops or workplaces are usually focused on a specific, contract-based construction processes that use specific machining technology and technological processes (machines and equipment). Thanks to engineering and technical processes the metalworking is becoming more and more modern.

Despite the achievements of the modern era some of metalworking workshops still use conventional machining technologies (especially in the production

of custom-made products), for example chip machining using center lathes, milling machines, drilling machines and carousels. In their work employees use hand and power tools which require enhanced safety at work measures.

Metalworking is a process during which a semi-product is shaped into a required shape and dimensions by machining or by changing its shape (e.g., bending).

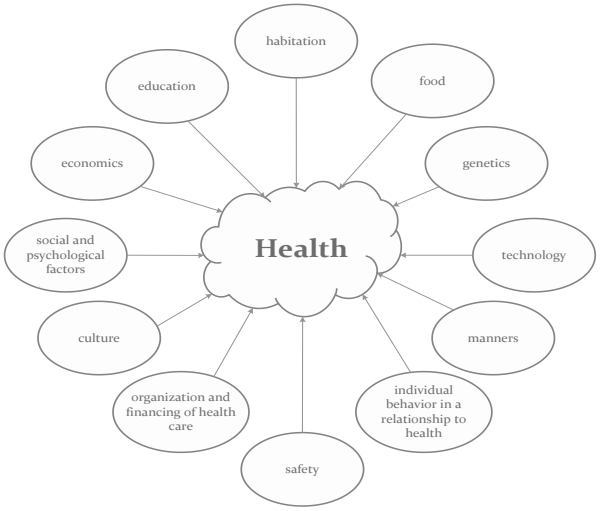

Figure 1
Factors influencing health status of a person

ASSESSING THE WORKING ENVIRONMENT USING COEFFICIENTS

Sizing of the analyzed factors is assessed using a difficulty factor Q_{dif}. This factor determines **how many times a burden factor exceeds the allowed limit**. It is calculated as follows:

$$Q_{dif} = \frac{Z_r}{Z_p}$$

where: Z_r – value of the actual workload factor,
Z_p – value of the permissible workload,
Z – overall workload factor $Z_{i,j}$ = 1, 2, ..., n.

In the course of the work employees are being affected by many factors as well as the work environment which have negative effects on the human body. **The sum of all burdensome factors** that affect humans in different ways is referred to **as a total workload *Z*.**

This workload factor can be assigned to a **specific degree of workload** using the workload coefficient Z_j with regard to other workload factors – ranging from α_1 to α_n – while keeping in mind that the sum of the values $\alpha_1, \alpha_2, ..., \alpha_n$ must be equal to one.

If the value of α **is close to zero**, then *Zj* has an **insignificant impact** on other factors. If the value of α **is closer to one**, it can be stated that Z_j **has a strong influence** on other factors.

This factor has a decisive effect on the final calculation of the load of the work environment.

TABLE I
ASSESSMENT OF THE IMPACT OF WORKPLACE RISK FACTORS ON HEALTH

Impact on health	Body burden and health and safety	Productivity	Status	Coefficients
WITHOUT AN IMPACT	-	-	optimal	0
INSIGNIFICANT – without permanent sequelae	the possibility of increased workload	occasional drop in work performance	good	0,2
LOW – low impacting sequelae	noticeable body burden	drop in work performance	satisfactory	0,4
MEDIUM – serious sequelae	possible risks	significant drop in work performance	acceptable	0,6
HIGH – life-long sequelae	very high risk	low work productivity	unfavorable	0,8
EXTREMELY HIGH – death	the possibility of fatal accidents	working is almost impossible	unacceptable	1

The value of the total instantaneous workload $q_c = \sum_{j=1}^{n} \alpha_j \cdot \frac{z_j^r}{z_j^p}$

$\alpha_j \cdot \frac{z_j^r}{z_j^p}$	reflects the actual body burden of the workload factor Z_j from the all resulting load factors $Z_1, Z_2, ..., Z_n$

To obtain specific data it is necessary to take into account **health statistics** (occupational diseases, the likelihood of the occurrence of occupational diseases), **the effect of risk factors on the accident rate in a particular operation, hygienic conditions of operation, health and safety measures and productivity.**

EXPERIMENTAL PROPOSAL

The health risk assessment process is essential for the safety and health of workers at work. Negative impacts on employees are greater when there are several negative influences present at the workplace.

The methods and procedures used in the assessment of the work environment **are intended to quantify the extent of damage inflicted to human health**. Therefore, it is necessary to properly select an appropriate method for a comprehensive assessment of the quality of the working environment. Using this method, it would be possible to determine the level of workload at the workplace.

Synergistic effect

The current status of the work factors and factors of working environment is assessed by assessing one factor at a time. Following the qualitative-quantitative assessment it is necessary to assess these factors in a comprehensive way.

Thus, **if one factor affects** the human body in a **negative** way and can harm the human organism, **the**

coexistence of such factors may increase the negative impacts by their synergistic effects (mutual active interaction) or by potentiating the factors, which means the factors are complementary to each other.

However, **the opposing effects** of work factors and factors of working environment are also well-known. When assessing effects of work factors and factors of working environment it is important to consider each factor and its effect on the human organism individually. However, if we want to quantify their overall effect on employees, it is essential to assess effects of work factors and factors of working environment comprehensively and never underestimate their negative effects on the human body, especially if the values of factors are below the limit, since their synergistic effect can significantly damage employees' health. Therefore, it is important to find a solution to the issues related to synergy.

It is necessary to highlight the fact that every phenomenon has its own specificities, and it is important to carefully examine and evaluate them gradually. The synergistic effect outlines the intensive and prolonged effect of factors which together create one final effect.

At the beginning, a number of negative effects may for some time seem **insignificant**. Likewise, positive effects may seem **unjust or inefficient.**

Even in terms of fictitious metalworking workshop, a synergistic effect of noise which exceeds upper exposure action values, vibrations transmitted to the whole body or hands not exceeding action values of the normalized vibration acceleration and microclimate conditions such as cold, dampness and physical stress can after a long-term exposure have an adverse impact on health or even cause an occupational disease.

Time frame proposal

For a more thorough analysis of the impact of risk factors it is necessary to develop a detailed time frame which will be used in initial measurements.

For the better assessment of synergy effects on employees the time frame includes periods of exposure to vibrations and noise for various activities carried out during the eight-hour working time.

In order to assess the combined effects of work factors and working environment factors we need information about **objectification, qualitative - quantitative assessment, information on employees' job positions** and other related documents regarding **data on the workplace, the subject matter, and various other documents.**

In order to obtain more relevant data needed for the assessment we have **proposed and designed a comprehensive questionnaire.** Its primary aim is to get information directly from employees working at a particular workplace. The questionnaire has not yet been filled out and only serves as a proposal for the assessment of combined effects. Due to the limited scope of this article we will not describe it any further.

Final evaluation and a flowchart

In order to eliminate occupational diseases at the workplace it is important to identify risk factors and monitor the incidence of health problems among employees. The professional assessment of the work environment, working conditions and the way of working it is necessary to consider each of the factors individually, but at the same time sensitively, responsibly and professionally in accordance with the qualitative-quantitative assessment and the current scientific knowledge. Moreover, it is also important to evaluate and assess comprehensively all the negative synergistic effects in order to eliminate or at least reduce their harmful side effects on the body.

Description of the flow chart:

1. The identification of hazardous risk factors at the workplace.
2. Sanitary survey at the workplace survey. Definition and determination of factors.
3. Definition of the time frame needed for the assessment and measurements.
4. Preparation of documentation and equipment for the measurement and assessment.
5. Measurement of noise, vibration and climatic conditions.
6. Assessment of physical activities.
7. Preparation of records, methodology descriptions, outputs from the measuring devices.
8. Are measurements carried out in line with the time frames for all job positions?
   A – The measurements are carried out in line with time frames
   N – Not all measurements have been carried out.
9. Processing of measurement results and the base documents for the assessment of physical load.
10. Adding professions and drafting / editing TF.
11. Carrying out additional measurements of physical factors.
12. Completing measurement results and base documents for the assessment.
13. Evaluation and assessment of the health risks.
14. Developing the risk assessment including the Risk Management Plan.
15. Submitting a proposal to the relevant Regional Public Health Authority for inclusion of the specific works into the third or fourth category of work/ submitting a proposal for changing or removing the works from the third or fourth category.
16. Implementation of measures of the Risk Management Plan, review the health risks, preparation of documents.
17. Have changes been implemented?
    A – Changes that have an impact on the inclusion / removal into / from the third and fourth category have been made.

N – No changes that would have an impact on the inclusion / removal into / from the third and fourth category have been made.

18. Checking the up-to-date nature of the risk assessment, checking the compliance with the Risk Management Plan, updating records:
    A – Reviews are valid; Risk Management Plan is being met.
    N – Changes to the risk assessment.
19. Updating TF, completing documents on the changes taking place at the workplace.
20. Implementation of complementary surveys and measurements of harmful factors.
21. Reviewing changes in working conditions, data update.
22. Additions and changes in risk assessment.
23. Informing the management.
24. Archiving documents.

The assessment of synergistic effect of work factors and working environment factors is not strictly governed by any legislation that would lay down assessment procedures or outline rates, levels and conditions of the harmful effects on employees.
We suggest the following assessment procedure:

- Risk assessment, categorization, and the decision on hazardous work. Time exposure and job descriptions. Reports on the measurement and assessment of harmful factors.
- Risk analysis carried out on the basis of a questionnaire.
- Detailed analysis of reported occupational diseases and threats of occupational disease.
- Analysis of health status of employees made on the basis of information contained in a medical opinion on work capability.

The first point of the assessment
For the purposes of the assessment we propose the following markings and score:

TABLE II.
DATA FOR THE RISK CATEGORIZATION

Noise	Vibration	Physical Exercise
category 2 **N2 - 4**	category 2 **V2 - 4**	category 2 **PE2 - 4**
category 3 **N3 - 6**	category 3 **V3 - 6**	category 3 **PE3 - 6**
category 4 **N4 - 8**	category 4 **V4 - 8**	category 4 **PE4 - 8**

The second point of the assessment
When analyzing the data received from the questionnaire we can obtain other important data as well. Such data is likely to be objective and fairly accurate since it is given by employees voluntarily and mostly on an anonymous basis.
The questionnaire provides very important data on the age range of respondents and information on their exposure to risk factors. Such data is important in determining the level of risk - whether it is a **medium, high or very high risk** with regard to the age of an employee or the probability of health damage given the length of exposure to risk factors - **low, medium, high and very high.**

The third point of the assessment
A detailed analysis of reported occupational diseases and threats of occupational disease at the workplace provide important data for the assessment of synergistic effects of the monitored harmful factors.
By analyzing the reported occupational diseases, we can obtain detailed information about minimum, maximum and average age of employees at the time of the occurrence of the occupational disease, as well as information about minimum, maximum and average exposure time prior to the occurrence of the occupational disease.

The fourth point of the assessment
The first medical restrictions stated in a medical opinion on work capability fitness or medical work restrictions supported by medical check-ups will give us information on the time of exposure to harmful factors which have not caused any harm yet, and the early signs of damage to health. From such data we can then calculate the minimum length of carrying out work in the work environment without inducing any harm or indicate time when such effect will start to appear. These conclusions can be the basis for a timely redeployment in order to prevent the impact of harmful factors.

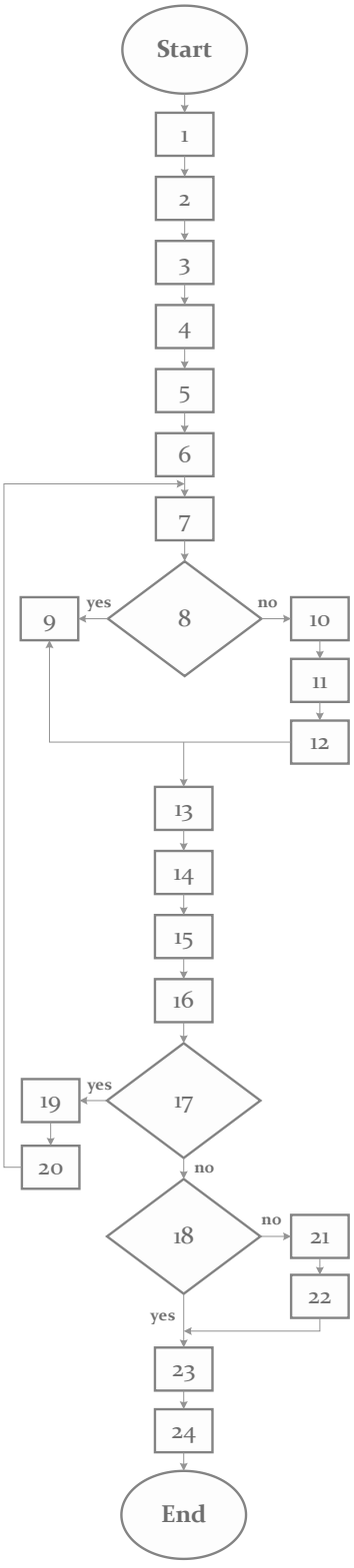

Figure 2
Evaluation of health risks – flowchart

In a similar manner were also proposed additional scales (*the scale of the occupational disease risk, the scale for the restrictions resulting from medical reports, etc.)*

A summary table assessing the combined effects of work factors and working environment factors serves as a basis for the resulting summary documents which were obtained from four basic sources, namely the risk assessment and work categorization, the analysis of data provided in the questionnaire, the detailed analysis of occupational diseases and threats of occupational diseases, the analysis of data contained in a medical opinion on work capability during regular medical check-ups of employees.

TABLE IV
THE SCALE OF THE OCCUPATIONAL DISEASES RISK

The number of reports at the workplace	**The word sign**	**Value OD**
≥ 3	Extremely High – **ODEH**	10
≤ 2	Medium – **ODM**	5
0	Without an Impact – **ODWaI**	0

The assessment of the combined effects of working as a profession fitter / lathe operator has given the related synergistic effects the score 8, i.e. very high probability of potential damage to health due to several factors related to the work environment and tasks performed. The employee performing the above-mentioned tasks was placed in the following categories: fourth category due to the noise factor, the third category for vibrations factor and fourth category due to physical load.

From the documents provided it was found that at least one occupational disease and more than three threats of occupational diseases were reported at the monitored workplace. Also, medical check-ups revealed more than three health restrictions. According to data provided the age of the employee in question ranged between 45-49 years, which was assessed as a high risk. The given employee had been exposed to the risk factors for more than 20 years, which was assessed as very high probability of a potential harm to the body.

On the basis of data obtained the profession of fitter/ lathe operator was assessed as a profession with a very high probability of harm to the body (if the work conditions will not change).

CONCLUSION

Proposing a method for assessing the combined effects of the risk factors in the chosen work environment and its implementation into practice is a long process. Since the risk assessment is not clearly defined in the legislation, the actual assessment of the combined effects of risks requires an experienced team of experts working in the field of qualitative-quantitative assessment and health risk assessment and a lot of work. Moreover, it is necessary to obtain the maximum

possible number of data on the employment in a given workplace.

ACKNOWLEDGMENT

This paper was written in frame of the work on the projects KEGA 039 TUKE-4/2015 (25%) and KEGA 049 TUKE-4/2015 (25%). This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0432-12 (50%).

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ANALYSIS OF ELV COMPONENTS FROM ASPECT INFLUENCE ON THE ENVIRONMENT

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Received: November 2016

Abstract

There are different types of wastes that have effect on the environment, including waste from motor vehicle at the End of life Vehicle (ELV). ELV components have a big ecological influence on the environment because of that their adequate recycling and disposal are very important. The paper presents ELV components which could have potential negative influence on the environment if they are not properly managed. Paper shows a brief comparative overview of recycling components in the world and Republic of Serbia. Paper also shows some of available technologies which are using in the purpose of quality ELV process as well as protection measures in the aim of adequate treatment with reference to European Union (EU) directives and Legislation of Republic of Serbia.

INTRODUCTION

Waste is part of the most important ecological problems of today which has an effect on the environment, thus quality of life. There are different types of waste including waste from motor vehicles which come to the ELV [1]. ELV presents a major source of environmental pollution but if it is used in the right way, it could be a great source of material resources, especially metals [2].

Comparation of situation of recycling ELV in the world and Serbia

Table 1 shows statistic state recycling motor vehicles which comes to the ELV in the developed communities. There is a no company in the Serbia which is recycling motor vehicles but it is developed and exist a good infrastructure of companies which can recycle waste materials that arise during the process of dismantling vehicles which come to the ELV [13].

In the aim of rising level recycling ELVs on the territory of Republic of Serbia and improvement according to recycling in the developed countries, it is a necessary to establish specialized factories which are dealing with mentioned area.

TABLE I
ELV STATISTIC IN DEVELOPED COUNTRIES [15]

Statistic - annual	**EU**	**Japan**	**USA**
Production (vehicles and trucks)	16 – 18 million vehicles	9 – 10 million vehicles	15 – 17 million vehicles
Vehicles in exploitation	200 million	about 50 million	200 – 210 million

New registered vehicles	14 – 14.5 million	5 – 5.5 million	15 – 15.5 million
Deregistered vehicles	14 – 14.5 million	about 5 million	13.5 – 14.5 million
Crushed / recycled vehicle	7 – 8 million	4 – 4.5 million	12.5 – 13.5 million
Thrown / vehicles in stock	about 5 – 7 %	about 1 %	about 6 %
Export of used vehicles	3 – 3.5 million	0.5 – 1 million	unknown
The average weight of vehicles	1000 – 1200 kg	1000 – 1200 kg	1200 – 1400 kg
The content of copper and copper alloys	1 – 2.2 %	unknown	1.4 – 1.5 %

Harmonization of the Serbian national legislation with the Directive 2000/53/EC

Recycling at the end of life cycle in the countries on the territory of European Union is defined by the Directive 2000/53/EC which is defined in accordance with sustainable development principles and examples of good practice of member countries which already had developed this type of recycling. Each of the member countries is obliged to follow regulation of the Directive modify their legislation to the requirements (economics, ecological, socially-economic, resources) on their territory. Harmonizing of national law acts with the Directive leads to:

- decrease of ELV influence on environment which contributes to the protection, improvement and preserving of the environment as well as saving energy.
- undisturbed labor on the domestic market and increasing the competition level on the world market.

Serbia's involvement with European integration processes, above all, means harmonization of the legislation portfolio for the environmental protection. In this case, there is a need for harmonizing the national legislation with the Directive 2000/53/EC and the related sub legal acts [8].

Rulebook about method and process of controlling motor vehicles determined that the controlling of waste vehicles is performed by the method which provides and secures the conditions for:

- preventing the formation of the waste of the vehicle,
- reusing, recycling and other forms of reusing such waste as well as the dump waste decreasing,
- development of environment protection standards by manufacturers, importers, distributers, sellers and end users during the life cycle vehicle particularly while providing treatments of waste vehicles [9].

ELV recycling technologies

Steps in the process of ELV treatment are:

- acceptance of ELV from the last owner,
- collection and storage,
- removal of pollutants / toxic materials,
- dismantling / disassembly / reparation,
- shredding / grinding,
- operation after shredding / grinding,
- reuse / recovery / recycling,
- final waste (burning, disposal on the land) [13].

Collection – Collected cars are storage at special places only for them. In that storages are not allowed doing any kind of treatment, except collecting. Wasted vehicles will be transported to the centres for different treatments.

Detoxification – To successfully recycling process of motor vehicle precede adequate detoxification and treatment of toxic waste from vehicles [3].

From detoxification process of fluids, i.e. removal pollutants as harmful on the environment stand out:

- fuels,
- motor oils,
- oils from gearshifts,
- oils from differential,
- hydraulic oils,
- antifreeze,
- acids from the accumulator,
- liquids from air-conditioner,
- brake fluids,
- other.

One of the available technologies for detoxification vehicles is Technical solution “Plant model for discharging liquids from vehicles in the process of ELV” developed under the project TR 35033, which is a fixed station for combined removal of all vehicle fluids with minimum influence on the environment, showed on the Figure 1.

By discharging fluids from the vehicle, vehicle becomes to have a treatment as dangerous waste which results to higher level of safety of environmental protection.

After elimination toxic waste materials from the vehicle which leads to further elimination and recycling of metal parts of vehicles which are comprising the biggest part [5].

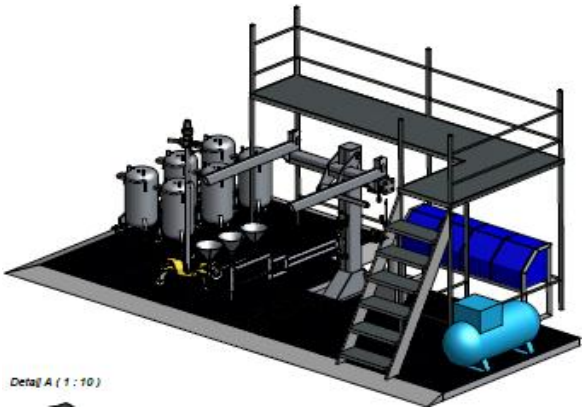

Figure 1
Plant model for discharging liquids from vehicles in the process of ELV [4]

Dismantling – After the de-pollution operations, the ELVs were transferred to the dismantling workshop for deconstruction. The operations were mostly manual ones, assisted by pneumatic and electric power tools. The mechanical parts destined to be reused were carefully removed and checked by a specialized operator, whereas the other parts were removed by the usual workforce [22].
Pressing – After dismantling, in the function of the easy transport to the next ELV process "stage", and all with aim of adequate and complete ELV process, vehicles are pressing. Pressing helps to the next "stage" of ELV process - shredding of motor vehicle [6].
Shredding – where the remainder of the ELV, so-called hulks, are turned into small pieces and the ferrous and non-ferrous metals are sorted by a series of mechanical and magnetic separation processes to be sent for recycling. The metallic fraction present in the shredded waste stream represents around 60 % of the total weight of the ELV [23].
Auto Shredder Residue (ASR) – is usually defined as the 15-25% of ELV's mass remaining after de-pollution, dismantling, shredding of the hulk, and removal of metals from the shredded fraction [18]. Auto shredder residue (ASR) is a solid waste, which is generated by the ferrous metal shredding industry. ASR is an extremely heterogeneous material [19].
Processing of materials – Many alternatives have been developed for processing of these types of residual (physical separation, incineration, pyrolysis) but it seems that the landfill is currently the most acceptable solution because of the high price of their processing [6].

Impact of ELV components on the environment

Every year in the world about 18 million vehicles come to the end of life cycle. If all vehicles are exposed as a waste would mean 20 million tons (70 million m^3 per volume) a new solid waste per year which burdened environment [10]. In the aim of cut that quantities it is developed concept of 3R (Reuse-Recycle-Recover).
Reuse – any operation by which components of end-of life vehicles are used for the same purpose for which they were conceived. For example the engine, if it still works properly and is undamaged, can be mounted in another similar vehicle.
Recycle – The reprocessing in a production process of the ELV waste materials for the original purpose or for other purposes. If the engine of the previous example no longer works or is damaged, the material from which it is made could be recycled.
Recover – Any procedure allowing reuse of the resources contained in the ELV, including incineration thereof with energy recovery. Tires are a good example [24].
Securing "safety" and quality environment for population is faced with problem of waste, which is considered for one of the most ecological problems of modern world [1].
Motor vehicles with all their components, metal parts and toxic fluids which come to the ELV present important contaminants of the environment [11].

Potential negative impact of ELV components on the environment

Table 2, as an example of the amount of material per vehicle, it is showed percentage and weight of material in the Zastava vehicle, produced in Serbia, which is total weight about 835 kg.
Removed pollutants and components with dangerous substances are collecting in the appropriate reservoirs and transport to the organization for recycling or landfills [13]. Some of the components are treated as more, and some as a less dangerous waste and some of components as a reusable but all of them demands appropriate treatment.
Ferrous metal: Mainly steel and iron for resmelting, generally known as scrap metal. It is obtained by shredding in specific plants where the vehicles arrive in crushed half-meter cubes from the ATFs themselves or an authorized manager. After decontamination, the parts that can be reused are then separated off. It is estimated that in the period 2005-2010 about 1,500,000 tons of this material was obtained from recycled cars, this then being sent on directly to the steel plants for recycling.
Nonferrous metal: This is also obtained from the shredding process, mainly made up by aluminum and copper, which are sent on to specific plants for recycling. Metal of this type is currently being more widely used in automobiles, mainly aluminum, of which about 95% is recovered. Seventy percent of the aluminum used in automobile manufacture comes from the resmelting of this metal from other

automobiles, closing the recycling circle almost completely [24].

TABLE II
THE STRUCTURE OF MATERIAL IN THE VEHICLE ZASTAVA [12]

Material	Weight [kg]	Participation [%]
Steel / Iron	626	75
Other metals	48.9	5.86
Plastic	41.7	5
Tires	25.9	3.1
Glass	30.9	3.7
Fluids	15.4	1.84
Rubber	8.3	1
Others	37.9	4.5
Total	**835**	**100**

Aluminum: In automotive industry aluminum is consider for material of the future. In present time grow of ecologic consciousness and unfair race in saving (economical) this material with its extraordinary technical characteristic and ecology acceptable recycling technology represents like ideal material [17].

Airbags: The ELV Directive requires all pyrotechnic devices, such as airbags or pyrotechnic seat belt pre-tensioners, to be either removed or deployed because they are classed as explosive components [16].

Motor cooling liquid (antifreeze): main structure of this agent makes basic fluid (formed mainly from mono ethylene glycol MEG or propylene glycol), additives (inhibitor corrosion, cavitations and precipitation, defamer, stabilizer and puffer) and water.

In used antifreeze, except ethylene glycol, can be find traces of heavy metals and other substances (e.g. lead, cadmium, copper, benzene and anticorrosive additives) which make it very dangerous. [1].

Brake fluid: must not be treated as used oil, as it has characteristics of toxicity. Mix with chlorinated solvents from spray, which is used for cleaning the brakes, makes the brake fluid extremely hazardous. Brake fluid shouldn't be dumped on landfills.

As we can see from the aforementioned, attention should be paid to the adequate treatment of this medium, which cannot be recycled or reused in its original use, which requires providing of safe and efficient system of gathering, treatment, storage and dumping [14].

Motor and transmission oils – are mineral motor oils, synthetic motor oils and half synthetic oils.

In waste motor oils large percent of very toxic and cancerogenic substances is contained which makes them very dangerous waste, especially because they are part fluid physical state and therefore can more easily penetrate into soil and water [1].

Fluid for washing windshield glass: Fluid for washing windshield glass contains alcohol, detergent, water and small amount of antifreeze.

If it is possible this fluid should be used again. Flooding into the soil may result in contamination of soil, groundwater and air due to their evaporation [3].

Asbestos: Some older ELVs may contain asbestos (e.g. certain brake pad linings). Regulations require the location of any components that may contain asbestos to be identified on the vehicle. A visual inspection of the vehicle must be made during the de-pollution procedure to identify if the ELV contains any notices indicating parts that contain asbestos. If any asbestos containing components are identified during this procedure, they must be removed. The procedure used to remove the asbestos containing components must follow all health and safety guidelines relating to asbestos [16].

Fuel: Fuel combustion emits gases which are one of the main causes of the greenhouse effect. Carbon dioxide is one of the main causes of global warming. The result of air pollution with fuel is smog, which occurs in urban areas and causing. The discharge of fuel into water systems and soil poses a danger [3].

Glass: The recycling of glass can save more than 19% of energy compared to the production of natural materials. For every 10% of used glass splinters saves 2.5% of energy, and with each tone used splinters of glass saves 1.2% tones of natural raw materials [20].

Of all the basic elements used in the production of glass from primary raw materials, soda most polluting environment. One ton of soda contained about 950 kg of sodium chloride (NaCl), which significantly increases the concentration of salts in the water. Increasing glass splinters in the preparation of the glass significantly improves the balance of the environment [21].

Tires: It is estimated that about 210.000 tons of tires were generated by end-of-life vehicles in the period 2006-2010. Tires are governed by a different regulation, according to whether they come from ATFs or repair garages. In both cases, however, depending on the state of the tire itself, we can speak of its reuse, recycling and recovery. This may well be one of the vehicle components with most applications nowadays [24].

With fulfilment legislature norms for managing with this materials and development of different technologies for their detoxification and recycling it can be achieved higher level for safety environment and all with the aim for creating a better place for leaving [1].

CONCLUSION

Community sustainable development largely depends on the use of strategic resources. Majorities a part of components which are analyzed by the paper are non-

biodegradable and because of that their adequate treatment are of the crucial importance for the environment and quality of life in it.

Recycling of the components which are mentioned in the paper could be economically profitable if recycling technologies using properly and if materials which could be reused are carefully treated.

Development and availability level of the recycling technologies in the Republic of Serbia is on the low level but with step by step scientific-technological development, with rising of awareness of population about the importance of the ELV recycling, with following examples of good practice of recycling in the countries where is that economic sector on the high level and also with fulfilling of Legislation norms it could be achieved certain level where ecologic community could survive.

ACKNOWLEDGMENT

This paper is a result of the research activities conducted under the project TR 35033, which is financed by the Ministry of Education, Science and Technological Development of Republic of Serbia.

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CHANGES IN THE FAUNA OF HYDROMELIORATION CHANNELS UNDER CHANGED AGRICULTURAL CONDITIONS

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Received: November 2016

Abstract

Over the past 30 years changed conditions and the occurrence of fauna have exhibited significant differences. Chemical composition of water has changed considerably. Indexes of zooplankton variation are very high and exceed 50% and 30% for macrozoobenthos, respectively. Both groups showed high diversity (zooplankton - 145 and zoobenthos - 96 species). The vegetation has changed as well with predominant riparian woody vegetation. The composition of zooplankton, especially the group of cladocerans, indicates moderate acidification of water. Changes that occurred reflect the conditions of fertilization, crop production, and also hydrological regime as a result of decreased functionality of hydromelioration systems, especially pumping stations probably including temperature conditions in the country as well.

Keyword: *Land use, acidification, zooplankton, makrozoobenthos*

INTRODUCTION

In the conditions of East Slovak Lowland (Východoslovenská nížina) lowland hydromeriolation channels represent a dominant landscape element stretching over 450 km in an area of 50 by 50 km. A hydromeriolation system was built in what was originally a wetland area in the 60s of the previous century. This system consisted of channels of various degrees and water was drained into river recipients with the use of pumping stations. The surrounding landscape was intensively used with the application of high dosages of fertilizers. This state changed significantly after 1989 when agricultural production underwent a great change. The production was no longer used and became gradually used with a changed structure of agricultural crops. No organization has taken control over the channel system. At present time especially intensive growth of water macrovegetation and bank shrub vegetation have led to successional processes in melioration channels. The originally lotic-lenitic biotope is becoming a quickly silting biotope with significantly changed ecological conditions.

In this paper, we used the published results (Terek 1990; Brázda, Terek 1996) and unpublished results gained in 2014-2015.

CHARACTERISTICS OF TERRITORY

The hydromelioration channel system is in the East Slovak Lowland (2l^{o}3´ - 22^{o}3´ of latitude, 48^{o}2´ - 49^{o}0´ of longitude) in the region of the former floodplain of the River Ondava. The geological base is formed by fluvial plain sediments with a prevalence of heavy soils, mainly clayish and gleyic. The region of interest has a warm lowland climate with January temperatures of l.5 - 4^{o}C and July temperatures of l8.5 - l9.5^{o}C. Annual precipitation is 500-700 mm, with peak rain in the vegetational season [1]. Before melioration interventions, the territory had a swamp character; at the present time it is utilized as arable land, pasture, and the waterlogged parts as extensive grass fields.

The water in the channels is mainly stagnant; streaming occurs at high water levels and during pumping. The basin of channel K-3 is characterized by a great portion of arable land. The main water source is the territory beyond the Trnavka River. The channel K$_{-4}$ has a great portion of extensively utilized grass fields, and it drains off the infiltration from Trnavka, and partly drains off the waterlogged grass fields.

During our observation, a pumping station was under reconstruction. The variation of the level regime was minimal; we found the visible changes during rainstorms, the lowest, i.e. -30 cm, at the end of the summer and in the winter. The channels' gradient is

l%. On the observed profiles, the cover corresponding with cycles was investigated. This is characteristic for surface water soil and in l989 the hollowing of the bed was done by heavy machinery.

K_3-l: the channel bed has a trapezoidal shape; maximal width in the crown is 8 m, the depth is l.5 m. There is no accompanying vegetational wood. The channel bed is formed by anaerobic mud with a large amount of organic matter. The macrovegetation is formed by submersed vegetation, to a lesser extent by natant vegetation. The community is dominated by *Ceratophylletum demersi* (Soó l927, Eggler l933), which has asserted itself against *Potametum lucentis* Hueck l93l, with *Myriophyllum spicatum* and *M. verticillatum*.

K_3-2: accompanying vegetation is formed by willows and alders. The channel profile is significantly covered with soil. Submersed vegetation is suppressed in comparison with K_3-l. *Elodeotum Canadensis* Eggler l933 prevails and has interfered with the sinuses of union *Lemnion minaris* R. Tuxen l955. In l989 *Stratiodes alloides* started to penetrate.

K_4: has arisen through hollowing of the existing Nöll channel, constructed in the 1940s. It has a double-trapezoidal shape, partly embedded; the bed is paved with concrete blocks. The width of the lower part is approx. 9 m (K_4-l); the width of the upper part is 4 m (K_4-2). The total length is 25l6 m, gradient 0.l%. It is without accompanying wood verdure.

K_4-l: The *Lemnatum minoris* community is dominant and is formed by the *Lemna minor*, *L. trisulca* and *Spirodela polyrhyza* species.

K_4-2: The *Hydrochari* community dominates with *Stratiocetum subasoc.typicum* (Hejný, Berta l972).

MATERIALS AND METHODS

The subject of observation is two channels differing in size and in the way of agricultural utilisation of the surrounding country. The observation of the limnologic features as well as sample acquisition of benthos has begun in 1986-1988 in profiles K_3-1 a K_4-1. (K_3-1, K_3-2 and on K_4 on profiles (K_4-1, K_4-2). Samples were taken by Birge-Eckman sampler (15 x 15 cm) x 3 and washed on sieve with mesh size 0.8 mm.

The samples for the observation of physico-chemical properties of waters (temperature, pH, conductivity, turbidity and oxygen content) were determined in situ by water analyzer HORIBA U-2; chemical properties: ammonia, nitrates, nitrites, phosphates, hardness, chlorides, calcium, magnesium and potassium were all determined according to ČSN 83 0532.

The samples of net zooplankton were sampled by Friedinger collector with 2 dm^3 volume (total volume 20 dm^3). The content was fixed in 4% formalin, and calculated in Kolkwitz chambers. All samples were taken at one-month intervals in l988-89.

During in 2014 -15 we collected representative samples once in the spring and summer and twice in the autumn. The consequences of changing climatic, socio - economic and agronomic conditions show a slight acidification. Evaluation based on the species diversity of cladocerans indicates [3] a low degree of stability in hydromelioration channels.

We took samples of submerged vegetation and macrofauna by the means of a device resembling a book with the dimensions 27x14 cm. Abundance of macroevertebrates of bentic, natant, submerged fauna were recalculated per m^{-2}.

The resemblance of species is stated by means of Sörens index (2S.100):(S1+S2).

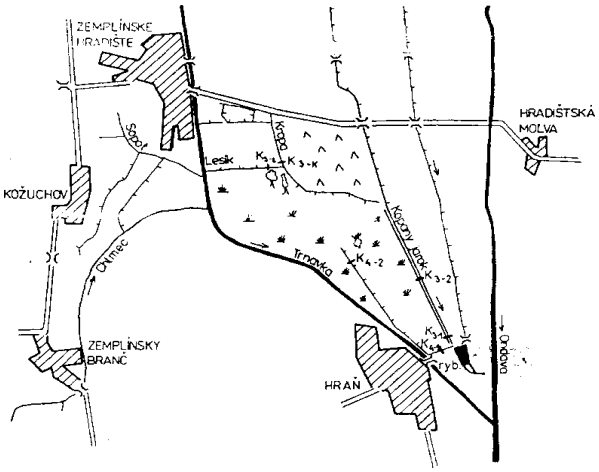

Figure l
Channel network in Hran region with sampling place

RESULTTS AND DISCUSSION

The work is an attempt to faunal analysis of zooplankton and macrozoobenthos artificial anthropogenic landscape elements - hydromelioration channels. Irrigation and drainage canals that are now neglected, but acquire an important function as connective, and stabilizing the gene landscape element. Fauna composition will vary depending on environmental factors related to climate change and the way the intensity of land use.

In spite of the small number of observed channels (2) and their profiles (4) a relatively high diversity of macrozoobenthos species was not perceived (96 taxons) with the weight dominance of Bivalvia and Isopoda. Rich revival was found on water microvegetation, in the sediment the dominant are microdetritofag forms (Chironomidae), in the submerged and natant vegetation macrodetritofags forms are dominant. Low index of species similarity (Sö-I) among individual profiles in both channels and years shows considerable different ecological conditions changing from collecting channels (collectors) to lower sections. Concerning biomass of zoobenthos we can characterise the observed

channels as highly to very highly productive. Biomass and abundance is relatively high, which is also important for the use for fish farming. The bulk of kategory belongs to the beta-mesosaprobite with inclination to alpha-mesosaprobite.

In two hydromelioration channels (four profiles) in the Hraň region in the East Slovak Lowland the net zooplankton was observed during three time intervals (1985-87, 1988-89, and 2014-15). High species diversity (43 taxa of Cladocera, 21 Copepoda, and 81 Rotatoria) was found and characterized by low abundance and biomass together with great alternation of species.

With regard to the fact that the sampling places include the scale of conditions, the dynamics have various characters. One of the important facts is that that the profiles K_3-l and K_4-l, which are connected with an artificial reservoir, have a course similar to that of other greater stagnant waters. The course of seasonal dynamics is significantly influenced by climatic conditions, which determine the hydrological ones.

Through analysis of this state we come to the conclusion that the reason for this state is the great heterogeneity of ecological conditions in time and space, which are caused by the changes due to variations of water levels, as well as the variable ratio of underground and surface water at the formation of physico-chemical and biological states.

The alternation of lenitic and lotic states causes frequent disturbances which play a key part in the structure and successive processes.

These processes are often interrupted, which forms the ecological niches that are permanently occupied by new species, the transfer of which is secured also by water birds, because the territory is one for the passage of birds.

The consequences of changing climatic, socio - economic and agronomic conditions show a slight acidification. Evaluation based on the species diversity of cladocerans indicates a low degree of stability in hydromelioration channels.

TABLE I
Values of the main chemical of channel water

Profiles	K-3-1		K-3-2		K-4-1		K-4-2	
Y.observed	1998	2016	1998	2016	1998	2016	1998	2016
Hardness °N	18,5	10,2	20,7	8,0	22,4	10,1	22,4	10,2
NH_4 mg.l^{-1}	1,3	0,05	1,4	0,9	1,9	0,04	1,9	0,05
NO_2 mg.l^{-1}	0,02	0,00	0,04	0,00	0,05	0,00	0,05	0,01
NO_3 mg.l^{-1}	2,52	2,2	2,63	2,2	2,4	2,0	2,4	2,1
PO_4 mg.l^{-1}	1,4	0,6	1,65	1,2	0,37	0,2	0,37	0,3
Ca mg.l^{-1}	89,7	48,7	105,9	37,2	91,8	41,5	91,8	41,6
Mg mg.l^{-1}	25,7	14,8	28,2	12,2	24	18,2	25	18,2
Cl mg.l^{-1}	46,8	31,0	54,2	27,7	47,6	29,5	47,6	29,6

CONCLUSION

In two hydromelioration channels (four profiles) in the Hraň region in the East Slovak Lowland the net zooplankton was observed during three time intervals (1985-87, 1988-89, and 2014-15). A high species diversity 43 taxa of Cladocera, 21 Copepoda, 81 Rotatoria) was found and characterized by low abundance and biomass together with great alternation of species. In spite of the small number of observed channels a relatively high diversity of macrozoobenthos species was not perceived (96 taxons) with the weight dominance of Bivalvia and Isopoda. Fauna analysis will serve to assess the impact of climate change and land use.

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ECOLOGICALLY ACTIVE SURFACES AND ZOOPLANKTON STRUCTURE IN THE FLOODED AREA OF LATORICA

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Received: November 2016

Abstract

The research was conducted in five localities of the inside and outside embankment areas in the protected landscape area (Chránená krajinná oblasť Latorica Protected landscape area. During the period of two years 118 taxa of zooplankton were detected. Of these, 76 were taxa of Rotatoria, 32 were taxa of Cladocera and 10 were taxa of Copepoda. Species diversity in the inside embankment area was lower (61 taxa) than in localities in the inside embankment area (107 taxa). The limiting factor underlying the development of zooplankton was the effect of floods accompanied by increased turbidity. The floods had an inhibitory effect on the abundance of zooplankton. During floods, the abundance of zooplankton was extremely low with mean abundance of 24.5 n.l^{-1}. However, decrease in water level led to a significant qualitative and quantitative composition of crustaceoplankton and rotifers. Water levels in particular localities were evidently associated with the abundance and species composition. In addition to generally known physical and chemical, hydrological and biological factors, the qualitative and quantitative parameters of zooplankton are also affected by the ratio of contact areas to volume (EAS). This factor is presented with respect to particular localities.

Keyword: *Cladocera, Copepoda, Rotatoria, dead arms, inside embankment area, outside embankment area*

INTRODUCTION

The issue of zooplankton origination in the flooded area and its effect on the main stream has been the subject of studies as early as the beginning of the previous century. Authors assume that the origin of the true potamozooplankton is in river arms, or other still water reservoirs along river basins [17]. Less attention is paid to its dynamics.

The structure of zooplankton is affected (physical and chcmical factors such as temperature, oxygen concentration, and the content of nutritional elements) especially by P-PO_4^{3-}, a N-NO_3^- and trophic conditions. Among other factors with a significant effect are water flow velocity and turbidity. In addition to the factors specified above, the presence of clay particles also has a profound effect on incidence of filtrators. This factor, although from other types of water, has been reported by Grimalský (1967) found an inverse relationship between the incidence of rotifers and flow and turbidity. Kirk, Gilbert [6], Akopian et al. [1] found a direct association between suspended clay and the dynamics of planktonic rotifers (Rotatoria) and cladocerans (Cladocera). The resulting turbidity limits the penetration of light, which leads to limited production of the biomass of phytoplankton [5], [8].

Changes in the structure of community caused by floods show a change in their abundance rather than in species composition.

Vranovský [17] found that the quantity of zooplankton in the arms of the Danube River increased significantly during stagnation longer than 30 days; during stagnation shorter than 30 days and at an increased water flow velocity the quantity of zooplankton increased minimally or not at all. Visser and Stipps [16] reported a negative association between turbulence and zooplankton ingestion rates.

Terek [11] connects high diversity of species in the flooded areas with high variability of ecological conditions in time and space, and also with permanent supplying species with rafting and transport by birds. The structure of zooplankton in flooded reservoirs in both inside embankment and outside embankment areas of the river Latorica, that is, the remnants of cutoff lakes and mining pits shows a high diversity of species detected in the long-term on the Latorica River [10], [11]. Similar findings were reported for the river Rhine [14], where high alternation of species was observed during a short monitoring period. Ecologically diverse conditions in a small area are subject to constant changes in contact, boundary

zones, or ecologically active surfaces (EAS), where border effect is manifested by increased species was observed during a short monitoring period. Ecologically diverse conditions in a small area are subject to constant changes in contact, boundary zones, or ecologically active surfaces (EAS), where border effect is manifested by increased species.
Diversity and its production [12]. Changes in the water column represent a significant factor that consequently determines physical-chemical and biological conditions. This state may be expressed as the ratio of water volume to the size of contact areas with another environment, that is, boundary zones, where the boundary effect is manifested by increased activity. The recommended evaluation of the ratio of contact surfaces per unit volume, or surface or weight unit may aid in clarifying this state. This ratio can be regarded as the degree of heterogeneity of the conditions after taking into account the environmental gradient. This ratio creates ecological conditions for changes that contribute to the abundance and diversity of species. The contact surface to volume coefficient (CS:V) includes several environmental factors and determines the potential and the direction in which a particular community develops. This coefficient plays a key role in comparing various morphometric characteristics, especially reservoir depth.

GENERAL CHARACTERISTIC OF THE MONITORED AREA

Geographic coordinates of the monitored area, which is also a part of the protected area according to Ramsar convention on wetlands, are 48º 28' N, and 22º 00' E. Altimetry (mean, minimum and maximum altitude) is 100 m (99 – 103 m). This area includes a part of an area flooded regularly by the Latorica River. The area extends from the embankments at the Slovak-Ukrainian border to the confluence with the Laborec River in the Chránená krajinná oblasť Latorica protected landscape area in the southern part of the Východoslovenská nížina lowland. The river channel itself consists of an artificial channel only. The orthophotomap of the area (Figure 1) shows 5 monitored localities (Balatón, Cesta, Pri hlavnom potoku, Kubík and Mimohrádzový priestor).

Figure.1
Orthophoto map of the observed area

HYDROLOGY

The Latorica River is a border river rising in Východné Karpaty Mountains in Ukraine. Hydrological regime is determined by the predominant flysch substrate with fan-shaped river basin rising in Východné Karpaty Mountains. Low permeability of the flysch and shallow circulation of subsurface water accelerate the surface runoff. Main rainfall runoff from this area is approximately 50%, which may increase up to 80% during extreme discharges. High discharges take place especially during snow-melt in the spring and after short-term heavy rain. Annual runoff of the Latorica river is 33.7 $m^3.s^{-1}$. During floods the annual runoff increases as much as twenty times. The Latorica River has the character of a typical lowland river. In the past the river consisted of a network of meanders and oxbow lakes.

DESCRIPTION OF STATIONARY AREAS

The research was conducted in five stationary areas (localities). Four localities (referred to as Balatón, Cesta, Mŕtve rameno pri hlavnom toku and Kubík) are located in the inside embankment area, where they join together during the overflow of the river Latorica. One locality (referred to as Mimohrádzový priestor) is isolated and situated behind the embankment. The localities Mimohrádzový priestor, Balatón, Cesta and Pri hlavnom toku in the inside embankment area represent a natural and original network of the Latorica river. The locality Kubík is an anthropogenic landscape element where the material for building the embankment was taken from. The locality is situated 10 meters from the toe of embankment.

SAMPLING METHODS

Samples were collected between 11:00 a.m. and 2:30 p.m using the Friedinger sampler with the volume of 2 liters and a total volume of 20 liters regularly every month from November 16, 2006 to November 2, 2008. To collect the samples we used a sampler hanging from a piece of rope from the immediate littoral area. After sampling, the content was filtered through sieve no. 16 and was quantitatively evaluated in Kolkwitz chambers (3 x 7 ml) in laboratory conditions, that is, from a total sample of 50 ml of thickened material and expressed per 1 liter.
The results were analyzed in a time sequence, that is, during 25 months, but also with regard to mean values of water level and the abundance and diversity of species. During the years of 2014-2015, we took qualitative samples on an irregular basis.
Chemical composition: During regular sampling, we used a portable water analyzer HORIBA to measure pH, the content of dissolved oxygen, conductivity, water temperature and salinity in situ. These properties were measured at a depth of 40 cm.

In addition to the measurements of physico-chemical parameters of water, we sampled approximately 0.5 l of water from every locality to evaluate chemical properties ($N\text{-}NO_3$, $N\text{-}NO_2$, $N\text{-}NH_4^+$, $P\text{-}PO_4^{3-}$, SO_4^{2-} and Cl^-). The properties were evaluated in laboratory conditions using the instrument Spectroquant NOVA 60.

RESULTS

To clarify the dynamics of the zooplankton abundance affected by floods during the period of two years we relied on the data about the water level fluctuation on the Latorica River obtained from the water gauge station of Veľké Kapušany. These data were obtained from regular measurements of the watersheds of the Bodrog River and the Hornad River and the Slovak Hydrometeorological Institute (Figure 2), as well as from our own observations of water levels and the degree of turbidity in the localities especially during floods. During the 25-month moinitoring period, we observed three flood periods with several maximum water stages. During these flood periods we observed stable inter-embankment localities with a low water level.

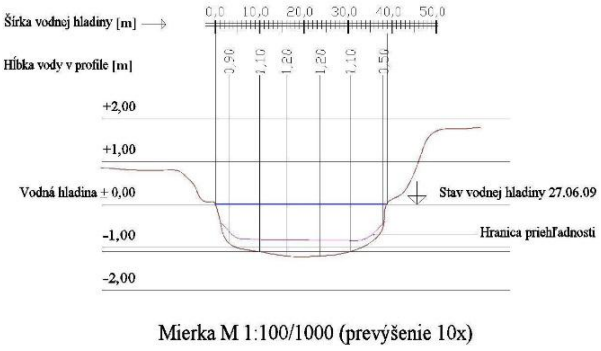

Figure 2
Cross section of oxbow lake of the locality Balaton

Approximately at the water level of 600 cm at the water gauge station of Latorica – Veľké Kapušany, the arms start to progressively fill with water and during the flood flow the water overflows also the river banks, and the entire inundation area gets flooded. When the flood wave subsides the arms get gradually empty until the moment when the total disconnection from the main stream occurs and the water in the arms remains almost without flow. Flood flows usually occur at the beginning of spring and also during the summer season [7].

Mean abundance of zooplankton as of 10 August 2008 inside the embankment area was 38.2 $n.l^{-1}$, and reached the second highest value of 257.9 $n.l^{-1}$ in the outside embankment area. This state is associated with sudden deterioration in ecological conditions, which even leads to the reduction in zooplankton density or to its outflow from the flooded objects (inhibitory effect of turbidity and turbulence, washout, reduction in water transparency, etc.). However the development continues under stable conditions without greater changes in the locality in the outside embankment area. Detected physico-chemical properties did not exceed the limit of values typical for this type of water.

TABLE 1
Species composition of particular groups of zooplankton and mean depth of monitored localities

Taxonomická skupina	Mimohrádzový priestor	Balatón	Cesta	Pri hlavnom toku	Kubík
Rotatoria	37	47	43	45	41
Cladocera	17	21	18	19	23
Copepoda	7	7	8	6	8
Zooplanktón spolu:	61	75	69	70	72
Priemerná hĺbka vody [cm]:	33,2	159,2	337,6	208,5	158,8

DISCUSSION

The contact between two media (bed sediment – air) leads to transformation and energy exchange, where synergic, antagonistic, and physical, chemical, biological processes interact. Biological activity in this area is much greater than that in the area of free water. The greater the area of "ecologically active surfaces", the higher the diversity of ecological conditions, which results in a qualitative and quantitative development. Regardless of varied bed morphology shallow reservoirs have a larger contact surface to water volume than deep reservoirs. Therefore, depth is one of the parameters having effect on biological activity through the area of ecologically active surfaces.

Ecologically diverse conditions in a small area are determined by constant changes at contact (boundary) zones, or ecologically active surfaces manifested by boundary effect showing increased species diversity, abundance and production [10]. Amoros [2] highlights the association between species diversity on a side arm through the design of a sinuous pathway combined with variation of water depth, wetted width, and substrate grain size. Figure 3 shows that species diversity in the localities of the inside embankment area increases with reducing reservoir depth. However, changes in the number of taxa are very small because these objects are not permanently isolated. Regular floods result in the mixing of species. We may agree with the findings reported by Nielsen [9] who found that changes in the structure of community caused by floods manifest by the change in their number rather than in species composition.

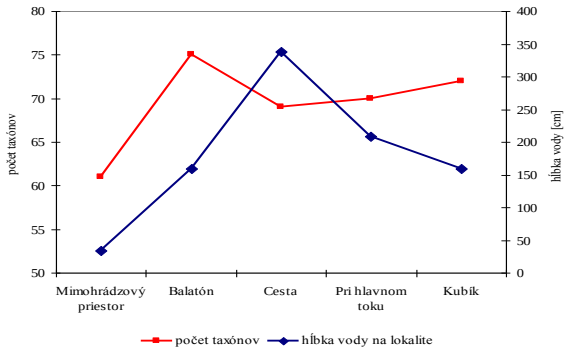

Figure 3
The relationship of species diversity to the depth of the study site

The trend of increase in species diversity with reducing reservoir depth does not apply to the locality of Mimohrádzový priestor, where the lowest number of taxa (61) was found at the lowest water depth of 33.2 cm. The result from different ecological conditions in comparison with the inside embankment area showed that there is a lack of already mentioned supply of species with zooplankton outflown from the surrounding dead arms (euplankton) and also species coming directly from the flow (potamoplankton). We assume that this is primarily caused by the size of contact areas and the volume, which does not lead to both changes in parameters and supply of new species by flush. On the other hand, there is larger abundance and biomass. Data about the number of taxa from three basic groups of zooplankton (Rotatoria, Copepoda, Cladocera) and the mean water depth in particular localities are presented in Table 2.

TABLE 2
Mean values of physico-chemical properties for particular localities

Ukazovateľ	Mimohrádzový priestor	Balatón	Cesta	Pri hlavnom toku	Kubík
pH [-]	7,0	7,6	7,5	7,5	7,6
konduktivita [mS.m^{-1}]	0,23	0,20	0,23	0,20	0,20
O_2 [mg.l^{-1}]	6,8	7,0	6,6	6,5	6,1
teplota [°C]	10,3	13,0	12,5	13,2	11,3
salinita [mg.l^{-1}]	0,00	0,00	0,00	0,00	0,00
N-NO^{-}_{3} [mg.l^{-1}]	0,91	1,07	0,96	1,13	1,34
N-NO^{-}_{2} [mg.l^{-1}]	0,03	0,03	0,03	0,03	0,03
N-NH^{+}_{4} [mg.l^{-1}]	< 0,03	< 0,03	< 0,03	< 0,03	< 0,03
P-PO^{-}_{4} [mg.l^{-1}]	0,13	0,14	0,08	0,14	0,15
SO^{-2}_{4} [mg.l^{-1}]	104,4	93,1	101,2	95,6	91,3
Cl^{-} [mg.l^{-1}]	9,3	7,2	8,6	7,4	6,3

Changes in depth parameters, that is, the ratio of volume to the contact area, lead to qualitative and quantitative changes with a certain delay. It is a fact that dilution caused by the tidal wave and the outflow of individuals into the main stream contributes to the decrease in the number of both individuals and species. According to Vranovský [17] time interval for reproduction / origination of a new generation is 30 days. The results were analyzed in a time sequence, that is, during a 25-month period, but with regard to mean values of water levels and the number and diversity of species.

The Sørensen index (Figure 4) and the Jaccard index showed the highest degree of faunistic similarity between the localities of Balatón and Cesta. Indexes of similarity according to Sørensen and Jaccard between the localities of Balatón and Cesta and other localities decrease in the following order: Kubík, Pri hlavnom toku and Mimohrádzová priestor. However, species similarity is significantly different and the proximity of localities is evident.

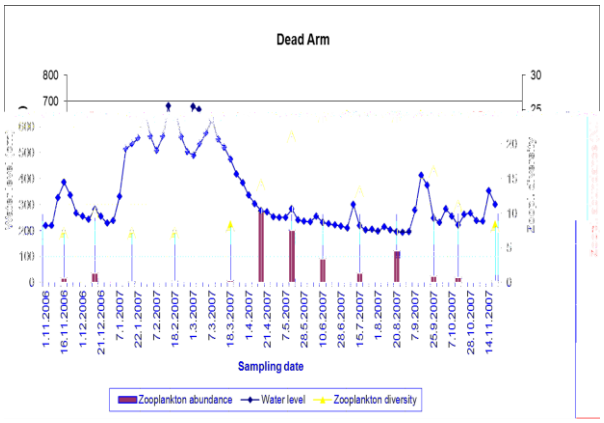

Figure 4
The relationship of species diversity to the depth of the study site

The greatest faunistic difference was found between the localities of Mimohrádzový priestor and the localities in the inside embankment area.

The subsidence of the flood wave leads to repeated increase in the abundance of euplanktonic species. The structure of zooplankton, especially species composition, abundance, biomass and seasonal dynamics are affected by the fluctuation of water levels in the arms of the river's inundation areas. This unstable hydrological regime prevents the development of planktonic crustaceans.

Abundance of zooplankton is subject to significant fluctuation during the year and the most important factors determining its development are water temperature, turbidity, water flow velocity, abundance of phytoplankton and consumption pressure of fish and birds [15]. The development of zooplankton in mining pits is inhibited especially by turbidity caused by outflow of clay elements off the banks of mining pits (Terek, 2005).

The associations may be observed for mean values of reservoir depth and also for dynamic changes during

floods. More shallow water areas multiply temperature and trophic conditions.

CONCLUSION

The association between depth and qualitative and quantitative proportions of zooplankton in the flooded areas was evident as shown in particular figures as well as by statistical significance. The abundance and species diversity manifesting in a time sequence are related to the water column. The reservoir depth reflects a variety of hydrobiological properties of the environment, especially the size of ecologically active surfaces, transparency and production.

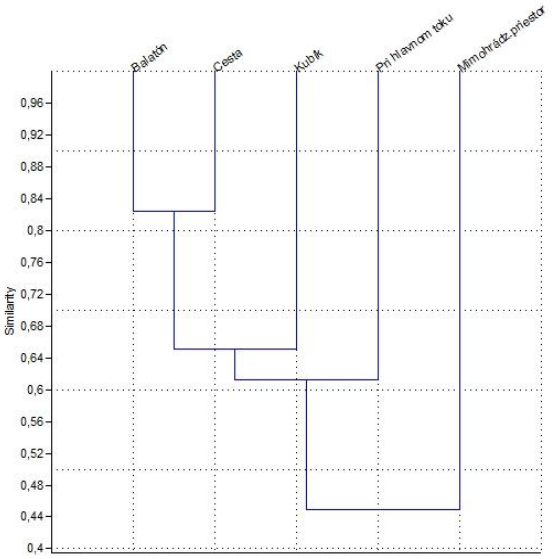

Figure 5
Cluster analysis faunistic similarities expressed by Sorensen index

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RESEARCH OF SOUND QUALITY IN INTERIOR OF AUTOMOBILE BY PSYCHOACOUSTIC EVALUATION METHODS

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Received: November 2016

Abstract

The presented paper is oriented into an area of sound engineering, an area of automobile research, development and production. The requirements of customers on drive comfort and with it vibration acoustic properties of automobile are growing and stricter ones in the last decade. The contribution presents the own research of authors, realised by evaluation with psychoacoustic methods of sound quality in the interior of chosen automobile marks. The authors used the original binaural measuring technique in the research – psychoacoustic (artificial) head, seven stage of rating scale and selected methods of statistical analysis. The vehicle crew is aware of the (formal) perceived quality of the vehicle based on the multi-faceted interconnected sensory impressions, which are subject to specific interactive effects. An assessment of vehicle noise also gets another dimension, when the person, on who are the noise effects, he may as survive the driving situation, but also interactively influence on the situation. The aim is to make possible conceptual formation of acoustics instead of responding to adverse on desirable, respectively unwanted sounds (so-called active sound design).

INTRODUCTION

There are several authors dealing with the problems of sound quality evaluation. For the needs of the evaluation (testing) of sound quality, there are several approaches available. They can be classified into two main categories: subjective methods and objective methods of sound quality evaluation. The paper focuses on the analysis of subjective methods of sound quality evaluation. There is the specific experiment presented.

ANALYSIS OF METHODS OF SOUND QUALITY EVALUATION

The evaluation of sound quality can be carried out by subjective or objective methods - Figure 1 [1].

SUBJECTIVE METHODS OF EVALUATION

There are many ways how to carry out the subjective evaluation of sound, from informal listening (monitoring) of a recording up to formal evaluation of sound quality. The respondents hereinafter referred to as (reviewers), can be chosen according to various criteria. The tests used at the subjective evaluation of sounds are characterized by certain problems or restrictions, which are to be kept in mind and minimized as possible.

Figure 1
Methods of Sound Evaluation

On the other hand, this type of evaluation has its advantages, including: it is fast, simple and financially viable. For the purposes of the testing, audio records are prepared in advance and they are successively played to a reviewer, who records his/her subjective opinion into a questionnaire prepared in advance. The quality of evaluating process depends on the test complexity and detail of the requested results. Psychoacoustic Evaluation Methods (PEM) use several techniques. In the table below (Table. 1), the most frequently used methods applied in connection with psychoacoustic measurements are presented. Every method has its advantages and disadvantages (Table. 2). By this reason, their combinations are also often used in the practice.

TABLE I
COMPARISON OF METHODS USED IN PSYCHOACOUSTICS

Method of Measuring	Brief Characteristics	Advantages of the Method	Disadvantages of the Method
Method of Constant Stimuli	It is the most accurate and used measuring method in psychoacoustics. By this method, absolute thresholds are detected. The basis of the measurements consist in the fact that the stimuli phases are chosen, from which approximately a half is of the size above the expected value of the absolute threshold and other are of the size below the expected value of the absolute threshold, which is to be ascertained. Every of the stimuli, in any order repeatedly (50 - 200 times) influences on a respondent the task of whom is to assign one of two options, whether he/she notices the given stimulus or not.	• wide application possibilities • high accuracy • simple task for a respondent	• time demanding method • large number of repetitions • distorted review of a testing person
Method of Paired Comparisons	The basis of the method consists in a sequential comparison of every of all n reviewed stimuli with every one of all other stimuli. The result of every comparison is the respondent's determination of more dominant stimulus according to the criterion specified in advance.	• wide applicability of the method	• time demanding method • the respondent fatigue, what could result in errors in the measurement
Method of Stimuli Ordering	The method consists in ordering of measured sound stimuli in the foreground by the respondent, while the respond assigns an order number to every stimulus according to the criterion specified in advance. It is not permitted to assign the same number to various stimuli.	• wide applicability • easy and fast measuring of relatively large number of objects	• dependence on time order, in which the stimuli act on the respondents
Method of Stimuli Adjustment	The method principle is in an automated change of measured signal acoustic pressure level (continuously rises or descends) and, at the same time, its frequency continuously rises. The intensity of sound signal (above-threshold frequency of 125 Hz) begins to descend continuously. When respondent cannot hear the sound any longer, he/she will press a pushbutton and the whole process repeats alternately until	• high efficiency • a respondent active participation • interesting method from the point of view of respondents	• the measurement is to be carried out with every respondent

Method of Measuring	Brief Characteristics	Advantages of the Method	Disadvantages of the Method
	the increasing frequency of the sound stimulus reaches the maximum (approx. 8,000 Hz).		

TABLE II
COMPARISON OF METHODS

Method of Measurement	Measurement Level	Time Demandingness	Difficulty for Respondents	Laboriousness of Experiment Preparation	Remarks
Method of Constant Stimuli	Ratio Scale	Large	Small	Medium	Suitable for measuring of absolute thresholds
Method of Paired Comparisons	Order to Interval Scale	Large	Small	Medium	Suitable at small differences among stimuli
Method of Stimuli Ordering	Order to Interval Scale	Medium	Small	Small	Suitable at large number of stimuli
Method of Stimuli Adjustment	Ratio Scale	Small	Small	Small	Suitable for fast detection of optimal value

There are many statistical techniques and tools, which are useful at sound quality analysis performance. The techniques range from relatively simple tests (t-test, chi squared test or ANOVA test) up to more complicated tests such as Principal Component Analysis (PCA). The employment of these tests depends on the sound quality test structure, hypotheses, which are to be tested and knowledge, which can be obtained from the tests performed. The design of every sound quality test should include the careful planning of selection of statistical methods that will be used.

OBJECTIVE METHODS OF EVALUATION

In the present, the technical means begin to break through for the needs of performance of psychoacoustic measurements. They include highly sophisticated systems designated for measuring and requiring highly specialized software support. This support creates a space for development of analyses and predictions with measured data.

Perception of sound by two ears is called binaural hearing. Such hearing enables to hear sounds from right and left ears and is able to localize more easily the sound direction. Binaural hearing depends, to the great extent, on geometrical parameters of a human body, especially of a main body, head and ears.

Psychoacoustic head (or so called artificial head) resembles a human head and it is equipped by two microphones built in the ears. It has similar aural and acoustic properties as a human head in Figure 2.

APPLICATION OF SUBJECTIVE METHOD OF ASSESSMENT OF SOUND QUALITY IN A CAR INTERIOR

For the needs of subjective assessment of sound quality in car interior, the method using a questionnaire survey has been applied. The basis was a preparation of the questionnaire with suitably chosen evaluation scale and preparation of played sounds.

Figure 2
Artificial Head HEAD Acoustics (FME TU Kosice Laboratory)

Psychoacoustic or artificial head enables to perform objective measurements of parameters given in Table 3.

TABLE III
COMPARISON OF METHODS

Speed¤	Speeds¤			Average·Value¤
	90·km/h¤	110·km/h	130·km/h	
Car¤ BMW·5¤	4.76¤	5.1¤	4.4¤	4.75¤
Audi·A4¤	4.43¤	4.67¤	4.72¤	4.61¤
Skoda·Octavia¤	2.33¤	2.24¤	1.86¤	2.81¤
Skoda·Superb¤	4.85¤	5.0¤	4.42¤	4.76¤

The records were made by binaural measuring technique in four different cars (BMW 525d, Audi A4 2.0 TDi, Škoda Octavia 1.6 GLX, Škoda Superb 2.0 TDi) at different speeds (90 km/ hour, 110 km/hour and 130 km/hour). The results of evaluation of pleasure of sound in car interior by respondents are clearly given in the Table 4.

In overall evaluation, it proved that the respondents identified the sound of Skoda Superb 2.0 TDi to be the most pleasant sound.

The car brands BMW525 d and Audi A4 2.0 TDi followed in a close proximity. The least pleasant sound determined by the respondents was the one of Skoda Octavia 1.6 GLX.

Taking the individual speeds of cars, e.g. at 90 km/h, the respondents determined that the most pleasant sound is the one of SKODA Superb 2.0 TDi, at 110 km/h, the respondents said that the most pleasant was the one of BMW525d and at 130 km/h, the respondents decided that the most pleasant sound or the least disturbing sound is the sound of Audi A4 2.0 TDi. The positions of cars depending on pleasure of perceived sound in a car interior are given on Figure 3.

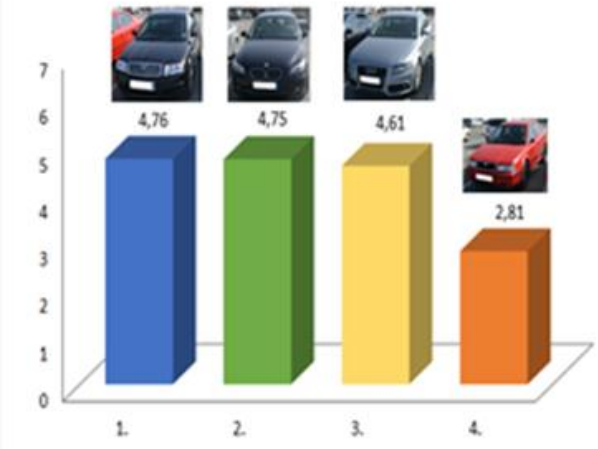

Figure 3
Placings of Particular Cars

TABLE IV
EVALUATION OF SOUND BY RESPONDENTS

Psychoacoustic Quantities	Characteristics	Unit of Measuring
Loudness	A property of aural perception, according to which it is possible to arrange the sounds on the scale from quiet to loud ones.	Designation: N Unit: 1 son
Harshness	It is one of the dimensions of a sound colour. The sound at higher harmonic components begins to be harsh and sharp. The harshness is a quantity which is not standardized yet. There are several methods of its calculation.	Designation: S Unit: 2 cum
Roughness	It characterizes a perception, at which the time changes of sound signal amplitude are so fast that human ears cannot notice them. It arises as a result of a modulation within the interval of modulation frequencies from 15 MHz to 300 MHz	Designation: R Unit: asper
Tonality	It expresses the size of perceived ratio of tone and noise quality of sound. The tonality does not depend on loudness. It descends with increasing level of acoustical pressure of rising white noise.	Designation: T Unit: 0

ACKNOWLEDGMENT

This work was supported by the Slovak research and development agency under the contract No. APVV – 15 – 0327.

CONCLUSION

A car is perceived interactively, by several senses at the same time and in complex and it is evaluated on the basis of parametrical findings. Customers do not distinguish among particular senses, they evaluate the specific categories and they derive overall complex reviews from the particular evaluations. In addition, a customer develops the perceived quality of a car on the basis of multiform and interconnected sensual impressions, which are subject to specific interactive effects. The reviewing of a car noise has another dimension if a person who hears them can not only experience the driving situation but also to influence it interactively. The sound adjustment for the purpose of an improvement of a car overall nature is and will remain very important in future. The aim is to enable to form acoustics from the point of view of design instead of reacting to undesirable or unwanted sounds (so called active sound design).

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IMPACT OF PLASMA TECHNOLOGY ON WORKPLACE

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Received: November 2016

Abstract

The present contribution deals with the research of plasma cutting of material and its influence on the environment. As each technology have an influence on the working environment. The first proposal of the progressive technology is to decrease the negative impact into environment, to facilitate and accelerate the production and from economical side to save money. The identification of hazard and risk of plasma workplace on employee belongs to the important requirements of health and work safety. Among the negative effect we can include the noise and dustiness that are the most controlled condition among the risks in plasma workplace. The main source of noise and dust is during the plasma cutting operation, when the plasma ray comes into contact with material and also depends on the technological conditions. In the paper is presented the results from the research of measuring of noise, measured with acoustic camera apparatus and dust, measured with IOM sampling head and sampling pump. These measurements were realized in workplace with manual plasma cutting and machine plasma cutting.

INTRODUCTION

Progressive plasma technologies create noisy and dusty environment in working place and also can minimize the production of waste.

Hazard identification, risk and environmental safety at the technological plasma workplaces create very important part of the determination of technology influence on environment. Specific plasma operations as welding and cutting allow to increasing the quality and productivity of work and decreasing the production waste. It reduces the possibility of threats to staff, but creates noise and dust into work surrounding.

The rules of the market are beginning to gradually expand about the environmental requirements. The main contribution of production firm to environmental sustainability is decision and act making in three directions:

- choice of environmentally suitable technologies,
- production of environmentally friendly products,
- optimum operation of existing technologies with the aim to the maximum limit of their negative impacts on the environment.

UTILISATION OF PLASMA TECHNOLOGIES IN MACHINERY AND ENVIRONMENT

Plasma torches or machines are usually used in technical praxis for:

- cutting of materials (greater thickness or heavy materials, high level of materials hardness),
- welding,
- renovation technologies - surfacing (building–up of materials, metals or spraying layers of materials with required properties on machine parts),
- surface finishing,
- melting of materials in the kilns,
- high temperature chemical gas synthesis.

Plasma operations can be divided from various point of working situations and working place, as utilization of:

- plasma technology in open air,
- plasma technology under the water,
- manual plasma cutting,
- plasma cutting machine.

Also plasma cutting technologies give us the possibility of dividing of various materials in dependence on:

- the shape of material,
- material dimension,
- thickness of materials,
- material quality.

In the Figure 1 is shown examples of plasma technology in practice.

Plasma cutting utilizes a high-velocity plasma gas jet formed by an arc and inert gas flow to create extremely high temperatures (up to 30,000°C), which melts the targeted material.

The source of environmental risk for plasma technology is most frequently:

- electrical current (up to 600A),
- radiation of all wavelengths, but especially ultraviolet, which is much more intensive than in open burning electric arc,
- arc rays,
- harmful gases and aerosols, mainly in particular ozone and nitrous gases,
- noise that reaches particularly high levels (up to 110 db), which dominates high-frequency component,
- fire hazard.

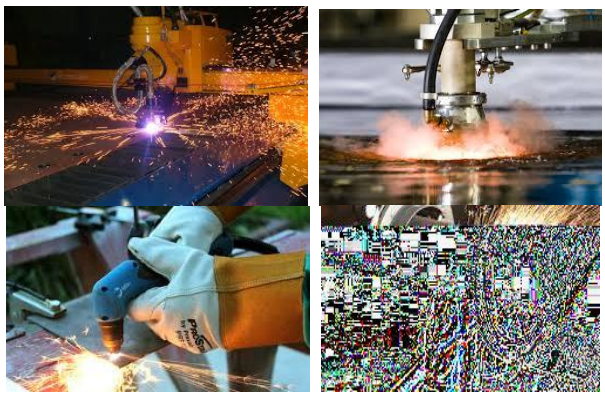

Figure 1
Plasma technology examples – work on air, under water, by hand, cutting of shaped material

Persons involved with welding exposes themselves to numerous risks, e.g.:

- flying sparks and hot pieces of metal,
- light from the arc, which can damage eyes and skin,
- hazardous electromagnetic fields, which endanger the lives of people using cardiac pacemakers,
- risk of electrocution from mains current and welding current,
- greater noise pollution,
- harmful welding smoke and gases.

Experimental measuring

The realization of measurements, the samples were prepared in the production. There were prepared and performed the testing of.

- dust in working surrounding,
- noise in working surrounding

as a most influenced parameters of environment.

DUST MEASUREMENt

The testing of dust in the working place was made according the European Standard STN EN 689: Atmosphere on the workplace. The guidelines for the evaluation of exposure by inhalation of chemical agents for comparison with limit values and measurement strategy. The standard defines the measurement procedure and also the measurement strategy.

The sampling was used for the following instrumentation:

- personal sampling pump, type AirChek2000 made by SKC,
- plastic sampling head, type made by SKC IOM,
- flow Calibrator, type DC-Lite from the company SKC, glass fiber filters from SKC company.

For evaluating of samples were used analytical balance with accurate to 0.1 mg, type AP250DE made by Ohaus and desiccator to stabilize of filters.

On the workplace, it was realized two types of donations and personal and stationary samplings. Both samplings were taken at the same time. Personal sampling was made at the employee, who was serving of plasma workplace (plasma operator), and who was working and moving on workstation and perform standard business operations. Stationary sampling was located 1.5 m from the plasma table at 1.5 m above the floor level of the production hall, Figure 2 and Figure 3.

Figure 2
Personal measuring of dust

Figure 3
Dust measuring in workplace

In the Figure 3 is shown the drawing with positioning of measuring apparatus.

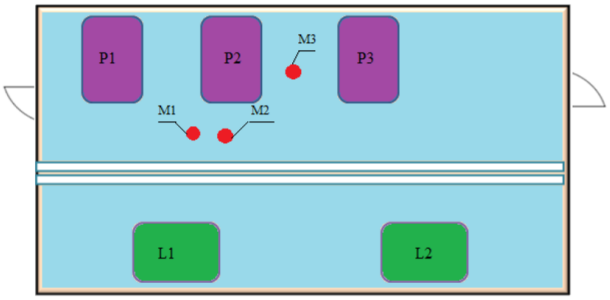

Figure 4
Schematic representation of personal and stationary sampling in the workplace

Location of measuring apparatus is shown in the following diagram:

- M1 (measuring point no. 1) - measuring acoustic camera,
- M2 (measuring point no. 2) - Measurement of sound level meter,
- M3 (measuring point No. 3) - measuring the sound level meter.

In the Figure 5 is shown the concrete measuring apparatus for dust measuring, technical parameters are: flow range 5-3000ml/min., range stability ± 5%, dimension 142 x 76x58 mm, weight 624 g, barometric pressure measurement accuracy ± 1 kPa, flow measurement accuracy ± 2.

Figure 5
Personal measuring apparatus

The sampling time was 90 minutes and flow rate pump was set to 2 l. min^{-1}. Before and after measurements were recorded climatic conditions at the place of measurement:

- air temperature: 21°C ,
- atmospheric pressure: 97.5 kPa,
- humidity: 47% .

The measured values are shown in the Table 1. Based on sampling and their evaluation, there was found that the concentration of solid aerosol exposure to the plasma at the workplace was at:

- personnel taking of 1.71 mg m-3,
- stationary collection of 1.07 mg m^{-3}.

Thus we can make a conclusion that TLV-c by Slovak Government Regulation no. 471/2011 was not exceeded in each case.

Accoustic measurement

Acoustic measuring equipment is shown in the Fig. 6.

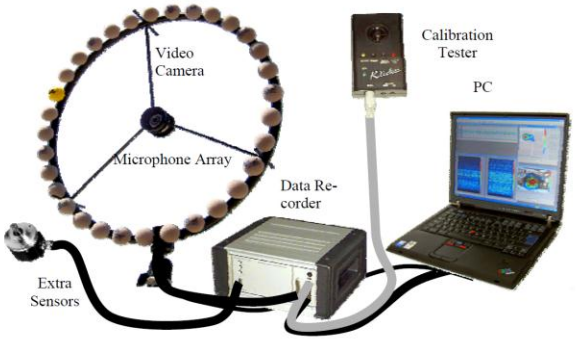

Figure 6
Acoustic measuring equipment

The measuring apparatus used in the workplace is shown in the Figure 7. There was used technical equipment:

- audio analyser with microphone - NORSONIC, type NOR 140,
- microphone NORSONIC, type NOR 118,
- acoustic calibrator- PIZZATO ELETRICA, type NOR-1251,
- distance measuring apparatus – Disto, type LEICA DISTO D5.

Figure 7
Measuring place in workplace

Measuring by acoustics apparatus was twice made., it. Means during the cutting of steel sheet with thickeness 10 mm and 40 mm at defined technological parameters. Location of apparatus was according the Figure 4. In the Table 2 are shown the results of measuring. For evaluating of processed measurements with sound level meter were used Figure 8 and Figure 9.

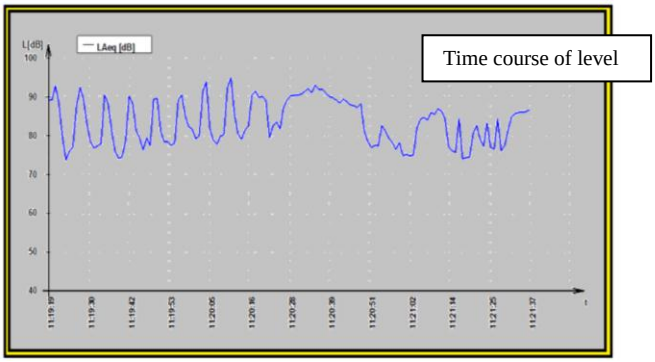

Figure 8
The time course of the sound pressure level M2

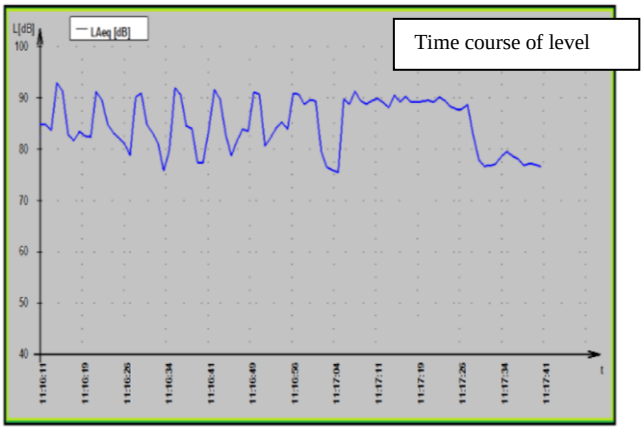

Figure 9
The time course of the sound pressure level M3

In the Table 3 is the measurement results of samples of noise exposure.
Assessment of compliance / non-compliance of the measurement results and determination of the exposure to noise, measured and calculated values are shown in the Table 4.
The calculated standard level of noise exposure raised with the uncertainty of measurement and compared with the limit and action values within the meaning of NV SR no. 115/2006 Z.z. on the minimum health and safety requirements to protect workers from the risks related to exposure to noise.

TABLE I
MESASUREMENT RESULTS

M	Measured place	Subscribe type	Profession	Duration of exposure [min]	Climatic condition	Measured concentration	time-weighted average value of exposure concentration [mg/ m^3]
1	Plasma cutting	stationary		440	19,6 ^{0}C, 97,5 kPa	1,13	1,07
2	Plasma cutting	personaly	Plasma operator	440	21,3 ^{0}C, 97,5 kPa	1,79	1,71

TABLE II
THE MEASUREMENT RESULTS OF SAMPLES OF NOISE EXPOSURE

Measured place	Position	Time of measured Interval [min]	LAeq,T [dB]	LCPK,T [dB]
M2	1,5 m over ground level, 2 m from machine	2,29	86,7	109,8
M3	1,5 m over ground level, 2 m from machine	2,18	87,2	111,5

TABLE III
MEASURED AND CALCULATED MEASURED VALUES

Profession	Sample	$L_{Aeq,T}$ [dB]	T [hours]	$L_{AEX,8h}$ [dB]	L[illegible]	[dB]	$L_{R,CPK}$
	1/M2	86,7	7,5	86,42	88,87	109,8	112,55
	2/M3	87,2	8	86,92		111,5	

time course of level

TABLE IV
DETERMINATION OF COMPLIANCE RESPECTIVELY INCONSISTENCY OF MEASUREMENT RESULTS

Profession	LRAEX,8h [dB]	LR,CPK	Exceeding of limit		
			LAEX,8h,DA [dB]	LAEX,8h,HA [dB]	LAEX,8h,L [dB]
Worker cutter	88,87	112,55	8,87	3,87	1,87

VISUALISATION AND IDENTIFICATION OF NOISE SOURCE

Measuring with an acoustic camera was made for the plasma cutting center no. 2 a measuring point is shown in the diagram as M1.
Acoustic camera was used primarily to identify the source of noise. The camera device was placed 2 m from plasma cutting centre and at given time intervals, we measured the acoustic energy of the machine. The results of the measurements are shown in the following Figure 10 and Figure 11.
At the time of measurement it has been switched on just one plasma cutting center. Acoustic camera was turned on for 10 minutes.

Figure 10
Visualization and identifying of the source of noise and emissions

Figure 11 presents the spectrogram of noise emitted from the measuring point M1. The biggest noise is emitted in the frequency range from 0 Hz to 2000 Hz. Critical frequencies are shown in red and pink color.

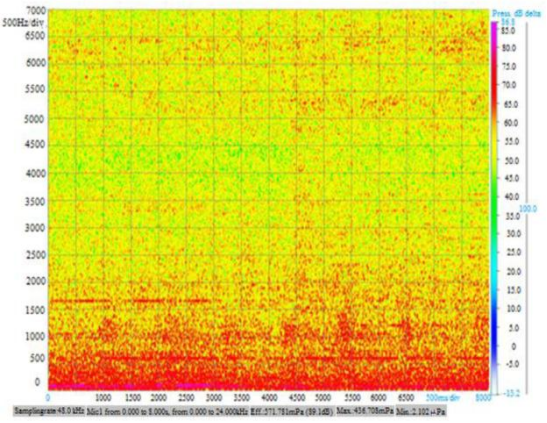

Figure 11
Spectrogram of emitted noise recorded at the measuring point M1

CONCLUSION

This document is intended to provide initial information regarding the environmental safety of plasma workplaces. It is important to note that the chemical composition of smoke, the intensity of their production size distribution (particle size and structure of the solid aerosol) depend on the mechanical technology, basic materials, shielding gases, procedures and process parameters, the maximum working temperature during the technological operations and the eventual finished working piece.
Nevertheless, there is a presumption that due to an expanding shortage of skilled workers in the Slovak labour market, employers will to sustain a skilled workforce care more about the health of their employees and provide them with relevant technology and technical equipment of workplaces with quality ventilation equipment, thereby achieving a quality work environment. Along with quality health care is the way to reducing the burden of workers harmful working environment factors.
To reduce noise in the workplace and also to prevent from spreading it into the environment, there are proposed the following technical and organisational measures.
Technical measures for plasma workplace:

- use of personal protective equipment, such as. absorbers hearing,
- machine guards, to mute the noise.

- wall insulation, the use of sound absorbing materials, which are due to its ability to absorb noise absorption excellent means of protection against noise, for example. sound insulation panels, foam and the like,
- if they were situated close to residential areas, separate them by engineering traffic noise barriers and screens of various materials, for example. glass, bricks, while protecting the environment

Organisational measures for plasma workplace:

- rational organization of work to reduce noise, introduce an appropriate timetable and adequate rest periods.
- instructing employees on the appropriate handling of machinery and equipment,
- spatial resolution workplace.

ACKNOWLEDGMENT

This work was supported by the Slovak Research and Development Agency under the contract No. APVV- 15-0327, Research and development of optimization methodologies of the acoustic performance of domestic appliances emitting noise.

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ECO-MONITORING FOR BIOAVAILABILITY OF CADMIUM AND LEAD IN CLAY LOAM CHERNOZEM MEADOW SOIL AMENDED WITH SEWAGE SLUDGE

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Received: November 2016

Abstract

The major benefits of sewage sludge (SS) application to agricultural environments are to increase the plant nutrients and improve the soil physical, chemical and biological properties. The SS application to agricultural land could affect potentially by availability of heavy metals. The solubility and mobility of metals throughout SS is controlled by organic matter and oxides that can prevent excessive heavy metals mobilisation. A pot experiment 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 SS (MSS). Corn plants were grown in the soils following the treatment with the MSS. The results showed that the addition of MSS significantly increased the average dry plant weight. The Cd and Pb uptake by corn plants generally followed the differences in metal inputs, but quantitative differences were found between the heavy metals. The availability and phytotoxicity of Cd and Pb were influenced by soil properties and organic matter content and metal content in the MSS as well. Furthermore, by sludge applications, Cd and Pb may accumulate in the soil and increase the phytotoxic concentrations for crop production, although at certain concentrations the Cd and Pb may be deficient for crop growth (at lower concentrations). Previous research work has shown that crop cultivation on MSS 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 MSS on agricultural soils. Therefore, strict monitoring procedures are necessary and the correct management practices. The value of SS 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 Cd and Pb in agricultural soils.

Keywords: *bioavailability, corn plant biomass, cadmium, lead, municipal sewage sludge.*

INTRODUCTION

Industrial effluents containing heavy metals may consider a major source of contamination causes serious environmental problems. Decontamination of heavy metals from wastewater has been a challenged for a long time [1]. Most of heavy metal ions are toxic to living system. These metal ions are non-degradable and are persistent in the environment. Therefore, the elimination of heavy metal ions from wastewater is important to protect public health.

Bioavailability of heavy metals is very complex and dependent on many interrelated chemical, biological, and environmental processes. Plant uptake of heavy metals is generally the first step of their entry into the agricultural food chain. Plant uptake is dependent on (1) movement of metals from the soil to the plant root, (2) metals crossing the biomembrane of epidermal cells of the root, (3) transport of metals from the epidermal cells to the xylem, in which a metals solution is transported from roots to shoots, and (4) possible mobilization, from leaves to storage tissues used as food, in the phloem transport system. Cadmium is a biotoxic heavy metal regarded as an important environmental pollutant in agricultural soils. Because of the potential adverse effects, it may pose to food quality, soil health and the environment [2]. But it is the labile fraction rather than the total Cd content that is critical when assessing Cd availability in soils, and consequent bioaccessibility in other forms of life. The extent of bioavailability is largely controlled by metal speciation or chemical sitting in soil, which determine solubility.

A number of soil testing methods and partial or sequential chemical extraction techniques and

methods are used to determine element behaviour [3]. Some of the chemical extractions are: (1) water or $MgCl_2$ at neutral or ambient soil pH for easily soluble metals, (2) solubility in weak base (pH 9) for humic materials, (3) weak acid or dilute acid in buffer solution (pH 2 to 5) to release metals associated with carbonate phases, and (4) a chelating (or complexing) agent such as EDTA (ethylenediaminetetraacetic acid) [4] or DPTA (diethylenetriaminepentaacetic acid) buffered to a pH of 7 [5]. Other possible extractants include (5) hydroxylamine hydrochloride for the "reducible" fraction associated with iron and manganese oxides/hydroxides, (6) strong acid (HCl, pH 1) to identify maximum mobility of most metals [6], (7) oxidation by hydrogen peroxide (H_2O_2) to release metals associated with organic matter and (or) sulfide minerals, (8) a strong oxidizing acid (HNO_3) to execute steps (6) and (7) simultaneously, and (9) a mixture of strong acid and HF to dissolve residual silicate minerals. The application of MSS or compost did not increase heavy metal concentrations in grain with respect to inorganic fertilizer-soil and also, the addition of SS or SS compost does not imply environmental risks and soil amended with SS and SS compost increased organic matter (2.5-fold). The addition of these organic wastes to the soil did not cause toxicity nor did it affect the number of leaves and corn cobs per plant [7]. Land application of biosolids increases the accumulation of toxic metals in corn tissues in slightly alkaline soils [8]. Mahdy et al. [9] showing significant positive relationships between the DTPA-extractable metals and the metal accumulation in plant tissues in biosolids amended soils. To understand the phytotoxicity and bioavailability effects of Cd and Pb in using MSS on plant dry weight production, their bioavailability and bioaccumulation in corn plants grown in clay loam chernozem meadow soil was investigated in greenhouse experiment for 9 weeks.

MATERIALS AND METHODS

A greenhouse pot experiment was conducted to determine the bioavailability, bioaccumulation and the impacts of different application rates (0, 30 45 and 60%, w/w) of stabilized MSS (Hódmezovásárhely's sewage water purification plant, Hungary) of high Cd and Pb content on the corn (*Zea mays* L.) transplants grown in 3 kg plastic pot of clay loam chernozem meadow for 63 days under natural day/night duration and at average temperatures of 27 ± 3°C and 18 ± 3°C, day and night, respectively. Some properties of investigated clay loam chernozem meadow soil (Szeged) were: $pH_{(KCl)}$ (6.20), organic content (20.4%), Cd (4.168 mg/kg) and Pb was (0.96 mg/kg) and for the municipal SS (MSS) of high heavy metals content (Hódmezovásárhely) were: $pH_{(KCl)}$ (7.8), organic content (3.55%), Cd (1.2 mg/kg) and Pb was (540.02 mg/kg). Air dried soil samples were treated with 0, 30, 45 and 60% (w/w) of MSS in triplicates and the moisture content of soil amended with MSS was adjusted to 60% of water holding capacity. After 63 days of cultivations: plants were assessed, and fresh soil samples were used for determining the Cd and Pb contents. Plant materials were air-dried at 65°C to constant weight. Plant samples were digested in concentrated HNO3 and analysed for Cd and Pb by flame atomic absorption spectrophotometry (FAAS) and soil samples were digested using aqua regia (75% conc. HCl and 25% conc. HNO_3) microwave digestion and then centrifuged and analysed using FAAS. The available metal contents were determined by extraction of the soils with 0.005 M diethylen-triamine pent acetic acid (DTPA) at pH = 7.3. For determining the distribution and bioavailability of Cd and Pb concentrations, the following indicators were used:

Translocation factor (TF) = MCshoot/MCroot (1)

Bioaccumulation coefficient (BAC) = MCshoot/MCsoil (2)

Bioconcentration factor (BCF) = MCroot/MCsoil (3)

Transfer coefficient (TnF) = MCplant/MCsoil (4)

If TF > 1 represent that translocation of metals effectively was made to the shoot from root [10] and BCF was categorized further as: hyperaccumulators, accumulator and excluder to those samples which accumulated metals > 1 mg/kg, and < 1, respectively [11]. Soil organic carbon (OC) was determined by reduction of potassium dichromate ($K_2Cr_2O_7$) by OC and subsequent determination of the unreduced dichromate by oxidation-reduction titration with 0.5 M ferrous ammonium sulfate according to [12] method. The amount of oxidized OC is multiplied by 1.334 to give the final amount of soil organic matter. The results were statistically analysed carried out to determine significant differences between the measured parameters.

RESULTTS AND DISCUSSION

The experimental observations showed that there are variations in shoot and root dry weight patterns of the corn plants grown at different rates of MSS in clay loam soil as shown in Figure 1. It was found that the addition of MSS markedly increased the average dry weight of the root and shoot of corn plants (Figure 1). The highest weights were obtained with 45% application rate of MSS as compared to the plants grown in control soil. One aspect which should be taken into account is that the addition of MSS not only results in an increase in the total concentrations of metals, but also in the quantity of organic matter, which may have a direct effect on the heavy metals solubility and bioavailability (Figure 2).

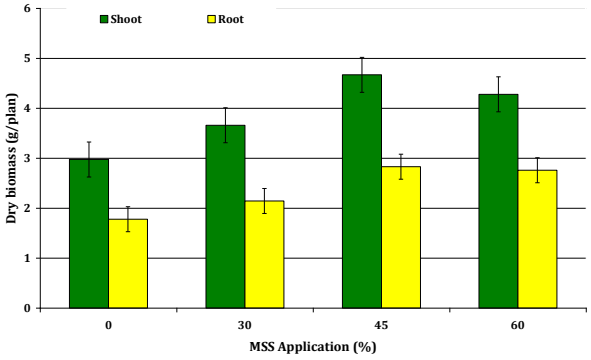

Figure 1
Corn plant dry weight under the effect of MSS application

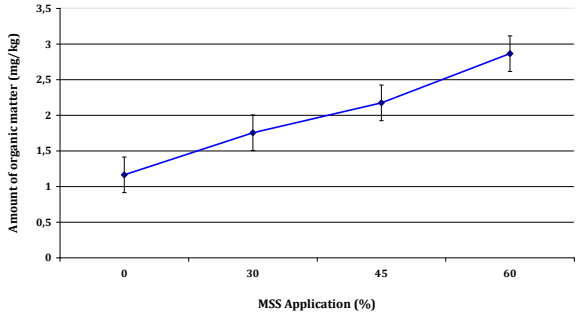

Figure 2
Changing of organic matter in clay loam chernozem meadow soil under the effect of different application rates (%) of MSS

The addition of MSS significantly increased the DTPA extractable Cd and Pb concentration compared to control due to higher metal contents. The increase in Cd availability could be explained by the fact that this element in organic substrates is associated with the more soluble fractions of organic matter, such as non humic (simple sugars and amino acids) fractions of MSS compost. Figure 3 shows that the bioavailability of Cd in MSS amended soil increased by increasing the application rate of MSS except at 45%, where the bioavailability of Cd in plant tissue is higher in root than the shoot. Similarly, Figure 4 illustrates that bioavailability of Pb in soil is gradually increased by increasing the MSS application rate, while it was found that in corn plant tissues, the bioavailability of Pb in root is significantly increased by increasing the application rate of MSS more than in the shoot system.

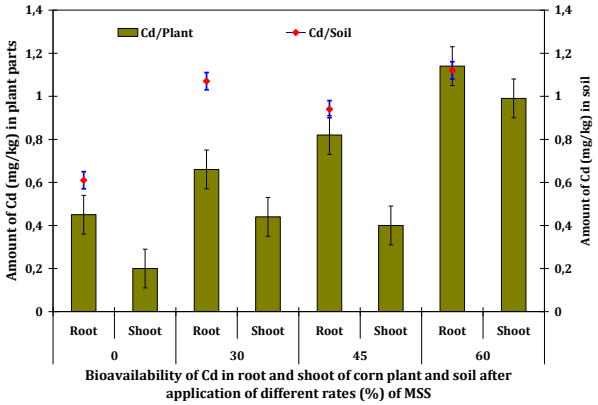

Figure 3
Bioavailability of Cd (mg/kg) in root and shoot of corn plant grown in clay loam chernozem meadow soil for 63 days after application of different rates (%) of MSS

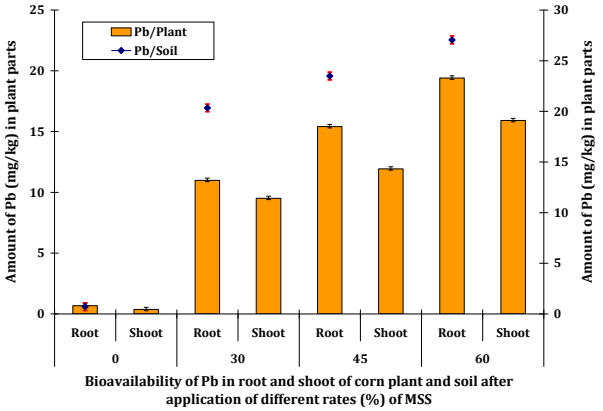

Figure 4
Bioavailability of Cd (mg/kg) in root and shoot of corn plant grown in clay loam chernozem meadow soil for 63 days after application of different rates (%) of MSS

In case of Cd, Figure 5 demonstrates that the TF, BCF and TnF index are increased by the increasing the application rates of MSS except at 30% which is not significant with the control. It is also shows that BAC is gradually increased up to 60% of application rate. Also, it is clear that the values of TF and BAC are below 1, and BCF also except at the application rate 60% which is relatively near to 1. The values of TnF are always more than 1 even at the control soil samples. But in case of Pb (Figure 6), the TnF values are higher in control soil samples than those treated with MSS and the lowest value obtained at 30% application rate.

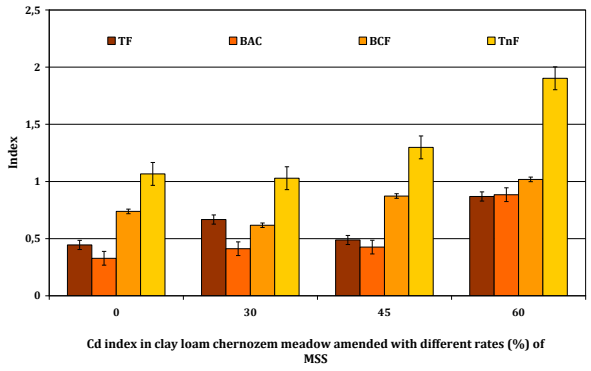

Figure 5
Index of Cd in clay loam chernozem meadow soil cultivated by corn plants for 63 days after application of different rates (%) of MSS

The values of TnF are more than 1 except at 30% which it is almost equal to 1. The values of TF, BAC and BCF are below 1. Meanwhile, the value of TF was at highest when the soil amended with 30% MSS and the lowest value recorded at control soil samples.

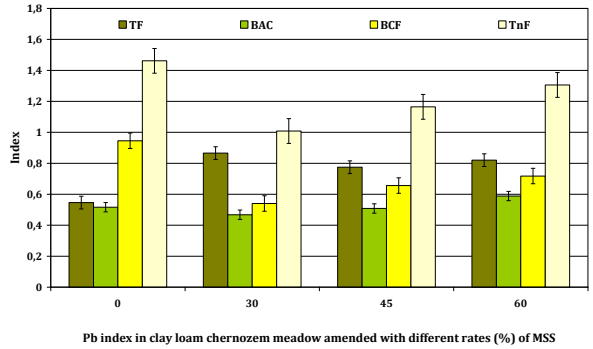

Figure 6
Index of Pb in clay loam chernozem meadow soil cultivated by corn plants for 63 days after application of different rates (%) of MSS

The values of BAC were than 0.6 at 60% application rate and lower than 0.6 in control, 30 and 45% application rates. Malik et al. [13] evaluated the concentration, transfer and accumulation of metals from soil to roots and shoots in terms of BCF, TF and BAC. This indicates that experimental conditions, that the SS treatments did not lead to detrimental conditions in terms of the investigated heavy metal uptake. Furthermore, the experiment was conducted soon after the application of the MSS and this left very little time for the metals to equilibrate with soil constituents upon its release from the MSS. The conclusion therefore is that at current application rates of use there is almost no risk of metal contamination of the food chain. This situation is bound to change if long-term continuous applications and possible changes in soil-use after a number of years are considered. Further research should be focused on continuous applications and soil-use scenarios. The availabilities of Cd and Pb were redistributed to other forms by incubation and addition of MSS at amendment rates 30, 45 and 60% as well as the corn growth for 63 days.

The reduction in availability of Cd concentrations in plant tissues can be explained by their retention by soil organic matter and in this case we are agreeing with the conclusion of McBride et al. [14] and Gray et al. [15] who reported that soil organic matter was important in controlling Cd sorption and desorption. It was observed that the rate of decrease in availability of Cd tended to decline as incubation progressed. Neal & Sposito [16] found that soil sorption of Cd was reduced by the formation of soluble–organic associations in the aqueous solution. In our soil, the reduction in extractability of Cd and Pb is attributed, in part, to the nearly neutral pH, the presence of low sludge application rate (30%) and, in part, the high organic matter content at high sludge application rate (60%). This result concurs with that of McBride et al. [14], who found that Cd and Pb were strongly retained in MSS amended soil, which has a high organic matter and lime content. Ong & Bisque [17] explained the phenomena of metal reduction by the fact that humic substances behave as negatively charged colloids, which may be coagulated by the electrolytes. Another phenomenon is that after the release of heavy metals from the MSS, they react chemically with the soil so that metal toxicity declines with time [18]. The properties of the MSS change rapidly as soon as it is amended to soil. This is particularly true where MSS is to be used in agriculture is high in organic matter, mineralisation rates prevail due to rapid microbial decomposition [19]. The organic material in the “fresh” sludge is unstable in soil and will therefore undergo extensive alteration before it becomes material resistant to mineralisation (humus). In this process a large fraction of the total C is lost mainly to the atmosphere [20].

A combination of environmental factors influences the rate at which the microbially mediated processes lead to the decomposition of organic material in soil. As general rule soil organic matter decomposition is curvilinear related to soil moisture and is slow at very wet and very dry conditions and temperature affects mineralisation where increases in temperature from 10°C to 35°C, also increase the breakdown rate [21]. Our experimental conditions are agreed with the conclusion of Sikora & Szmidt [21]. Below and above these temperatures the rates decrease drastically. Similarly, once accumulated, heavy metals are highly persistent in the topsoil [22] and can cause potential problems such as phytotoxicity [23]. The phytoavailability of heavy metals present in the SS depends on many factors such as the nature and

amount of metal, degree of metal association in the sludge, soil, plant characteristics and weather conditions [24].

The accumulation of sludge-borne metals in soil could not be proven to be in excess, even at a higher application rate (60%). Furthermore, accumulation of heavy metals in corn plants did not reach phytotoxic levels. A significant increase in certain yield aspects was seen after MSS amendment to the soil. The application of MSS to agricultural soil could provide an economical way to dispose of the increasing amounts of sludge generation. The improvement of the soil properties through the increase in organic matter could play an important role in promoting the agricultural application of MSS in the future and rapid decomposition by microorganisms and the use of mineral fertilizers. Large number of factors control metal accumulation and bioavailability associated with soil and climatic conditions, plant genotype and agronomic management, including: active/passive transfer processes, sequestration and speciation, redox states, the type of plant root system and the response of plants to elements in relation to seasonal cycles.

Figure (4) shows the results of Pb concentrations in the shoot of corn plants. Little absorption of metal by the corn plants was detected. Pb concentrations in plant samples (dry weight of plant tissue) may be classified according to levels of metal toxicity in plant species tabulated by Kabata-Pendias & Pendias [25]: a) normal concentration, 5-10 µg/g; b) excessive or toxic concentration, 30-300 µg/g; c); tolerance in agronomic crops, 10 µg/g. Many researches showed that distribution of metals concerning depth in the profiles of sludged soils presented little downward movement [22]. Nyamangara & Mzezewa [26] reported significant EDTA-extractable metal accumulation in the topsoil (Pb: 0-15 cm) with no evidence of further movement. Increases in metal concentrations below the depth of 30 cm, however, did not appear to be significant when compared to background values. This suggests that the movement of metals downward in the soil profile was minimal [27]. The level of uptake of heavy metals by plants growing in sewage-amended soils will depend on the bioavailable levels of the metal in the soil [26] and the bioavailable levels are depend many factors e.g., type of soil, organic matter content, pH. However, other authors have reported a more pronounced movement of metals within the profiles of amended soils [28]. Among the metals in this investigation, Pb is often mentioned as the less mobile. Miller & Boswell [29] mentioned that the rates of sludge application to land that are economically feasible in terms of both crop production and waste disposal should be determined. Sludge treatment of strip-mine soil increased yields of corn without causing significant differences in heavy metal content of the grain [30]. Garcia et al. [3] investigated translocation and accumulation of heavy metals in various tissues of corn plants. Generally, the highest concentrations of metals were found in roots and leaves and the lowest in grain and cob. Increases in Cd in leaf tissue occurred as a result of sludge application, with the increase in Cd being greatest. Although SS provides nutrients for plant growth, its successive use may result in the accumulation of heavy metals to levels detrimental to the environment. Pb behaviour in red nitosol with twice-treated contaminated SS at interval of 18 months was analysed and the Pb concentration, detected in maize plants cultivated in soil treated with SS, is considered normal and lies below the phytotoxic interval reported in the literature [32]. The little absorption of Pb by maize plants may be attributed to its probable retention in the roots and to its high retention in the soil complex system [33]. Lead is a common pollutant in the environment and could adversely affect seed germination [34], induct leaf chlorosis, inhibit root and shoot growth, and decrease photosynthesis [35]. The accumulation of Pb to the surface soil depth may be attributed to the high affinity of metals to organic matter [36]. In this study, the process may have also been facilitated by pH values in the surface soil of the sludge treatment. Organic matter and pH are the most important factors that control the availability of heavy metals in the soil [37]. Cadmium is more soluble and mobile than other heavy metals in soils [38], whereas Pb is relatively immobile and thus less available to plants.

Rhizosphere effects of plants may affect the heavy metal bioavailability to the cropping cycle e.g., lupines are known to release citric acid, which may increase the Cd lability. Oliver et al. [39] reported from two different locations that Cd concentration in wheat is highest when grown after lupines and Cd accumulation behaviour varies not only on the species level, but also between cultivars and individual plants e.g., large genotypic variation of Cd accumulation was found for maize shoots [40], where two main groups of inbred were distinguished: a group with low shoot, but high root Cd contents (shoot Cd excluder) and a group with similar shoot and root Cd concentrations (non-shoot Cd excluder). The corn plants grown in the clay soil had a higher assimilative capacity for uptake of Cd and Pb than other soils. The uptake values of heavy metals followed the following order: clay > calcareous > sandy soils [41]. Dry matter of wheat, concentration, uptake, and extractability of Cd and Pb were greater in sandy loam soil compared with those in sandy clay loam soil irrespective of amendments [42]. Soil amended by MSS showed tendency to higher biomass production due to their higher content of nitrogen, phosphorus and carbon.

CONCLUSIONS

The results had shown that crop cultivation on MSS amended soils can be done without contamination risk to soils or phytotoxic uptake by the crop plants. This research work forms part of a broader research programme where the following aspects are being investigated (1) The short term impact of using MSS in agricultural practices; (2) Establishing the impact of long term application of MSS under non-beneficial conditions; and (3) Establishing the MSS qualities (metals, nutrients and organic pollutants). The long term effects of the agricultural use of MSS needs to be assessed. The parameters of concern would be: (1) Recommended dosage for different crops and different soils to obtain maximum benefit from the MSS and (2) Protecting the environment against pollution. Soil organic matter showed a strong relationship with this order due to the formation of soluble and insoluble complexes with the metals. Further research is needed to find more efficient bioaccumulators, hyperaccumulators that produce more biomass. Researches involving the interactive effects of various environmental factors on plant response to heavy metal on different soil types are required before generalizations can be made.

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SOUND QUALITY ASSESSMENT METHODS OF HOME APPLIANCES

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Received: November 2016

Abstract

The acoustic properties of the electronic products become important factor for the most of customers. Aim of this article is to describe term psychoacoustics as well as more closely specify used equipment for an evaluation of acoustics parameters of products. Results of the psychoacoustic analysis show characteristics similar to human hearing and offers possibilities for objective valuation of sound quality. The most effective tool for psychoacoustic measurement and analysis is binaural measurement technique – artificial head. Artificial head has two ears that are positioned at about equal height at the two sides of the head. Currently, manufacturers of electrical home appliances that emit noise trying to reduce the noise. For some product groups, manufacturers must declare the level of acoustic power according to accepted standards. This is perhaps the most important driving force for reducing noise of household appliances. However, not in every case, is the most important quantity of the emitted sound, but also the sound quality i.e. customer perception of sound. Just the sound quality is engaged in a scientific discipline psychoacoustics, which brings a new perspective and ways to optimize acoustic performance of household electric and electronic appliances.

Keywords: *psychoacoustics, binaural measurement, sound quality*

INTRODUCTION

Human have two ears that are positioned at about equal height at the two sides of the head. Physically, the two ears and the head form a perception system, mounted on a mobile base. This system receives acoustic waves emitted by the source of the sound. The two waves received and transmitted by the two ears are the physiologically adequate input to a specific sensory system, the auditory system. Specifically, it is the basic biological role of hearing to get information about the environment, particularly about the spatial positions and trajectories of sound sources and about their state of activity.

SOUND QUALITY AND PSYCHOACOUSTICS

Sound quality testing is an important design concept in the automobile and audio industries. Marketing studies in these areas can demonstrate a relationship between sound and non-auditory concepts e.g. luxury, power, speed, safety, expense [3] making the sound of a product an important design consideration. There are a large number of metrics, some of which are well defined and others which are not. Very few have been standardised and the usefulness of a particular metric is dependent on the nature of the sound being tested. The majority of sound quality metrics can be divided into those that quantify some physical aspect of the sound (e.g. pressure level, frequency content) and those that try to quantify some physical effect taking place in the ear (e.g. impression of loudness, tone etc.) Some frequently used metrics are: roughness, sharpness, loudness, fluctuation strength, tonality. Hardly anybody would evaluate a sound with closed ears. However, this is still common practice for conventional acoustic and vibration measurements. Recordings with conventional measurement microphones are not suited for an aurally - accurate evaluation of an acoustic scenario, because substantial acoustic information such as the spatial array of sound sources and the selectivity of sound perception gets lost.[2,6] The aim of the artificial head measuring technique is, to get apart from the conventional possibilities of the evaluation, acoustic data with which the actual situation at the item under test is at any time callable.

The noise analysis ability of the hearing is not attainable or replaceable by any other analysis. So that the noise analysis with the hearing functions, is necessary a binaural input signal. This is made

available with the help of the artificial head measuring technique.
Binaural hearing cannot be simulated by simply using two measurement microphones as "ear replacements". Only after having taken the acoustic filter characteristics of the head and ears into account, do aurally-accurate, unaltered recordings become possible [6,7].
Binaural technique:

- recording with an artificial head (figure 1),
- more close to the function of the human hearing,
- makes all information e.g. for the direction hearing available.

The binaural measurement system is a stand-alone, mobile measuring device that is ready to perform aurally accurate binaural recordings immediately. The patented artificial head geometry offers [7]:

- a mathematically describable reproduction of the human head and shoulder geometry,
- an accurate reproduction of all acoustically relevant parts of the human outer ear.

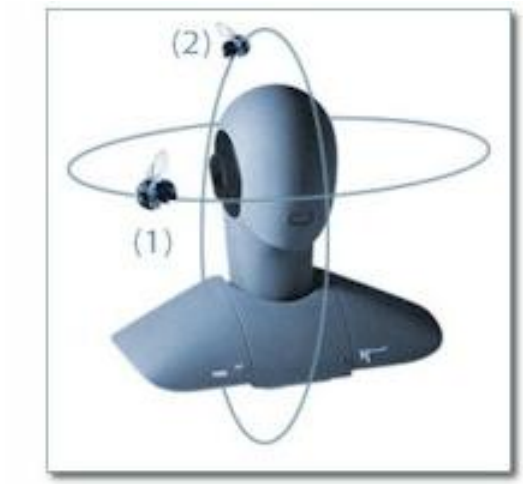

Figure 1
Artificial head – Head Acoustic (Binaural measurement system) [7]

ASSESSMENT METHODS

The sound quality assessment is realized by the two basic methods: approach of subjective testing using juries and objective assessment using metrics.

JURY TESTING

Asking customer's opinions of products is important part of sound quality testing. Jury testing is subjective testing done with a group of persons, rather than one person at a time. Subjective testing can be realized with a single person or many people. Subjective testing and analysis involves presentation of sounds to listeners, then requesting judgment of those sounds from the listeners and finally performing statistical analysis on the responses. However, this has to be done with care to prevent results being biased. A major technical problem centre around context - the assessment of sound quality is very dependent on the context, for instance the expectation and emotional state of the listener. It is also important that appropriate statistical analysis is carried out, otherwise you risk drawing incorrect conclusions from the data. The main problem of quality assessment sounds by the audience is dependent on various circumstances, such expectations and emotional state of the humans. These effects can be removed only appropriate selection and instruction of the respondents. It is very important to select the appropriate methods of statistical processing of data obtained of questionnaires in order to avoid distortions in evaluation of the data obtained. In general we can say that subjective evaluation through respondents allows the assessment and determination quality products based on their sounds e.g. designation better and worse in terms of sound perception customers, it means identifying best and worst products in terms of quality sound can design the product to be minimize annoying sounds. Manufacturers are often motivated to address the issue of sound quality when exposed customer complaints in case the product produce increased noise. Evaluation of sound quality by the respondents it can also be used in case of a required audio performance. If we want achieve product sound more powerful, more robust, stable etc. To rate sound through respondents are currently available on the market specialized software applications that all optimize the testing process [4].

OBJECTIVE ASSESSMENT

While jury testing evaluates the opinion of the user directly, it is time demanding to carry out if done many times. For this reasons, acoustic engineers like to draw up metrics that directly relate to the subjective response. There are a variety of metrics in use for sound quality measurement and testing. Once you have established appropriate metrics, this means that quick and easy measurements of sound quality can be made using competent instruments. However, it can sometimes be very difficult (if not impossible) to define appropriate sound quality metrics. Objective evaluation methods of psychoacoustic sound quality based on ratings binaural recordings is made by special measuring devices. These devices are called artificial heads and subsequent software evaluation of the audio signal leads to determination various psychoacoustic parameters (sharpness, roughness, fluctuation, tonality etc.). Sound recordings and records captured by the classic microphones are not suitable for hearing accurate assessment of acoustic environment and sources of noise, as it is lost significant acoustic information such as spatial and directional distribution of noise sources, masking

effects, selective hearing, and more. Man is able to locate the source of the noise three-dimensionally in horizontal and vertical plane. Localization is performed automatically based on time delay and different level acoustic signals incident on both ears. The outer ear causes directionally dependent filtering of audio signals. Anatomy of the head and shoulders and earlobes itself has vital importance. The ability of the human hearing system to locate the noise source one is able to perceive the different sources of noise from the overall noise and background noise. Binaural perception is not possible simulated simply by using two microphones as replacement ear. Such recordings may be used only after application of the acoustic filter, which takes account of properties and the geometry of the human head, ears and shoulders. Processing of acoustic signals by the hearing apparatus is complex and acceptor provides comprehensive and holistic perception of sound events. Sound field is affected by head arms and ears. Artificial head is simulation human head and shoulder, not only with regard to the shape of but also the surface properties which correspond to the properties of human skin. With this form of artificial head allows modify the sound field as in fact, thus able to recognize differences such as human ear [5]. The ear has placed microphones, to be used to record audio signals. Artificial head enables the recording and subsequent play sounds as though he heard them, if it was at the time of measurement at the place where it is located artificial head.

Figure 2
Sound quality measurement of washing machines

CORRELATION SUBJECTIVE AND OBJECTIVE ASSESSMENT

Objective measures that are used in sound quality assessment to measure human response without the effort of undertaking jury testing. Not all objectives measures are applicable for every product group. Before using objective measures, it is necessary to carry out jury testing to see which measures are useful and important for product sound characteristic. Sound quality is measured by computing metrics, which represent the objective data. In parallel, sound quality is subjectively assessed by performing jury tests where different sounds are presented to jurors who are asked to express a preference or opinion. The valuation of sound quality can be realized following different possible approaches, however if the results has to be correlated to objective sound quality metrics, it is recommended to perform a controlled experiment, where jurors and answers can be checked for consistency and repeatability [8]. Figure 3 shows basic steps of complex sound quality assessment.

It is appropriate to seek links between the two methods in order to achieve real results of psychoacoustic evaluation of sound quality individual product groups. In practice, it will be a correlation experimental measurements and determination psychoacoustic parameters results evaluation questionnaire for the same sound. On the base of this correlation will be designed mathematical model, which would be able to assess psychoacoustic sound quality only on the basis binaural measuring technology followed by determining the psychoacoustic parameters. As inputs in the mathematical model, are the values of individual psychoacoustic parameters and their correlation with the results of the questionnaire. On the base of correlation will be determined importance of individual psychoacoustic parameters. These model however, is not generally applicable to all products, but only for a given product group.

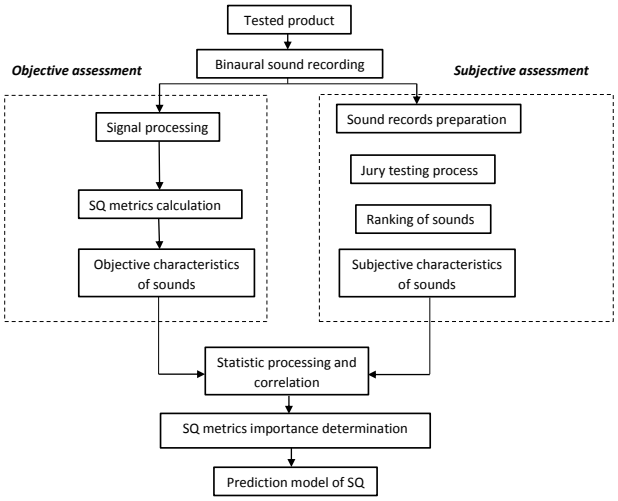

Figure 3
Sound quality assessment process

CONCLUSIONS

The sound quality of the noise emitted by the product has increasing importance when assessing the total quality of the product. For products ranging from cars to hand tools, not only the level of noise but also the quality of the noise is part that makes product more

attractive for customer; the right sound can lead to better sales. Many factors come into play in the sound quality evaluation process. Traditional objective measuring and analysis methods, such as A-weighted sound pressure and FFT analysis, are not enough for complex analyse of product sound. To obtain correct results is necessary realize significant correlations jury study results with objective metrics. Customer expectations and jury testing are also important factors for determining acceptable sound quality because, in the end, only the human ear can tell the designer whether or not the product has the right sound.

ACKNOWLEDGEMENT

This paper was supported by the projects VEGA 1/0537/15 and ITMS 26220220182.

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NEW POSSIBILITIES IN CLEANING OF MATERIALS AND ENVIRONMENT

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Received: November 2016

Abstract

The contribution deals with the possibilities of metal cleaning focused on environmentally friendly cleaning as laser cleaning technology of materials. The aim of this contribution is to present the new abilities of cleaning of product and tool surfaces in very short time with minimising of waste 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 sphere of products and materials. This technology minimises the harmful impact on the working environment and environment as a whole area.

Keywords: *environment, laser technology, cleaning, material*

INTRODUCTION

Degreasing of metal materials in the mechanical industry is an important technology for cleaning materials to further processing as a finishing surface treatment or as a pretreatment before surface operation of workpieces, or is used in the maintenance of machinery parts and tools. By degreasing of metal surfaces not only removes lubricant from surfaces, but also cleans mechanical particles from dust, abrasive parts and others. With the continuously deteriorating of environment, it is necessary to use such degreasing technologies of materials that have minimal negative impacts on the environment. Also the environment protection is encompassed by standards and decrees of REACH. [1]
The cleaning technology of materials must be quick, clear and short one. We can divide the cleaning technologies from various points of view as decreasing of materials, rust removal and surface pre-treatment of materials and also according to various methods of cleaning as [2]:

- Mechanical cleaning technologies,
- Chemical cleaning technologies,
- Progressive cleaning technologies.

The cleaning of metal materials by mechanical technologies belongs to the oldest method of the material cleaning as brushing, blasting technologies. The cleaning process takes a relatively long time and is usually dusty and noisy, with waste as used sand, metal balls. Chemical cleaning technologies requires the using of various degreasers, chemicals, which are very dangerous for the environment in terms of storage of new and pure chemicals, their utilisation, storage of the waste chemicals and their neutralisation or recycling and joined with chemical vapors and with the necessity of rinsed water operations.

PROGRESSIVE CLEANING TECHNOLOGIES

Progressive cleaning technologies as ultrasonic cleaning technology, water jet and abrasive water jet technologies, dry ice cleaning technology, laser cleaning are based on the utilisation of the physical parameters. They enable to work more quickly, save the time, effectively and can clean accessible parts of machines and tools, reduce waste, which are very important requirements of producers.
Ultrasonic cleaning technology transforms the high frequency energy on acoustic mechanics oscilations. Absorbent materials and degreasing parts due to the absorption causes the change of the ultrasonic energy on the thermal energy. By effect of the temperature changes occurs between degreasing substances and dirt to the partial separation and thus the scouring medium gets between subject degreaser and the dirt.

In US cleaning process we need chemicals, rinse water and also the waste occurs, which creates ballast from the environmentally point In the Figure.1 is shown the principle of the ultrasonic cleaning of materials. This technology enables to clean also the shape complicated product with cavities, shown in the Figure 2, which is one of the advantages of this type of cleaning. [3].

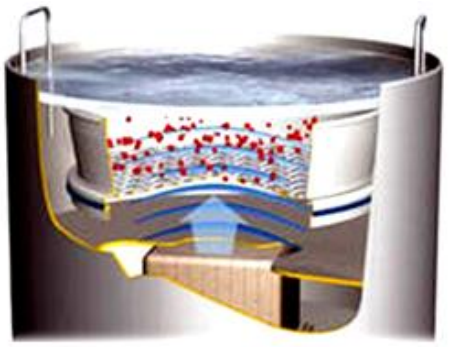


Figure 1
Principle of the US cleaning technology[3]

Figure 2
Example of US cleaning of product before and after cleaning

Dry ice blast cleaning technology 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 3 is shown the principle of dry ice blast cleaning [5].

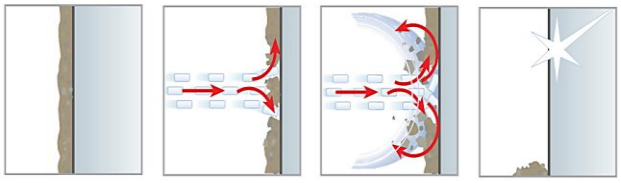


Figure 3
The principle of dry ice blast cleaning [4]

Dry ice blast cleaning offers comprehensive cleaning benefits over traditional methods, and can save up to 80% over current cleaning costs, Figure 4[6]. In the Figure 5 is shown the necessary equipment of dry ice cleaning. Except of degreasing, it can be used at the plastic cleaning from the extrusion screws at the plastic production, Figure 6.

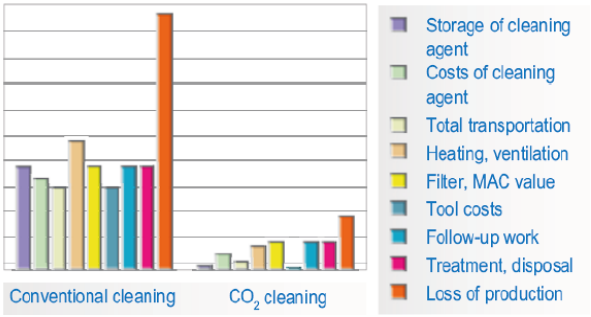


Figure 4
Incidental costs [5]

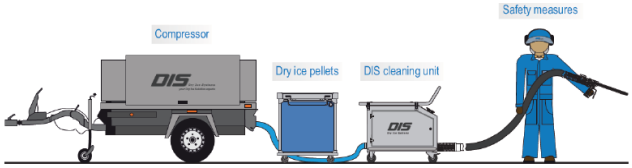


Figure 5
Equipment of dry ice cleaning [4]

Figure 6
The extrusion screws before and after cleaning operation [7]

Table 1 shows the comparison of blasting technologies according to environmental requirements.

Table 1
Comparison of blasting technologies according to environmental requirements [8]

CLEANING METHOD	NO SECONDARY WASTE	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 TECHNOLOGY

Laser cleaning technology offers a highly selective, reliable, precise and safe cleaning method of

removing layers of corrosion, pollution, unwanted paint, lubricants, other surface coatings and are environmentally friendly, using no water or chemicals and producing no effluent. Primarily laser cleaning technology is used for industrial cleaning in the automobile, aerospace, bakery, food, electronics, restoration industries and surface treatment, renovation and paint removal applications. It also removes 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. The innovative laser cleaning systems combine power and versatility, with the lowest operating cost of all industrial cleaning methods. [17], [18].

The cleaning surface reflects laser energy and is minimally affected; however, any contaminants on the surface absorb the laser energy and are quickly vaporized. The fumes or particulates are removed by an in-built filter of laser machines. 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 irradiation time will allow the laser energy to penetrate deeper so as to raise the material substrate temperature. In the Figure 7 is shown the dependence Optical absorption depths for several materials over a range of wavelengths [9].

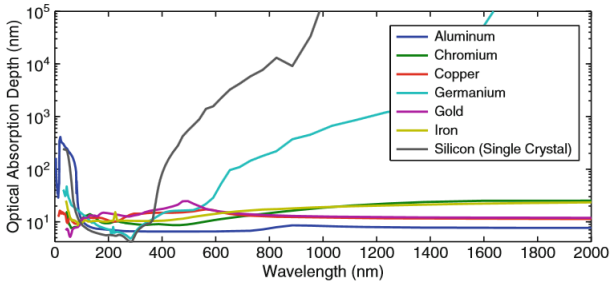


Figure 7
Optical absorption depths for several materials over a range of wavelengths [9]

The different effects of laser power flux and irradiation duration on the temperature elevation in the material can influence on the quality of laser cleaning.. For the purpose of laser cleaning, higher surface temperatures are desirable for the removal of machining debris. However, the elevation of temperature may damage the tested/ cleaned material structure, which should be prevented. Therefore, high power flux and short irradiation laser pulses are likely to be optimum for laser cleaning purposes. [10]. In the Figure 8 is shown the focus position of laser beam, which is a one way how we can prevent the damage of material structure and surface during the cleaning operation. [11]

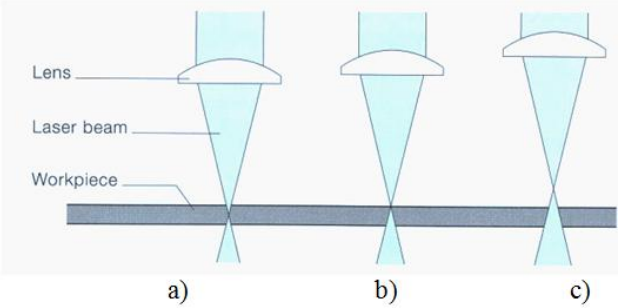


Figure 8
The focus position of laser beam: a) in the workpiece, b) on the surface, c) above the part [11]

MATERIALS AND METHODS

The realisation of the experimental testing of laser cleaning was made in Technical University in Kosice together with the cooperation of the firm Trumpf, Slovakia s.r.o., Figure 9. Used materials for the experiments were following:

a) Material: Steel sheet **KOSMALT 190**, dimension of table: 100x50 mm, thickness: 2 mm, mechanical properties were according to standard STN 038737
b) Synthetic lubrications [12],[13],[14]:
   1. **Berutox M21 EPK 420**, temperature range: -5°C to + 200 ~ + 220°C, viscosity of the basic oil: 490 $mm^2.s^{-1}$, at the temperature t = 40°C,
   2. **Berutox M 21 KN,** temperature range: -5°C to + 200 ~ + 220°C, viscosity of the basic oil: 490 $mm^2.s^{-1}$, at the temperature t = 40°C,
   3. **Beruplex** LI-EP 2, temperature range: -30°C to + 150°C.

There were used 5 tested pieces for each material and lubricant combination for the experiment. In the Figure 10 is shown prepared tested pieces greased with three types of lubricants.

After degreasing with technical white gasoline, the tested samples were weighed on laboratory scales MS, METTLER TOLEDO. The three types of lubricants were applied on the samples 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 8. The condition of the laser parameters are shown in the Table 2.

Figure 9
Laser cleaning – position of the sample

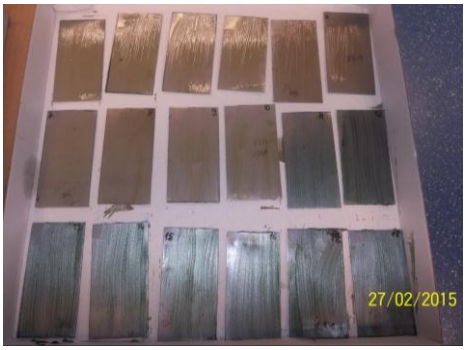


Figure 10
Tested materials KOSMALT 190

Table 2
Testing parameters of laser beam at the degreasing of testing sample

beam source	TruMark 6130
Optics	F 163
wavelength λ	1604 μm
The speed of the laser beam v	1000 mm/s
frequency	50 kHz
defocus	1,5 mm

Table 3 shows the chemical parameters of the steel KOSMALT 190. [15], [16]

Table 3
Chemical elements of steel KOSMALT 190

	Chemical element							
	C	Mn	Si_{max}	P_{max}	S_{max}	Al	Cu_{max}	Ti_{max}
content [%]	max. 0,04	max. 0,19	0,01	0,015	0,012	0,02 – 0,06	0,060	-

RESULTS

After laser cleaning operations, 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 4.

Table 4
Examples of the values of the tested samples cleaned by laser beam

	Weight of tested sample			
Sample	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

After preparing of tested samples with three types of lubricant, Figure 11, the laser beam passed only one time through the surface samples during the laser cleaning. During the experiments we changed the setup of the laser focus on the position +2, +1,0, -1, -2 regarding to basic position (according Figure 8).These results are shown from the Figure 12 to Figure 14. In the Figure 13 and Figure 14 are shown the laser paths with the cleared areas and areas with the rest of lubricant. From the practice of laser testing is known, that the synthetic lubricants remove very hardly. The experiment confirmed this assumption.
The details of tested samples were examined in the microscope Olympus at mag. 50x, mag. 100x. In the Figure 15 and Figure 16 are shown the path of laser cleaning on the sample, that can be observed as a macrostructure of tested material with the remains of lubricants in the form of drops. In the Figure 17 are shown the examples of the microstructures of tested samples with using of two lubricants, where can be seen the laser points (as the path) and residual of lubricants drops.

Figure 11
Tested samples No. 14, 7, 29 before degreasing by laser cleaning

A No-14 Beruplex | B No-7 Berutox M21 EPK/420 | C No29 Berutox M21 KN

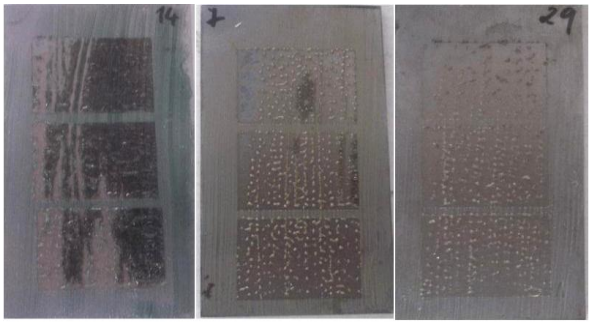


Figure 12
Tested samples No. 14, 7, 29 after laser cleaning
A No-14 Beruplex | B No-7 Berutox M21 EPK/420 | C No29 Berutox M21 KN

Figure 13
The sample after laser cleaning Lubricant Berutox M 21 EPK 420, mag.50x

Figure 14
The sample after laser cleaning Berutox M 21 KN, mag.50x

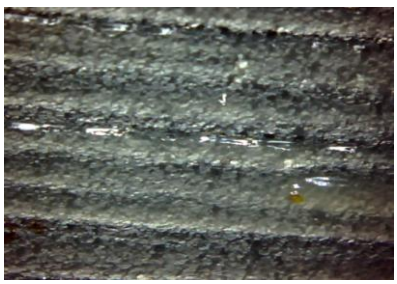


Figure 15
The sample after laser cleaning Berutox M 21 KN, mag.50x

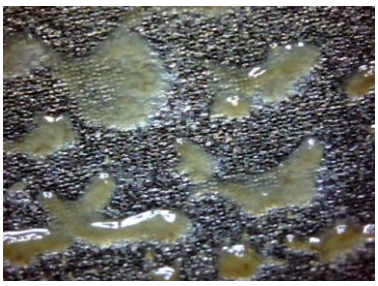
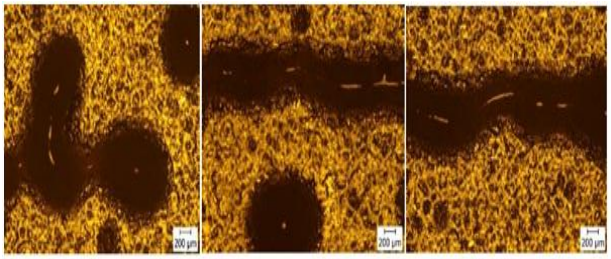


Figure 16
Detail of degreasing of lubricant Berutox M 21 KN, mag.50x



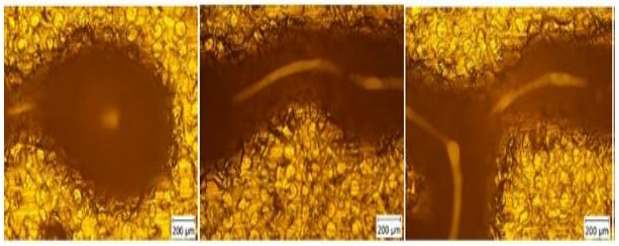


Figure 17
The samples after laser cleaning
Detail of degreasing of lubricant Berutox M 21 EPK 420, mag.100x and Berutox M 21 KN, mag. 100x

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 18.

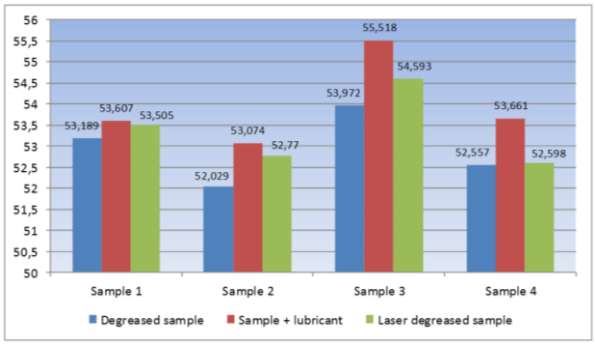


Figure 18
Degreasing of tested sample by laser beam, sample 1 – Berutox M 21 EPK 420, sample 2 – Berutox M 1 KN, sample 3 – Beruplex LI-EP 2, sample 4 – Berutox M 21 KN

CONCLUSIONS

Due to the ongoing problem of environmental protection of living and workplace environment, we

try to find ways how to minimize production waste and reduce the number of technological operations on the products.. The engineering industry as a whole is greatly utilize the lubrication of materials for the rust protection, for technological operations and od the other hand we must degrease the workpieces befora surface finishing oparations . Also during the life-service of machines occurs the necessity to do the maintenance or to remove the dust from functional parts. That is why we try and look after new progressive technologies, which enable to minimize the number of technological operations, save the amount of chemicals. This is the new way how to minimize the impact on the environment. One of these ways was to try degrease of the testing samples by laser technology and as itcan be in ultrasonic machines with the using of chemicals and rinsing water.

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,it is shown that during the laser cleaning tests of the samples, it is necessary to define the exact conditions of cleaning, how to set parameters of laser beam, to define the material properties as reflexivity, mechanical properties to reach the best results.The samples were greased by the synthetic lubricants BERUTOX M 21 KN and the lubricant Berutox M 21 EPK 420, where the worst results were reached with the samples, which were greased by the lubricant Berutox M 21 EPK 420. Organical lubricants, as suflower oils or fat burn during the cleaning operations that is why we did not used them.

ACKNOWLEDGEMENT

The work was supported by Ministry of Education of Slovak republic KEGA 048TUKE-4/2015.

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LAND USE ANALYSES OF ANTHROPOGENOUES PROCESSES IN THE 19-20TH CENTURIES IN THE GÖDÖLLŐ HILLSIDE, HUNGARY

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Received: November 2016

Abstract

In the last 200 years, the landscape gradually changed in Hungary. The study analysed former military, historical maps 1770s until 1890s and later EOV (Maps of the Unified National Mapping System) and CORINE Land Cover maps. The experimental analysis observed the transition direction of aerial distribution of various land uses with prepared land cover maps. Former surveys showed relevant changes in some type of land uses (e.g. arable lands, meadows and pastures). The main objective of this research work was focused on only built up areas, because due to the urbanization processes, and also, it was found that the great transformation in its distribution. Although, the second research point was to survey which type of land uses transformed to build up area. The increase of urban population and the prosperity of regional economy were the major driving forces of built-up area expansion. The study indicated that alterations were urgently needed in land management system and high-efficiency use of agricultural land. Promoting the compact development of built-up area was also crucial for striving toward regional sustainability.

Keywords: *land use, urbanization, historical map.*

INTRODUCTION

The Gödöllő Hillside is situated close the capital; it is rich both in nature and landscape values. It belongs to the Northern Mountain Ranges macro region according to the micro-region classification. The area of Gödöllő Hillside is 550 km^2, and it consists of 16 settlements. The landscape varies between 130 and 344 m above sea level, which reduces towards the south-east [1]. The highest point of the hillside is Margita (344 m) which is situated near the village of Szada, located in a suburban region, and the lowest point is near to Gyömrő (130 m). It is a diverse micro-region with twofold natural characteristics. Due to its landscape characteristics, the micro-region is a transitory area between a plain terrain and medium-height mountain ranges from the aspect of geological, climatic, botanical and soil features. Besides the natural conditions, the land use in the micro-region is determined by its role in the country's economy, good accessibility and ecological conditions. The change in land use happened in parallel with the transformations in the population number [2].

This analysis focuses on four inner settlements of Gödöllő Hillside (Veresegyház, Szada, Gödöllő, Isaszeg), where significant changes happened in the studied period. This present survey is concentrated on only built up areas, because due to the urbanization processes I found great transformation in distribution of different landscape types, mainly in the ratio of built up and arable land areas. In my previous study I have dealt with arable lands [3] and now changes in built up areas more detailed.

The Hungarian literature in the past decades several review studies were written about the Gödöllő Hillside. These studies are presented the topography, geological, climatological, hydrological, botanical, pedological features of the area and of course there are some were showed suburbanization changes in the agglomeration in Budapest [1], [4], [5], [6], [7], [8], [9], [10], [11], [12]. These overviews are focus on the natural factors duality, which are basically between northern and southern part of the hillside. Similar research objectives have been investigated in various regions of Hungary [13], [14], [15], [16], [17] and in other countries as well [18], [19], [20], [21].

MATERIALS AND METHODS

Similar to my previous study for the analyses I used former military maps from 1770s until 1890s and later EOV and CORINE Land Cover Maps. Firstly I

prepared land cover maps of the area. Secondly I separated different seven main land use categories (1. built up areas, 2. forests, 3. wetland areas, 4. meadows and pastures, 5. arable lands, 6. orchards and 7. vineyards). Finally I observed how and which directions changes the built up areas (I marked with "1"= changes areas or non-stable areas," 0" = no changes or stable areas).

To the mapping I used following maps:

1. 1st (1763-1787) Military Survey Map (Scale=1:28,800) (Arcanum Ltd.)
2. 2nd (1806-1869) Military Survey Map (Scale = 1:28,800) (Arcanum Ltd.),
3. 3rd (1872-1885) Military Survey Map (Scale = 1:25,000) (Arcanum Ltd.),
4. Maps of the Unified National Mapping System (Scale = 1:10,000),
5. Corine Land Cover Maps of 2006 (Scale = 1:100,000).

RESULTS

The spatial structure of Gödöllő Hillside becomes more and more fragmented in the last 200 years. Parallel to an intensive land use and suburbanization processes have changed the proportion of built up areas.

In the end of 18th century the area of 0.74% was inhabited, during the Ottoman rule the area was underpopulated.

In the 19th century the proportion of built up areas increased but not tremendously (1.27%). To the end of 20th century population of the area was extremely increased (app. 20% in 2006).

Transformation of between 1st and 2nd military Map

In this studied period (1763-1869) the share of stable areas in built up areas is more considerable than non-stable areas. 62.92% of built up areas weren't changed in this term.

The main directions of changes are the following: 1st orchard (51.41%), 2nd forest (33.6%), 3rd wetland (10.17%). Surveyed in each settlement Gödöllő was where the highest transformation happened (Table1).

Table 1
Distribution of non-stable areas in built up areas in each settlement on 1st and 2nd Military Maps (1763-1869)

Surveyed settlements	Non-stable areas (%)	Direction of changes (%)					
		Forest	Wetland	Pasture, meadow	Arable land	Orchard	Vineyard
Veresegyház	6.63	0.00	0.00	15.25	0.92	83.83	0.00
Szada	12.33	0.00	9.74	0.00	4.74	79.16	6.36
Gödöllő	66.82	50.29	13.34	0.97	0.00	35.40	0.00
Isaszeg	14.21	0.00	0.39	12.10	0.00	87.51	0.00

Transformation of between 2nd and 3rd Military Map

During 19th century the built up areas weren't changed significantly in the Gödöllő Hillside, although in the four-centered settlements considerably reordering occurred. In this case, most part of built up areas were transformed (64.16%).

The main directions of changes are the following: 1st pasture and meadow, 2nd orchard, 3rd forest. In that case the southeast town, Isaszeg where 48.02% of built up areas were changed (Table2).

Table 2
Distribution of non-stable areas in built up areas in each settlement on 2nd and 2rd Military Maps (1869-1885)

Surveyed settlements	Non-stable areas (%)	Direction of changes (%)					
		Forest	Wetland	Pasture, meadow	Arable land	Orchard	Vineyard
Veresegyház	15.21	0.00	0.36	2.43	3.56	93.65	0.00
Szada	8.30	0.00	0.00	0.04	1.01	98.94	0.00
Gödöllő	28.46	38.53	3.65	20.21	11.82	24.85	0.95
Isaszeg	48.02	10.97	1.28	86.41	0.29	1.05	0.00

Transformation of between 3rd Military Map and EOV MAP

In the next studied period the share of built up areas was increased. Its maximum coverage was 13.78% at the end of 20th century. The rate of changeable and non-changeable territories is app. similar, share of stable areas are 54.99% and non-stable areas are 45.01%.

The main directions of changes are the following: 1st orchard, 2nd pasture and meadow, 3rd arable land. Out of four centered towns Gödöllő and Veresegyház where one-third of the built up areas transformed (Table3).

Table 3
Distribution of non-stable areas in built up areas in each settlement on 3rd Military Map and EOV Map (1885-1990)

Surveyed settlements	Non-stable areas (%)	Direction of changes (%)						
		Forest	Wetland	Pasture, meadow	Arable land	Orchard	Vineyard	Other land
Veresegyház	26.11	1.37	0.44	7.21	12.09	34.85	2.37	41.68
Szada	22.64	7.81	2.89	9.71	1.27	56.85	12.33	9.13
Gödöllő	33.73	5.33	10.87	30.58	8.12	40.67	2.03	2.40
Isaszeg	17.51	16.49	0.00	16.90	55.59	11.02	0.00	0.00

Transformation of between EOV and Corine Land Cover Map

In the last analyzed term (in the end of 20th century) the coverage of built up areas were continuously increased. However the share of stable built up areas were more significant (78.65%) than non-stable built up areas (21.35%).

The main directions of changes are the following: 1st other land (i.e. other agricultural land, other semi-nature land) (77.87%), 2nd forest (14.12%), 3rd arable land (6.4%). Gödöllő is a city where the transformation is considerable (Table4).

Table 4
Distribution of non-stable areas in built up areas in each settlement on EOV Map and Corine Land Cover Map (1990-2006)

Surveyed settlements	Non-stable areas (%)	Direction of changes (%)						
		Forest	Wetland	Pasture, meadow	Arable land	Orchard	Vineyard	Other land
Veresegyház	3.68	34.87	9.70	0.18	17.06	0.00	0.00	38.19
Szada	30.80	4.27	0.00	0.00	2.66	0.00	0.00	93.07
Gödöllő	48.07	21.14	1.45	0.00	6.03	0.00	0.00	71.38
Isaszeg	17.46	7.78	3.14	0.00	11.80	0.00	0.00	77.29

From different cultivation forms in each settlement other land type (i.e. other agricultural land, other semi-nature land) is determinate.

CONCLUSION

In the Gödöllő Hillside, more precisely in the four chosen settlements the land use forms has been transformed. Spatial structure has become fragmented, which is clearly indicated increasing in the number of polygons. The most dominated land use forms in the Gödöllő Hillside were forest, arable land and at the end of 20th century were built up areas. The main directions of transformations were orchards, pasture and meadows, again orchards, and other lands. The transformation was not only due to physical characteristics of the area but suburbanization and economic processes, too (expansion of settlements).

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ENDOPHYTE PGPR AND SIDEROPHOREGENIC FLUORESCENT PSEUDOMONADS ISOLATION FROM COMMON BEANS RHIZOSPHERE

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Received: November 2016

Abstract

Fluorescent pseudomonads used in this study were isolated from an agricultural area of sandy loam brown forest of Gödöllő, treated by 30% sewage sludge. Seven of the 45 screened rhizobacterial isolates were able to Plant growth promoting rhizomicrobiomes. The isolates gave orange halos in the assay with Chrom Azurol Sulphonate (CAS). The isolates were identified as an endophytic Pseudomonas isolated from roots of beans showed the highest siderophore production on CAS agar. The sizes of orange haloes were correlated with the concentration of siderophore production. Pot experiments revealed that bacterization of bean seeds with different fluorescent pseudomonads isolates showed significant increase in germination percentage and plant health compared with untreated controls. Maximum shoot and root length and dry weight were observed. Our results highlight the value of a substantial understanding of the relationship of the PGP properties of endophytic Pseudomonas to the plants. Endophytic Pseudomonas, therefore, can be applied as potentially safe and environmentally friendly biocontrol in agriculture when inhibited some important phytopathogens like: Alternaria sp., Fusarium oxysporum, Rhizoctonia solani and Pythium ultimum. Pseudomonas fluorescens is an essential for biocontrol activity and increased the plant health.

Keywords: *PGPR, siderophore production, antagonism, plant health*

INTRODUCTION

The interface between the soil and the plant root is known as the rhizosphere. In this region, root activity greatly influences the soil physical, chemical, and biological properties compared with those of the soil that does not contain plant roots. The plant roots penetrate the soil and secret and increase organic matter contents such as organic acids, sugars, amino acids, and enzymes, which change the soil pH, redox potential, microbial activities, biomass, organic matter content, and the chemical speciation of elements.

Plant-microbe interactions in the rhizosphere are the determinants of plant health, productivity and soil fertility. Several important bacterial characteristics, such phosphate solubilisation, and production of siderophores and phytohormones, can be assessed as plant growth promotion (PGP) characters. One of the greatest challenges that faces world is our knowledge that it needs to double production or halve the amount of food wasted in order to feed more than 9 billion people by 2050. The growing human population requires increasing amounts of food, but modern agriculture has limited possibilities.

A certain groups of bacteria and fungi are present in waste organic matter (WOM) produce metabolites, such as siderophores and antibiotics, with specific suppressive activity against soil-borne plant pathogenic fungi: among these WOM bacteria, species of *Pseudomonas* which are very important. The root colonization efficiency of plant growth promoting rhizomicrobiomes or rhizomicrobiotas (PGPR) which include beneficial rhizobacteria and rhizofungi is

closely associated with microbial competition and survival in the soil.

Many bacteria utilize siderophores to help the process of ferric iron uptake in the environment. This process can be found across all three domains and is necessary for many microorganisms to obtain the environmental iron needed for essential processes. Siderophore production can also be a major factor in the ability of pathogens to cause disease because free iron is very limited, and often tightly bound to many proteins, such as haemoglobin, transferrin, and lactoferrin [1].

Siderophores are organic compounds with low molecular weights that are produced by some microbiomes and plants growing under low iron conditions. Iron (Fe) is one of essential micronutrients for plants and microorganisms, as it is involved in various important bioprocesses, like photosynthesis, respiration, chlorophyll biosynthesis, etc. The excretion of siderophores by PGPR might stimulate plant growth, thereby improving nutrition (direct effect) or inhibiting the establishment of phytopathogens (indirect effect) through the sequestration of Fe from the environment. One of the primary biogeochemical functions of siderophores in soil is to increase Fe bioavailability by promoting the dissolution of Fe-bearing minerals.

Plant growth promoting rhizomicrobiotas (PGPR) are benefit soil microorganisms that are stimulating plant growth and suppressing plant disease. They are the rhizosphere bacteria and fungi that can enhance plant growth by a wide variety of mechanisms like phosphate solubilisation, siderophore production, biological nitrogen fixation, rhizosphere engineering, production of 1-Aminocyclopropane-1-carboxylate deaminase, quorum sensing signal interference and inhibition of biofilm formation, phytohormones production, exhibiting antifungal activity, production of volatile organic compounds, induction of systemic resistance, promoting beneficial plant-microbe symbioses, interference with pathogen toxin production etc. Bhattacharyya and Jha [2] mentioned that the potentiality of PGPR in agriculture is steadily increased as it offers an attractive way to replace the use of chemical fertilizers, pesticides and other supplements. Growth promoting substances are likely to be produced in large quantities by these rhizosphere microbiomes that influence indirectly on the overall morphology of the plants. Recent progress in our understanding on the diversity of PGPR in the rhizosphere along with their colonization ability and mechanism of action should facilitate their application as a reliable component in the management of sustainable agricultural system. Martinez-Viveros et al. [3] mentioned that PGPR in accordance with their degree of association with the plant root cells, PGPR can be classified into extracellular PGPR (ePGPR) and intracellular PGPR (iPGPR). Gerhardson [4] established that PGPR can act as biocontrol agents for suppressing plant diseases, and inducers of disease resistance in plants [5]. In particular, strains of *Pseudomonas*, *Stenotrophomonas*, and *Bacillus* have been successfully used to control plant pathogens and increase plant growth [6]. The widely recognized mechanisms of PGP by PGPR are production of phytohormones, diazotrophic N_2-fixation, and solubilisation of phosphate. Mechanisms of biocontrol action include competition with phytopathogens for an ecological niche or substrate, as well as production of inhibitory compounds and hydrolytic enzymes that are often active against a broad spectrum of phytopathogens [7]. The various modes of action of a *B. subtilis* strain, FZB24 against phytopathogens are examined by Kilian et al. [8] suggesting the role of bacterium in plant vitality (Figure 1).

The rhizosphere has attracted much attention since it is a habitat of several microbiotas of biologically important processes and ecological interactions with plants. This zone around the plant root is populated by various biodiversity of useful microbiomes. The beneficial rhizosphere microbiomes include PGPR which form significant components of plant protection and production management strategies.

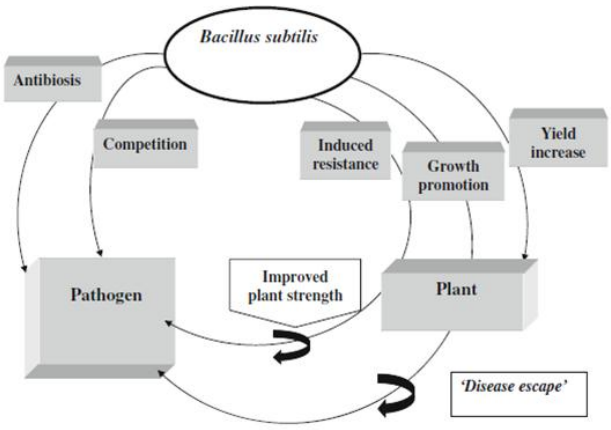

Figure 1
B. subtilis mode of action [8]

Various rhizobacterial species such as *Pseudomonas*, *Azospirillum, Azotobacter, Klebsiella, Enterobacter, Burkholderia, Bacillus* and others have been mentioned to improve the plant growth [9], germination and seedling of maize [10]. The PGPR group promotes the plant growth through production of antibiotics, enzymes, phytohormones, siderophores and fungicidal compounds [11].

Fluorescent pseudomonad rhizobacteria are a group of PGPR which are the well-studied. They maintain soil health and they are metabolically and functionally most important soil biodiversity. Presences of fluorescent pseudomonad bacteria as bioinoculants

play an effective role in stimulating plant growth and yield production [12].

This paper focusses on the performance of fluorescent pseudomonad PGPR isolates on common bean plant growth promotion and their ability to produce siderophore under greenhouse conditions.

MATERIALS AND METHODS

Common bean (*Phaseolus vulgaris* L.) root samples were collected from brown forest soil (Gödöllő) treated with 30% sewage sludge originated from Nyíregyháza. For isolation of rhizobacteria, 5 g of fresh roots were washed several times with sterilized distilled water (SDW) and root surface was sterilized with 5% (v/v) sodium hypochlorite (NaOCl) for 1 min. After washing and sterilization, root samples were ground with a sterilized mortar and pestle. Serial dilutions were prepared from the ground roots, and 100 µl aliquots from each dilution of 1×10^{-5}, 1×10^{-6}, and 1×10^{-7} CFU mL^{-1} were spread on potato dextrose agar (PDA) and King's B agar plates and incubated for 2 days at 28 ± 2°C. After purification, some morphologically distinct rhizobacterial colonies were selected for further purifications.

Colony morphology, size, shape, colour, and growth pattern were observed after 24 h of growth on PDA and King's B plates at 28 ± 2°C. The Gram stain and some biochemical examinations were carried out to characterize the cultures of isolates according to Bergey's Manual of Systematic Bacteriology [13].

Finally, seven pure endophyte rhizobacterial isolates were randomly selected based on their fluorescence production under UV were further characterized using the methods of Aneja [14].

For the KOH solubility examination, rhizobacterial isolates were mixed with 3% KOH solution on a clean slide for 1 min and observed for formation of a thread-like mass under aseptical condition.

The motility of each isolate was investigated according to Kirsop and Doyle [15] in sulfide indole motility (SIM) medium. Turbidity and growth away from the line of inoculation was a positive indicator of motility.

Catalase (It was done by adding a drop of 3% H_2O_2 to freshly grown rhizobacterial isolate on a sterile slide using a sterile wire loop. The effervescence indicated catalase activity) and oxidase examinations were conducted according to Hayward [16] and Rajat et al. [17], respectively.

Oxygen requirement test using the citrate test was carried out as described by Simmons [18] using Simmons citrate agar medium.

Qualitative [19] and quantitative [20] analyses of indole acetic acid (IAA) were carried out. After 24 h of incubation, colonies were observed for orange halo formation. Absorbance of supernatant mixture was measured at 520 nm and quantified using tryptophan standard.

For quantitative measurement, fresh rhizobacterial cultures were inoculated and grown for 48 h on nutrient broth at 30°C. 10 µl culture was inoculated in 20 ml broth. Fully grown cultures were centrifuged at 7000 rpm for 15 min at 4°C. The supernatant (2 ml) was mixed with two drops of ortho-phosphoric acid and 4 ml of the Salkowski reagent (50 ml, 35% of perchloric acid, 1 ml 0.5 M $FeCl_3$ solution). Development of pink colour indicates IAA production. Optical density was taken at 530 nm with the help of spectrophotometer.

Rhizobacterial isolates were investigated for hydrogen cyanide (HCN) production using the method of Lorck [21]. Nutrient broth was amended with glycine (4.4 gl^{-1}). After incubation, tubes were observed for the development of orange to red colour.

Qualitative cyanide determination as carried out by Lorck method [22]. The production of HCN was detected after inoculation for 48 to 72 h, using picrate-Na_2CO_3 (paper saturated with 1%, picric acid solution) moistened with some drops of a 10% Na_2CO_3 solution] paper fixed to the underside of the Petri dish lids which were scaled with parafilm before incubation at 28°C. A change from yellow to orange, red, brown, or reddish brown was recorded as an indication of weak, moderate, or strongly cyanogenic potential, respectively. Then, cyanogenic isolates were determined and identified.

In one of the dishes the yellow picrate paper obtained a strong reddish-brown colour after incubation at 26°C for 24 or 48 h. From this raw culture a cyanogenic bacteria strain was isolated.

Rhizobacterial isolates were tested for ammonia production in peptone water according to Joseph et al. [23] and incubated at 36°C for 48 to 72 h. After incubation, 0.5 mL of Nessler's reagent [10% HgI_2, 7% KI, 50% aqueous solution of NaOH (32%)] was added to bacterial suspension. The development of faint yellow colour indicates a small amount of ammonia and deep yellow to brownish indicates maximum production of ammonia.

Biofilm formation was studied using overnight culture of bacterial isolates in LB broth diluted to OD_{600} = 0.3, using crystal violet following the procedure of Iijima et al. [24]. Crystal violet attached to the biofilm was dissolved in 5 ml of 95% ethanol and quantified by measuring absorbance at 590 nm.

Siderophore production by the rhizobacterial isolates was qualitatively detected according to Schwyn and Neilands [25] using Chrome Azurol Sulphate (CAS) and following the protocol of Louden et al. [26]. After 24 h of incubation, colonies were observed for orange halo formation. The isolates were evaluated for the quantity of siderophore produced. The amount of

siderophore was then calculated in terms of percent siderophore units (% SU) using the following formula: Siderophore units (%) = [(Ar – As)/Ar]*100, where, Ar = absorbance of reference at 630 nm (CAS reagent); As = absorbance of sample at 630 nm.

Root colonization by rhizobacterial isolates was determined according to the protocol of Hossain et al. [27]. Roots were harvested from plants at 7, 14, and 21 days of growth. Root systems were thoroughly washed with SDW to remove adhering soil particles, then were rinsed 3 times with SDW and blotted to dryness, weighed and homogenized in SDW. Serial dilutions were prepared on PDA and King's B agar plates and the number of CFU/g root was determined after 24 h of incubation at 28 ± 2°C.

Seed germination and vigour index: Bean seeds were considered for this investigation. The rhizobacterial isolates were grown in King's B broth at 37 ± 2°C for 48 h and harvested by centrifugation (6000 rpm) for 15 min and re-suspended in phosphate buffer (0.01 M, pH 7.0). Concentration of endophytic rhizobacterial suspension was adjusted to about 1 x 10^7 CFU/ml (OD_{600} = 0.3) and used as inoculant. SDW treated seeds were considered as control. Germination was studied using top of the paper method [28]. Germination percentage (G %) and vigour index (VI) were calculated using the procedure of Baki and Anderson [29]. Control and inoculated seedlings were weighed (initial weight) and then dried at 65°C for two constant weights (final weight). Actual dry weight of the biomass was the difference between initial and final weight.

Antagonistic activity of selected rhizobacterial isolates against some phytopathogenic fungi was measured by inoculated 3 cm apart on the same agar plate. Fungal growth on each plate was observed, and the inhibition zone, if present, was determined as described in Riungu et al. [30]:

% Inhibition of mycelial growth = [(X–Y)/X] × 100

Where: X = Mycelial growth of pathogen in absence of antagonists, Y = Mycelial growth of pathogen in presence of antagonists

All experiments were done with three replications for each rhizobacterial isolate.

RESULTS AND DISCUSSION

Fifteen rhizosphere, rhizoplane and endorhizosphere of common bean seedlings root samples grown in 30% sewage sludge treated soil were collected and used for further study. The endophytic rhizobacterial isolates from the roots named rhizobacteria. The pure cultures of rhizobacterial colonies appeared creamy, smooth, shiny, circular, 1-2 mm in diameter and convex. Microscopic examinations showed that the isolates were Gram negative rod-shape, motile, and were studied for utilization of sucrose, dextrose, mannitol and lactose. Results showed that these rhizobacterial isolates were positive only for catalase, oxidase, organic acids, citrase, amylase, indole and caseinase. The rhizobacterial isolates utilized sucrose, mannitol and lactose differently. The morphological and biochemical examinations of the isolates were indicated that these isolates are belonging to the genus *Pseudomonas*. Battu and Reddy [31] showed that Gram negative, rod shaped bacterial colonies that produced yellowish green pigment on King's B medium and were positive for gelatinase and oxidase which were identified as Pseudomonas fluorescens.

The seven characteristic fluorescent pseudomonad rhizobacterial pure cultures of were coded as: GCB-01-96, GCB-04-96, GCB-09-96, GCB-10-96, GCB-13-96, GCB-27-96, and GCB-35-96 and considered for further study. The selected colonies on King's B agar, at λ at 265 nm, showed yellowish-green fluorescence and were maintained on King's B slants at 4°C for further investigations. Further analyses were done to proof the ability of these rhizobacterial isolates as PGPR by their production of IAA, HCN, ammonia, biofilm, siderophores, root colonization, seedling germination, vigour index and the antagonistic characterization.

It was found that all of the seven rhizobacterial isolates were able to produce these compounds with various extents. The results showed that out of the 7 endophytic isolates of fluorescent pseudomonads, GCB-10-96 showed highest PGP properties followed by GCB-27-96.

Qualitative analysis of IAA showed pink colour production on the Whatman number 1 filter paper demonstrated its production. The differences in colour intensities showed variation in IAA production. Spectrophotometric analysis showed that a maximum production of IAA was between 78.62 µg ml^{-1} produced by GCB-10-96, and 28.15 µg ml^{-1} by GCB-35-96 as showed in Figure 2. This is supported by the studies of Gundala et al. [32].

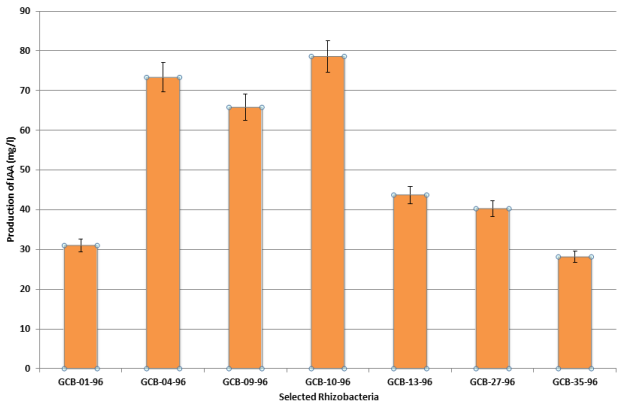

Figure 2

Production of IAA by the selected rhizobacterial isolates. Bar indicate standard error

Recently, there are many studies based upon the ability of PGPR to produce phytohormones like IAA

and their influence over the morphology, nutrition and plant growth and development. In most of these studies, IAA influences most of the root system [33] that promotes the plant growth. These investigations showed that all of the rhizobacterial isolates indicated the IAA production with different rates. Similar observations were made by Kumar et al. [9] from the isolates of bean rhizosphere. Karnwal [34] screened 30 strains for their ability to produce IAA. They showed the significance of bacterial IAA in different microbiomes–plant interactions which highlighted the use of IAA as part of their colonization strategy. The rhizobacterial isolates showing positive reactions for HCN production varied qualitatively in the amounts detected based on colour intensity developed on the picrate/Na_2CO_3 impregnated papers (Table 1)

Table 1

Production of HNC, NH_3 and siderophore by the endophytic fluorescent pseudomonad rhizoendobacteria

Isolates	HCN	NH_3	Siderophore
GCB-01-96	+	+	+
GCB-04-96	+++	+++	+++
GCB-09-96	++	++	++
GCB-10-96	+++	+++	+++
GCB-13-96	++	++	++
GCB-27-96	+++	+++	+++
GCB-35-96	+	+	+

HCN production is the primary mechanism of biocontrol. Ahmad et al. [35] observed that HCN production was a common character of *Pseudomonas*.
The results showed that the 7 selected rhizobacteria isolates of fluorescent pseudomonads were able to produce HCN. A change from yellow to orange, red, brown, or reddish brown was recorded as an indication of weak, moderate, or strongly cyanogenic potential, respectively.
Development of brown yellow colour was observed after addition of Nessler's reagent indicating production of ammonia (Table 1). Similar observation was earlier made by Yadav et al. [36] in chickpea plant under *in vitro* conditions using PGPR.
So, the ability of rhizobacterial isolates to form biofilm was examined using crystal violet. Results showed that all the rhizobacterial isolates had different biofilm forming ability (Figure 3) and the highest biofilm formation was with the isolate GCB-10-96 and the lowest was with the isolate GCB-35-96.
Most of plant–rhizobacterial associations rely upon the physical interaction between rhizobacteria and phytotissues. Direct illustrations of bacteria adhered to plant surfaces have revealed formation of biofilms [37]. Root-associated fluorescent pseudomonad rhizobacteria have been examined extensively, and many of these rhizobacteria promote the growth of host plants and may be used as biocontrol agents [38].
Species of *Pseudomonas* form dense biofilms on both abiotic and biotic surfaces, and are primary models in biofilm research [39]. In the present study, results showed that all rhizobacteria isolates had biofilm forming ability but in different quantities.

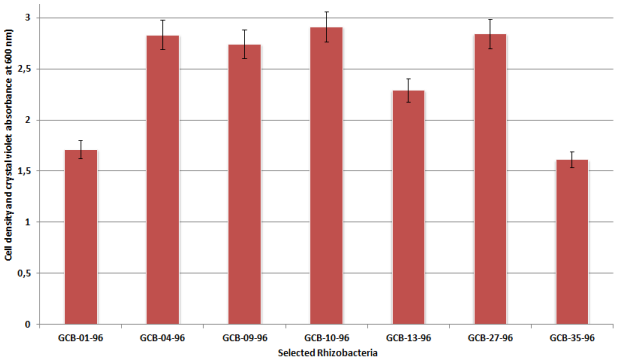

Figure 3
Formation of biofilm by selected rhizobacterial isolates. Bar indicate standard error

Enhanced siderophore production is an important factor contributing towards PGP. Fluorescent pseudomonads isolates inoculated on to CAS agar formed orange halo around the colony showing their ability to produce siderophore (Table 1).
The study was conducted on the estimation of siderophore production at λ_{630} for 5 days at 24 h intervals. All the 7 rhizobacterial isolates indicated an increase in siderophores production, but, the quantity of siderophore produced by each of the rhizobacterial isolate was varied. Of all the selected rhizobacterial isolates, GCB-10-96 showed highest siderophore production of 112.5% units after 4 days which was reduced to 87.3% units after 5 days (Figure 4).
This was followed by GCB-27-96 which produced 100.8% units of siderophores after 4th days of incubation, and it is significantly different from the isolate GCB-10-96. The potent of selected rhizobacterial isolates to produce siderophore after 5 days of incubation was as following: GCB-10-96 > GCB-27-96 > GCB-04-96 > GCB-09-96 > GCB-13-96 > GCB-35-96 > GCB-01-96.
At the 5th day of incubation the quantities of siderophore production were gradually. Results showed that the siderophore production by all rhizobacterial isolates increased till 4th days of incubation and decreased later.

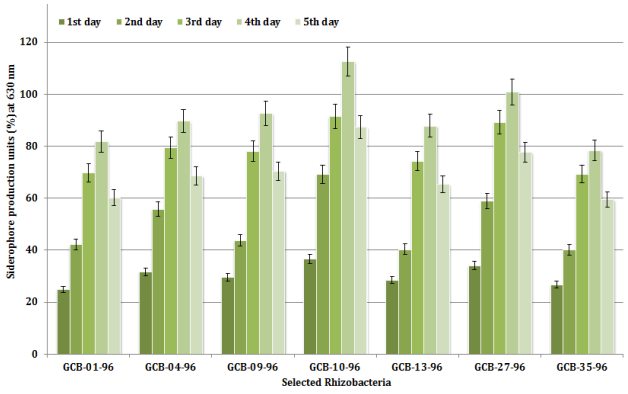

Figure 4

Production of siderophore (% units) as function of time by the selected rhizobacterial isolates. Bar indicate standard error

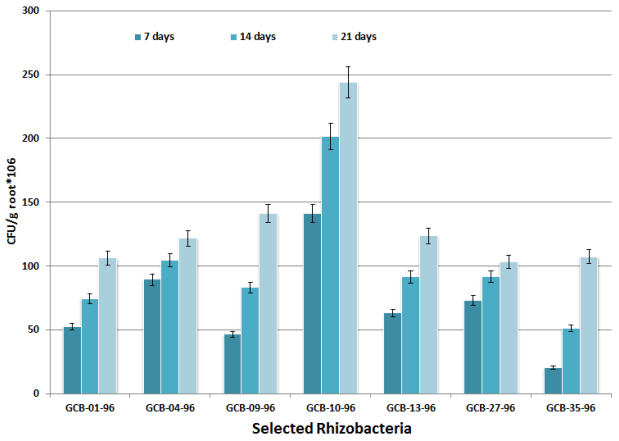

Figure 5

Root colonization by the selected rhizobacterial isolates. Bar indicate standard error

Wahyudi et al. [40], on screening of *Pseudomonas* sp. isolated from soybean rhizosphere showed siderophore production. Siderophore plays a very important role in plant growth as it sequesters Fe and help in plant nutrition [41]. Marques et al. [42] illustrated that growth promoting abilities of 6 bacterial isolates using *Zea mays*, and established that some isolates indicated siderophore production.

Soil microbiomes, especially rhizobacteria have developed a strategy to scavenge available iron (Fe^{3+}), which involves secretion of high-affinity, low-molecular weight iron-chelating ligands called siderophores [43].

The root colonization assays showed that all the tested rhizobacterial isolates successfully colonized the bean roots after only 7 days of seedling growth. The inoculated populations were even higher on 21-day-old roots. The largest root population was observed by the isolate GCB-10-96, and the lowest population was found by the GCB-35-96 (Figure 5).

The ability to colonize the root system is essential for rhizobacteria to be effective plant growth promoters. These results demonstrated that specific interaction between bean plant roots and the rhizobacterial isolates as well as the root population densities varied widely among the isolates.

The results indicated all 50 seeds were germinated under controls and treated seeds. This means that the germination rates were 100% for each isolates and the seeds were high quality and healthy. Studies indicated that increases in germination, shoot and root length were occurred in comparing with those treated with SDW controls.

The investigated PGPR isolates promote the growth of common bean seeds. The vigour index and plant dry biomass as a result of plant-endophytic isolate interaction as well as the antagonistic activity of the rhizoendophytic isolates against phytopathogens are present in Table 2.

Table 2

Effect of endophytic fluorescent pseudomonad rhizobacteria on vigour index, plant dry biomass and antagonistic activity against phytopathogens

Isolates	VI	Dry biomass	Phytopathogen suppression (%)
Control	1233	0.312	0
GCB-01-96	1253	0.330	53.67
GCB-04-96	1767	0.525	79.33
GCB-09-96	1533	0.447	64.33
GCB-10-96	2050	0.817	86.67
GCB-13-96	1517	0.381	72.36
GCB-27-96	2002	0.603	82.67
GCB-35-96	1250	0.320	61.07

In the present study, higher vigour index and dry weight, which are indices of PGP, were observed in treated seeds in comparison with control. The present study indicates the significant role played by endorhizobacteria in PGP could be a promising isolate in the development of a new formulation for growth promotion in common bean plants.

The use of synthesis and industrial products such as mineral fertilizers, pesticides, and growth regulators in agriculture causes a real public health problem. Moreover, the heavy metals contained in these agrochemicals pollute the groundwater and harvested products and also transferred to humans by feeding and/or direct contact, these heavy metals are reported to be involved in the cancer apparition [44]. Increased vigour index was observed in treated when compared to SDW controls. Seedlings treated with GCB-10-96, showed highest vigour index of 2050, which was followed by GCB-27-96 and GCB-04-96 which showed 2002 and 1767, respectively.

The rhizoendophytic bacteria were able to suppress different kinds of phytopathogenic fungi such as *Alternaria* sp., *F. oxysporum, F. solani, Pythium* sp.,

Sclerotinia sp. and *Rhizoctonia solani.* Also, Table 2 shows that the two rhizoendobacterial isolates GCB-10-96 and GCB-27-96 have high potent to suppress the phytopathogenic fungi.

Kumar et al. [45] observed that inoculation with bacteria isolated from the maize rhizosphere resulted in significant enhancement in growth, grain yield and yield attributing characters. Similar observations have also been reported in different plants treated with PGPR, which showed increased growth under different conditions [9; 46; 47]. In the present study, PGPR strains showed highly root-colonizing capacity. Agbodjato et al. [48] confirmed the potential of the 3 studied rhizobacteria (*A. lipoferum, P. fluorescens,* and *P. putida*) to promote seed germination and vegetative growth of maize plants.

CONCLUSION

The present study demonstrates the development of PGPR in biological PGP system. Most of the PGPR isolates significantly increased root colonization, plant shoots height, root length and dry matter production in common bean plants. The development of high potent antagonistic PGPR in sustainable agricultural systems is another promising function replacing the use of agrochemicals. PGPR are protecting natural environments and bioresources by playing a significant role in integrated pest management system. In accordance with their mode of action, PGPR can be classified as biofertilizers, phytostimulators and biopesticides with isolated rhizoendobacterial strains having overlapping applications. However, screening strategies for selecting the best rhizoendobacterial strain for rhizosphere competence and studies on the ecology of introduced new PGPR with the naturally resident PGPR in the soil and other microbial species in the plant rhizosphere will require more comprehensive knowledge, although the involvement of siderophore, phosphate solubilisation, phytohormones, nodulation, disease suppression, etc., and their coordinated expression to be responsible in enhancing the plant growth, yield and nutrient uptake of various crop plants in different agroecosystems. However, carefully controlled field properties of crop plants inoculated along with rhizoendobacteria are necessary for maximum crop production with the application of PGPR strains.

Now, it is very urgent to find as alternative agricultural practice that do not use the agrochemical products or significantly limit their use and increasing the agro-products to face the increasing of global population. The present study also, explored the eco-friendly approach of utilizing PGPR inoculation to improve the germination and growth of common bean plants.

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RELATIONS BETWEEN GLOBAL CHALLENGES, URBANIZATION, SOCIAL SECURITY AND ENVIRONMENTAL SECURITY FOR SUSTAINABLE DEVELOPMENT

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Received: November 2016

Abstract

The world is faced with challenges in three dimensions of sustainable development: economy, social and environmental factors. At the same time, the unsustainable consumption and production patterns have resulted in huge economic and social costs and may cause difficulty in the behaviour of the life on the Earth. The present paper gives the basic concepts about the relationships between the environmental security and the role of global urbanization in the global sustainable development. Meanwhile, the increase and worse management of urbanization can increased the pollution of the atmosphere, the lithosphere and hydrosphere and increase the dangerous impacts on human security. By the definition, the sustainable development is the development that meets the needs of today without destroying the future. If it is well managed, urbanization can bring important benefits for further development. The globe faces a serious environmental, social and economic challenge throughout the climate change, environmental pollution, public health as well as the world population increases. Soil is the fundamental unit of the landscape and ecosystem that provides biophysical, economic, cultural and spiritual services to the humanity and to all global biotic factors. Food and water securities, climate change limit, ecosystem development, biodiversity protection, energy sustainability, etc. are the main fundamental elements of global societal challenges and the concepts of the securities of soil, water, air, energy and food can be used to provide a useful links between themselves and important basic elements in sustainable development. A fully functioning soil lies at the centre of solving the issues of food and water securities, biodiversity, climate change and fresh-water regulation and other global environmental problems. The most significant threats to soil function at the global scale are soil erosion, loss of soil organic carbon and nutrient imbalance. Increasing human demands on soil-derived ecosystem services requires reliable data on global soil resources for sustainable development. This paper comes to the final conclusion that the (1) increased environmental, social and economic problems associated with rapid urbanization pose impendence to sustainable development and human security; (2) the decisions on development and sustainability depend on access to consequent well-organized information, raising global public awareness about the global environmental problems and cooperation between the governments and world-wide populations and (3) it is true that the humans that secure their own land will sustain it.

Key words: *Urbanization, Global issues, Global societal challenges, Soil security, Sustainable development*

GLOBAL URBANIZATION

Urbanization provides new jobs and new opportunities for millions of people in the world, and has contributed to poverty eradication efforts worldwide. At the same time, rapid urbanization adds pressure to the resource base, and increases demand for energy, water, and sanitation, as well as for public services, education and health care. People migrate to urban centres hoping to secure a better future for themselves and their families. It is obvious that the issue of urbanization is multidimensional complexity. Urbanization can basically be caused by 3 factors: 1) natural population increase, 2) rural–urban migration, and 3) annexation [1]. However, large urban areas have become focal areas in our world, selling dreams and become at the same time a conglomeration of individual dreams. More people are pushing faster into cities. The phenomenon of increasing the proportions of the population living in urban areas is called urbanization [2]. Birch and Wachter [3] mentioned that in 2010, a majority of the world's population lived in cities, an important milestone actually reached in 2008; and by 2050, this proportion

will approach 70%. These simple facts point in 2 directions: 1) looking back, they confirm the intensity with which the world has urbanized over the past 50 years and, 2) moving forward, they mark the world's cities as the central terrain on which the critical issues of human development will play out over the course of the 21st century. Cohen [4] said that the decade ending in 2010 spanned three unique, important transitions in the history of human-kind. Before 2000, young people always outnumbered old people. From 2000 forward, old people will outnumber young people. Until approximately 2007, rural people always outnumbered urban people. From approximately 2007 forward, urban people will outnumber rural people. From 2003 on, the worldwide median number of children/woman/life-time at current fertility rates was at or below the number required to replace the parents in the following generation, even though the declining average total fertility rate remained above the replacement level. Malpezzi [5] stated that the world's population, roughly 6.7 billion people, spreads over about 13 billion hectares of land. Much of this land is arid or otherwise inhospitable to settlement, but more on that later. Variously considered, people live in nations, regions, cities, and neighbourhoods. The study of their urbanization is, more or less, the study of density as it occurs in these venues. Yeh [6] mentioned that China has experienced rapid urban growth since the adoption of Economic Reform and Open Policy in 1978. Not only is more than 1/3 of the country's population now living in cities, but the remaining population is becoming increasingly dependent on cities and towns for its economic survival and livelihood. Already, more than half of the world's population live in towns and cities, and most future population growth will occur in the urban areas of developing countries (Figure 1).

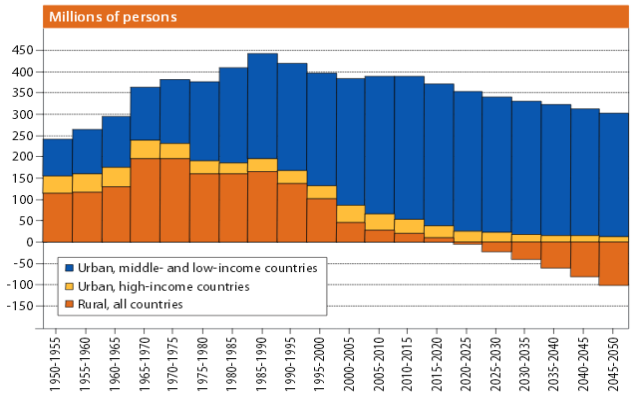

Figure 1

Urban and rural population growth, high-, low- and middle-income countries, 1950 to 2050 [7]

Montgomery and Balk [8] concluded that as urban populations continue to grow, poor countries and international aid agencies are likely to face mounting pressure to rethink their development strategies and set priorities with both rural and urban interests in mind. To plan for future growth, they will require informative forecasts of city size that are free from systematic bias. Unfortunately, demographic researchers are not yet in a position to deliver these scientific inputs. Sheppard [9] mentioned that from the perspective of global urbanization, the first decade of the 21st century will be seen not as the time when the problems associated with urbanization first became apparent, nor as the time when the basic outlines of policy solutions first attained widespread recognition, if not agreement. The importance of infrastructure provision, the need for legal institutions that recognize and seek to internalize the externalities (positive and negative) intrinsic to high-density settlements, and the connection of housing provision to human health and social order have all been understood. Landis [10] said that once known as urban activity models, urban growth models emerged in the mid-1960s out of advances in regional science, huge improvements in computing speed and storage capacity, a newfound surplus of detailed activity data, and federal mandates coupled with funding for metropolitan planning organizations to back up transportation funding requests with careful projections and hard-headed analysis. Overhyped and underdeveloped, early urban models soon proved unreliable. Seto [11] concluded that the size of the world's growing urban population gives urgency to the need for accurate estimates of the location, size, and growth of existing urban areas as well as forecasts of likely regions, magnitudes, and configurations of future urban growth. However, to date, there exists no global database that accurately describes and maps which portions of Earth's habitable land are urbanized, or how those portions have changed over the recent decades. Ottichilo [12] recognized the fast-growing Nairobi (Kenya), the most populous city in East Africa, offers an important example of how a municipality that lacks modern maps and databases turns to spatial technologies, especially remote-sensing and geographic information system technologies, to track urban growth and development and inform public and private infrastructure investments and other decision-making.

Urban population growth is expected to continue setting the pace of world population growth, and in the next 10-15 years, for the first time in history, the world rural population is expected to decline (Figure 2).

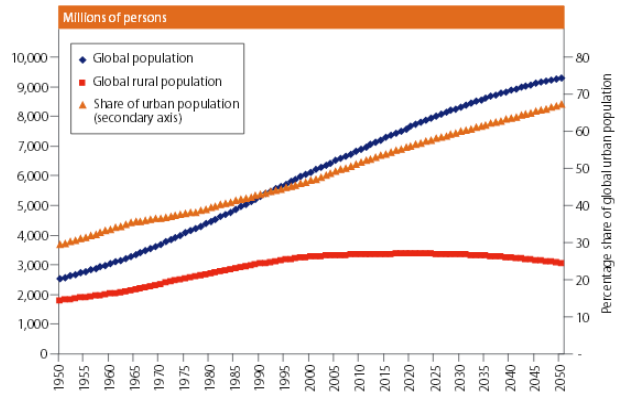

Figure 2

Population trends and projections, 1950-2050 [7]

Today cities are the home of more than 50% of the earth's population [7]. In Europe even 75% of the population live in urban areas, which cover only 4% of the area [13]. Consequently, urbanization is not local, regional or national, it is global phenomenon. The worldwide phenomenon of urbanization is exceptionally dynamic in upcoming developing countries, where unprecedented urban growth rates have occurred over the last 30 years [14]. It is along with climate change arguably the most dramatic form of irreversible land transformation. The dynamics of urban development in recent history are nothing else than awesome.

A basic framework proposes systematization for a chronologic workflow to approach the global problem of urbanization from the problem statement to the benchmarking of success or failure (Figure 3).

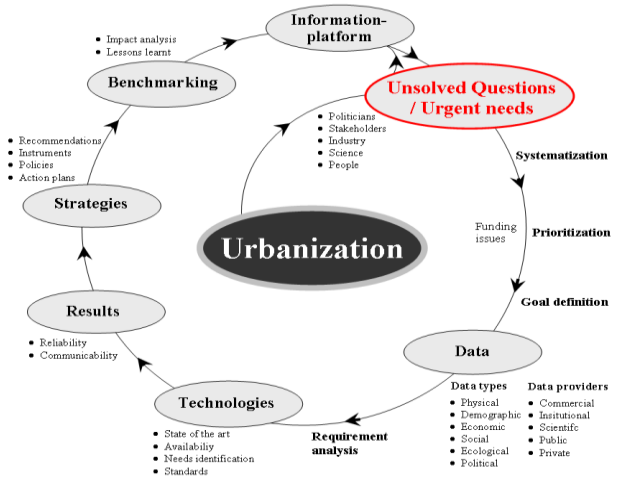

Figure 3

A framework for holistic strategy development to address the global challenge of mega-urbanization [15]

There is considerable regional diversity in the patterns of urbanization and an even greater variation in the level and pace of urbanization of individual countries. For example, on average more than three quarters of the Latin America and the Caribbean region is highly urbanized, whereas least developed countries and landlocked developing countries are still predominantly agricultural - although their path towards urbanization is expected to accelerate in the next decades (Table 1).

The late urbanization in Asia and Africa is expected to gain speed and concentrate the majority of the additional 3 billion urbanites during 2010-2050. Similarly, the number of urban agglomerations (750,000 inhabitants or more) and the number of inhabitants per agglomeration are expected to grow significantly in Asia and Africa by 2025 [7]. It is expected that over 80% of the urban population added in the next 15 years will be found in middle-income countries such as China, India, South Africa, Nigeria, Indonesia and Pakistan.

The Global Risks 2015 Report looks at four areas that face particularly daunting challenges in the face of rapid and unplanned urbanization: infrastructure, health, climate change, and social instability. While the challenges posed by large-scale urbanization are immense, the future of human development requires that we find ways to promote socially inclusive growth, environmental sustainability, and resilient infrastructure. The timely and relevant scholarship assembled in *Global Urbanization* will be of great interest to scholars and policymakers in demography, geography, urban studies, and international development. Urban people change their environment through their consumption of food, energy, water, and land. And in turn, the polluted urban environment affects the health and quality of life of the urban population.

Table 1

Expected regional figures for share of urban population [7]

	Percentage in year				
Country/region	1975	2000	2012	2025	2050
World	37.7	46.7	52.6	58.0	67.2
More developed regions	68.7	74.1	78.0	81.1	85.9
Less developed regions	27.0	40.1	47.1	53.6	64.1
Africa	25.6	35.6	39.9	45.3	57.7
Asia	25.0	37.4	45.7	53.1	64.4
Europe	65.2	70.8	73.1	76.1	82.2
Latin America and the Caribbean	60.7	75.5	79.4	82.5	86.6
North America	73.8	79.1	82.5	85.0	88.6
Australia and New Zealand	85.4	86.9	88.9	90.3	92.4

Oceania	71.9	70.4	70.7	71.1	73.0
Least developed countries	14.7	24.3	28.9	35.2	49.8
Small island developing States	45.8	55.5	59.5	62.4	67.3
Landlocked developing States	22.2	26.1	28.3	32.6	45.6

THE SUSTAINABLE ECO-CITY

The eco-city aims to curb all the negative factors that urbanisation has had on the natural environment. This includes reducing air pollution, water pollution, waste dumping and increasing use of space and energy resources. An eco-city aims to do many things such as:

- absorb rainfall to prevent flooding and pollution of fresh water supplies
- maintain arable land in surrounding areas to provide food
- increase public transport and fuel efficient vehicles; and
- improve energy use, technology and recycling.

SMART GROWTH CITIES

The smart growth city requires increasing the number of people within smaller areas of city living. Smart city planning requires a condensation of people, buildings and goods and services as well as eliminating individual cars. Smart city planning allows for people to live, work and play all within walking distance. The concept of eliminating all cars in urban areas and reducing public transport within the city centres is believed to help reduce pollution, a major issue of urbanization. Smart growth cities promote walking or cycling as primary means of transport within the city centre.

URBANIZATION, FOOD SECURITY AND SUSTAINABLE DEVELOPMENT

To minimise the negative effect, Hu and Chen [16] suggested to better deal with the relationships between market and government, between dispersion and concentration and between economic development and social development in the process of urbanisation [16]. Estimates indicate that food production will have to increase 70% globally to feed an additional 2.3 billion people by 2050. Food demand is anticipated to continue to shift towards more resource-intensive agricultural products, such as livestock and dairy products, thereby exerting additional pressure on land, water and biodiversity resources.

Current agricultural practices are a leading source of greenhouse gas emissions, while also leading to other problems, such as loss of soil fertility and water pollution from run-off. Increased temperatures and more volatile weather patterns caused by climate change may already be affecting crop yields, affecting incomes and agricultural production. Currently, it is estimated that 32% of the total food produced globally is wasted. In order to substantially reduce the quantity of food lost and wasted, changes have to take place at different levels of the food chain: production, storage, transportation and consumption. In developed countries, efforts are most needed at the retail and consumer end, owing in part to management practices and consumption habits. In developing countries, interventions are needed at the producer end, before food reaches the market, to address inadequate harvesting techniques and storage conditions.

Nutrition outcomes are largely determined not only by food production and accessibility but also by food quality and diversity. A considerable potential for increasing the nutritional status of people and the efficiency of the whole food chain lies in encouraging changes in diet and consumption patterns, as well as designing pro-nutrition policies in other sectors, such as health and education.

An increase in food production will also require integrating sustainable practices, particularly regarding the use of natural resources. Many of the current agricultural practices have relied on cheap energy and abundant water and land, and are a leading source of greenhouse gas emissions. These practices are now proving unsustainable for the environment and health, due to contamination of air, land and water sources. At the same time, they have led to substantial productivity losses, thereby posing risks to food security. Thus, increasing food production and improving distribution to respond to population growth, urbanization and a change in consumption patterns will require an integrated approach to addressing several challenges simultaneously along the entire food chain. Such an integrated approach to food security and environmental sustainability should also take into consideration the nexus of food, water, energy, environment and climate, while reorienting food production, distribution and consumption.

- The first challenge is to increase food production, while minimizing the environmental impact and increasing natural resource efficiency. This will require increasing agricultural productivity, in particular in developing countries where the agricultural sector contributes an important share of gross domestic product and where large productivity gaps still exist.
- The second major challenge will be to improve the access to food and markets, as hunger often occurs in countries where there is enough food produced.

Income poverty is a major factor preventing access to food.

- The third challenge is to orient food consumption towards "sustainable diets", that is, diets that are less resource-intensive and more nutritious, which will be crucial for the sustainability of the food system.
- Finally, in an increasingly interconnected world, improving agricultural productivity and the allocation of food within and across countries requires well-coordinated actions at local, national and global levels.

An increase in food production will also require integrating sustainable practices, in particular in the use of natural resources. Many of the current agricultural practices have relied on cheap energy and abundant water and land, and are a leading source of green-house gas emissions. These practices are now proving unsustainable for the environment and health. At the same time, they have led to substantial productivity losses, thereby posing risks to food security. Thus, agricultural productivity and an efficient use of natural resources, as well as climate-related adaptation and resilience-building, should be part of an integrated policy approach.

United States, it has been demonstrated that in the long term, organic agricultural methods can outperform conventional chemical farming in terms of crop yield, sustainability and profit.

The urbanization process is also increasing competition for arable land and wetlands. So far, urban areas occupy about 1% of the total land surface, but urbanization is projected to continue at a fast pace in the next decades. Between 2012 and 2050, the world urban population is expected to increase by 69%. At the same time, renewable energy strategies, such as use of biofuels, are increasing demand for land resources. Hence, developing the potential to create more sustainable land management systems, in order to reverse current trends in food insecurity and unsustainable land degradation, is desirable and possible.

FAO has estimated that meat consumption in 2050 will amount approximately to 4.65 billion tons. Poultry meat consumption level is expected to be 2.3 times higher than in 2010, while consumption of other livestock products is expected to be between 1.4 and 1.8 times higher [20]. The world's average daily calorie availability is projected to raise from an average of 2,789 kilocalories per person in 2000 to 3,130 kilocalories per person in 2050, a 12% increase. Further, current food waste is around 30-50% of total production [21].

Water is another essential natural resource for agriculture, whose limit of sustainability may have already been reached in many regions. Global water withdrawals have tripled over the last 50 years and water withdrawals for irrigation are expected to increase by almost 11% by 2050 [20]. Yet, today, 80% of the world's population lives in areas with high levels of threat to water security, particularly in developing countries. In addition, it is expected that the increasing and competing demands for water will aggravate the serious depletion of surface-water resources. Water scarcity represents an important challenge for agriculture, which uses 70% of global freshwater [22].

In the coming decades, it is expected that climate change will continue to have adverse effects on agricultural production. Even a modest climate change of about 2°C can change rainfall patterns, resulting in a shorter growing season and lower agricultural production, particularly in areas that are already hot and dry, for example, in Africa and South Asia [18].

There are several factors contributing to the problem of climate change. Current agriculture practices, including land clearing for cultivation and inefficient use of fertilizers and organic residues, constitute one such factor, being responsible for 25-33% of greenhouse gas emissions [18]. While agriculture is a major contributor to global greenhouse gas emissions, it can also be part of the solution to the problem of climate change.

SUSTAINABLE DEVELOPMENT

The world is faced with challenges in all three dimensions of sustainable development: economic, social and environmental. More than 1 billion people are still living in extreme poverty and income inequality within and among many countries have been rising; at the same time, unsustainable consumption and production patterns have resulted in huge economic and social costs and may endanger life on the planet. Achieving sustainable development will require global actions to deliver on the legitimate aspiration towards further economic and social progress, requiring growth and employment, and at the same time strengthening environmental protection.

Globalization is not a new phenomenon. In the nineteenth century, the world economy underwent its first process of globalization, driven by technological progress in the form of lower transportation and communication costs. World trade expanded at close to 4% annually on average throughout the century, much faster than in previous centuries [23]. The global community has made great strides in addressing poverty, but a mere continuation of current development strategies will not suffice to achieve sustainable development. Economic and social progress remains uneven, the global financial crisis has revealed the fragility of progress, and accelerating environmental degradation inflicts increasing costs on societies. There are a number of economic, social,

technological, demographic and environmental megatrends underlying these challenges to which a sustainable development agenda will have to respond. These trends influence and reinforce each other in myriad ways and pose enormous challenges.

Urbanization is proceeding rapidly in developing countries, globalization and financialization are perpetuating inequalities, while exposing countries to greater risks of contagion from crises, and food and nutrition as well as energy security is threatened by competing demands on land and water, as well as environmental degradation. Information and communications technologies have also made the diffusion of information easier, and have facilitated better access by developing countries to the global knowledge pool. Because of the critical role of science and technology in addressing the social, economic and environmental challenges faced by countries, this wider diffusion is contributing to the progress of development in a wide range of areas. At the same time, innovative activity and technology development continue to be concentrated in a small number of advanced economies. Only very few countries such as Brazil, China and India, have entered this segment in recent decades, because core research and development activities are very rarely outsourced and remain overwhelmingly centred at corporate headquarters in developed countries [24].

Sustainable development is a multi-dimensional way of thinking about the interdependencies among natural, social, and economic systems in our world. It represents a process in which economics, finance, trade, energy, agriculture, industry, and all other policies are implemented in a way to bring about development that is economically, socially, and environmentally sustainable. Thus, the goal of sustainable development is to meet the needs of the present without compromising the ability of future generations to meet their needs. Sustainable development calls for improving the quality of life for all of the world's people without increasing the use of our natural resources beyond the Earth's carrying capacity. While sustainable development may require different actions in every region of the world, the efforts to build a truly sustainable way of life require the integration of action in three key areas:

- Economic Growth and Equity
- Conserving Natural Resources and the Environment
- Social Development.

Sustainable development is the parallel consideration of healthy environments, life, and human well-being. This includes issues of population, climate, economic prosperity, energy, natural resource use, waste management, biodiversity, watershed protection, technology, agriculture, safe water supplies, international security, politics, green building, sustainable cities, smart development, community relations, human values, etc. All these "pieces" are parts of the sustainable society puzzle, because they are the basic ingredients of everyday life.

Overall, globalization has provided opportunities for emerging economies and developing countries, and in recent years their growth rates have been consistently higher than growth rates in the developed world. There are two critical caveats with respect to this broad trend of convergence, however. It has not made developing countries immune to cyclical stocks: indeed, globalization has increased countries' vulnerabilities; and it is far from uniform, with some developing countries not only excluded from this convergence process but falling further behind. Average per capita growth also hides increasing inequalities within countries, which are also partly related to globalization. A significant part of the global population therefore does not benefit from convergence [25].

Sustainable development will need to be inclusive and take special care of the needs of the poorest and most vulnerable. Strategies need to be ambitious, action-oriented and collaborative, and to adapt to different levels of development. They will need to systemically change consumption and production patterns, and might entail, inter alia, significant price corrections; encourage the preservation of natural endowments; reduce inequality; and strengthen economic governance.

The world reached the poverty target 5 years ahead of the 2015 deadline. In developing regions, the proportion of people living on less than $1.25 a day fell from 47% in 1990 to 22% in 2010. About 700 million fewer people lived in conditions of extreme poverty in 2010 compared with 1990. Still, results fall short of international expectations and of the global targets set to be reached by the 2015 deadline. It remains imperative that the international community takes bold and collaborative actions to accelerate progress in achieving the Millennium Development Goals [26]. Continuation of current development strategies will not suffice to achieve sustainable development beyond 2015. Moreover, relying on "business as usual" scenarios presents clear risks, because evidence is mounting that:

(a) The impact of climate change threatens to escalate in the absence of adequate safeguards and there is a need to promote the integrated and sustainable management of natural resources and ecosystems and take mitigation and adaptation action in keeping with the principle of common but differentiated responsibilities;

(b) Hunger and malnourishment, while decreasing in many developing countries, remain persistent in other countries, and food and nutrition security continues to be an elusive goal for too many;

(c) Income inequality within and among many countries has been rising and has reached an extremely high level, invoking the spectre of heightened tension and social conflict;
(d) Rapid urbanization, especially in developing countries, calls for major changes in the way in which urban development is designed and managed, as well as substantial increases of public and private investments in urban infrastructure and services;
(e) Energy needs are likely to remain unmet for hundreds of millions of house-holds, unless significant progress in ensuring access to modern energy services is achieved;
(f) Recurrence of financial crises needs to be prevented and the financial system has to be redirected towards promoting access to long-term financing for investments required to achieve sustainable development.

Three of cross-sectoral issues with immediate implications for realizing sustainable development, namely:

a) sustainable cities,
b) food and nutrition security and
c) energy transformation are under the focusing today.

An important sustainable development challenge arises from unsustainable consumption and production patterns that have evolved in developed countries, a pattern that is increasingly being followed by developing countries. For example, per capita green-house gas emissions levels in developed countries are 20-40 times greater than needed for stabilization of the atmospheric greenhouse gas concentration. The per capita ecological footprints in developed countries are 4-9 times greater than their bio-capacity. The high degree of inequality that accompanies and promotes these patterns makes them socially unsustainable and constrains achievement of the human development goals.

The outcome document of the UN Conference on Sustainable Development [26] provides guidance for achieving the transition to sustainable development as a means of increasing the well-being of current and future generations in all countries. Sustainable development strategies need to be inclusive and take special care of the needs of the poorest and most vulnerable. Strategies need to be ambitious, action-oriented and collaborative, taking into account different national circumstances. About 1 billion people still live in slums lacking access to basic infrastructure and services such as water, sanitation, electricity, health care and education. There might be 3 billion slum dwellers by 2050 unless decisive actions are taken.

Sustainable development of urban areas requires integration and coordination, including regarding land-use issues, food security, employment creation, transportation infrastructure development, biodiversity conservation, water conservation, renewable energy sourcing, waste and recycling management, and the provision of education, health care and housing. Investment in the reduction of waste production and improvement of waste collection and recycling systems is needed in most cities across the world. Providing access to modern energy services is a real challenge to urban authorities in developing countries which often do not have enough capacity to respond, nor the ability to raise the needed long-term financial resources for investment.

FINANCING SUSTAINABLE DEVELOPMENT

A significant share of the investments necessary to achieve sustainable development will have to come from private sources, which nonetheless will depend on the availability of public funds to match those investments, through the provision of guarantees and/or regulation to assure future revenue streams. Public financing, regulation and private market-based financing will therefore have to be combined, based on the specific characteristics of the newly created assets. Financing strategies for sustainable development in cities can draw upon a wide range of instruments. Sources of finance can have different degrees of stability and predictability. Innovative financing mechanisms can also make contributions to developing countries in respect of mobilization of additional resources for financing for development. Sustainable financing needs to be ensured across sectors, including agriculture, forestry, energy, health and education, as well as across economic segments, such as small and medium-sized enterprises, infrastructure and innovation, in both developed and developing countries. Special attention needs to be directed towards financing the global commons (e.g., the atmosphere, oceans, biodiversity and forests) and global health. A close partnership between local and national authorities is needed to finance the sustainable development of cities. While cities need to raise financial resources from capital markets directly, financial oversight mechanisms must be in place to manage risks so that municipal borrowing does not result in an excess of non-performing loans in the banking system or the incurring of huge financial liabilities by the central government. Thus, for poor and rich cities alike, part of the financing would have to be directed towards addressing global environmental challenges and the livelihoods of present and future generations. Achieving the sustainability of cities can be conceived as entailing the integration of four pillars: social development, economic development, environmental management, and urban governance.

Figure (4) presents the four pillars for achieving urban sustainability encompassing the balanced accomplishment of social and economic development, environmental management and effective governance.

Figure 4

Pillars for achieving sustainability of cities [7]

The integration of the four pillars can generate synergies, for example, between waste and recycling management (environmental management) and access to water and sanitation (social development); between air quality conservation and green public transportation; and among production and distribution of renewable energy sources, green energy access, and adaptation to and mitigation of climate change, as well as between the goal of reducing inequities (urban governance) and that of ensuring adequate access to green housing, education and health (social development). Investment is the catalyst behind the realization of each of the component goals of urban sustainability.

ENVIRONMENTAL DEGRADATION

The unusually stable global environment has been the precondition for unprecedented human development over the last ten thousand years; this stability is now under threat from human activity. Most critically, energy consumption has skyrocketed owing to rapid population and economic growth, resulting in unprecedented concentrations of CO_2 in the atmosphere and anthropogenic climate change. If greenhouse gas emissions, global resource consumption and habitat transformation continue at or above current rates, a state shift in the Earth's biosphere is likely [27], irreversibly changing the environmental conditions so favourable to human development in recent millenniums. Damage to the global environment is reaching critical levels and threatens to lead to irreversible changes in global ecosystems. Most visibly in climate change, critical thresholds have already been exceeded.

Climate change poses numerous and stark challenges for sustainable development and its effects will be felt in all regions of the globe, although the intensity of exposure will vary. Degree of vulnerability will vary even more, with developing countries and the poor, which have contributed the least to global warming, likely to suffer the most. Climate change also puts pressure on natural resources that are essential for sustaining human civilization. In the past, resource scarcity was often presented as a critical challenge, but for much of the twentieth century, resource prices actually fell. The combination of rapid economic expansion, continued population growth and a changing climate raises the spectre of resource scarcities. In the medium and long term, it may lead to a strong sustainability challenge. There is significant scope for substitution in many areas, yet certain forms of natural capital including the ecological services they provide cannot be replaced by man-made capital. Their exploitation has thus to be limited so as to preserve the overall capacity of ecosystems to provide those services [28]. Figure 5 presents a framework within which both human development and environmental protection can become universal goals and be integrated, ending the current separation between their domains of application. This framework can provide the basis for the post-2015 agenda. The ideas and the causal linkages presented in Figure (5) are abstract and very general. It is necessary to make them more concrete.

Soil, water and energy in particular are critical resources for humanity, and their availability and use are tightly interconnected, with multiple feedback channels between them. All of them have strong links to agriculture and food production. Large unmet needs at the global level require and will inevitably lead to a further expansion in their use and exploitation. Combined with the additional impact of climate change, this expansion may very well lead to much tighter supplies, and thus to price volatilities and sustained price increases.

Stresses in water supplies arise from the increase in consumptive use and pollution of freshwater, for which agriculture is overwhelmingly responsible. The consumption of agricultural products accounts for 92% of the global freshwater footprint, an indicator for humans' appropriation of freshwater resources [29].

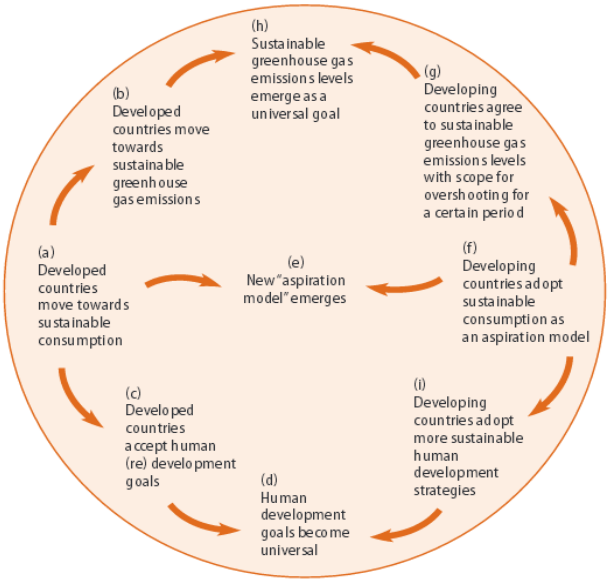

Figure 5

Framework for integrating human development and environmental protection goals and making them universal [7]

SOIL SECURITY "TO SAVE THE PLANET, WE MUST FIRST SAVE THE SOIL"

As noted earlier there are existing concepts which have been proposed that are similar to soil security, namely: Soil Quality, Soil Health and Soil Protection. Soil security, an overarching concept of soil motivated by sustainable development, is concerned with the maintenance and improvement of the global soil resource to produce food, fibre and freshwater, contribute to energy and climate sustainability, and to maintain the biodiversity and the overall protection of the ecosystem. Security is used here for soil in the same sense that it is used widely for food and water [30]. Soil degradation is a critical and growing global problem. As the world population increases, pressure on soil also increases and the natural capital of soil faces continuing decline. International policy makers have recognized this and a range of initiatives to address it have emerged over recent years. However, a gap remains between what the science tells us about soil and its role in underpinning ecological and human sustainable development, and existing policy instruments for sustainable development. Functioning soil is necessary for ecosystem service delivery, climate change abatement, food and fibre production and fresh water storage. Yet key policy instruments and initiatives for sustainable development have under-recognized the role of soil in addressing major challenges including food and water security, biodiversity loss, climate change and energy sustainability. Soil science has not been sufficiently translated to policy for sustainable development. Two underlying reasons for this are explored and the new concept of soil security is proposed to bridge the science–policy divide. Soil security is explored as a conceptual framework that could be used as the basis for a soil policy framework with soil carbon as an exemplar indicator. There are 6 major challenges for society and soil security are present the Figure (6).

Soil delivers the ecosystem services on which human life depends. It provides functions imperative to society, such as food and fibre production, water filtration, and the recycling of carbon by the decomposition of plant and animal residues. These processes, with many being carried out by microorganisms in the soil, are also linked to some of the greatest challenges facing humanity.

Figure 6

Soil functions and the major challenges for society and soil security

SUSTAINABLE SOIL MANAGEMENT:

Table (2) summarizes and describes the 4 main ways to manage the soil.

Consequently, the ability to deal with these challenges directly depends on our understanding of these microbes and how they interact with the minerals and plant roots in soil (the rhizosphere). A better understanding of this soil powerhouse could even enable us to engineer this layer to increase nutrient uptake by plants and reduce agricultural greenhouse gas emissions. Every year, the world loses 75 billion tonnes of crop soil as a result of erosion due by wind, water and through agriculture. That's more than 205 million tonnes a day, and represents a cost of US$ 70 per person per year. As it is estimated to take about 100 years to form 1 cm of topsoil, fertile soil is being lost much faster than it can be replaced through natural processes. It is therefore effectively a non-renewable and limited natural resource, and needs to be protected.

Table 2

The aims and strategies main 4 ways for soil management

Aim	Strategies
1. Water efficiency and productivity	
Increase plant water availability in rained agriculture	Minimise run-off; Maximise rainfall infiltration and storage in the soil
	Reduced non-productive evaporation
	Harvest and concentrate rainfall through run-off to crop area or for other use
Increase plant water availability in irrigated agriculture	Minimise water looses from irrigation system
	Efficient and effective and application of water
	Recharge aquifer/groundwater; water collection to enable off season irrigation
Increase plant water up-take	Increase productive transpiration
2. Soil fertility	
Improve nutrient availability and up-take	Reduce nutrient mining and loose
	Improve soil nutrient holding capacity and plant nutrient up-take capacity
3. Plants and their management	
Maximise yield	Use best suited planting material and optimise management
4. Microclimate	
Create favourable growing conditions	Reduce evapotranspiration
	Optimise temperature and radiation
	Reduce mechanical damage of plants

Because of this the security of soil in itself should be promoted to the status of a global existential challenge. Also, Soil Security can be defined as in McBratney et al. [30] as being concerned with the maintenance and improvement of the world's soil resource to produce food, fibre and freshwater, contribute to energy and climate sustainability, and maintain the biodiversity and the overall protection of the ecosystem. In this definition, security is used in the same sense that it is used for food, water and energy. To frame this concept a set of dimensions need to be established and defined and, as with other concepts such as food and water security, these dimensions should account for the quantity, quality and accessibility of the soil.

The European Union Soil Protection Strategy is based on soil function and the threats to soil. As described earlier (Bouma and Droogers, 2007), there are seven functions defined. If we consider soil security, the function of the soil to (i) produce food and other biomass would be related to soil capability and soil condition, while soil capital would relate to (ii) storing, filtering and transformation and (iii) the provision for a habitat and gene pool. The cultural environment for mankind (iv) is related to soil connectivity and valued through the soil capital, where (vi) acting as a carbon pool is related to soil condition and capital, and being an archive for archaeological heritage (vii) is covered by soil condition and its connectivity. Although described as a function we would consider (v) source for raw materials, as a threat. The European Commission has identified five threats classified as erosion, compaction, contamination, organic matter decline, salinization, landslides, and surface sealing. Many of these would relate largely to soil condition, capability and capital. It is clear that the concepts of soil quality, health and protection are directly and implicitly related to the concept of soil security and its dimensions, but it would be suggested that the soil security concept is wider with clear dimensions to frame the value of soil and how people interact with it. Most importantly the soil security concept is strengthened by the proposal of the soil capability, capital, connectivity and codification dimensions, which are not explicitly identified in the other concepts being compared.

DEFINITIONS OF THE 16 ENVIRONMENTAL QUALITY OBJECTIVES

1. REDUCED CLIMATE IMPACT In accordance with the UN Framework Convention on Climate Change, concentrations of greenhouse gases in the atmosphere must be stabilised at a level that will prevent dangerous anthropogenic interference with the climate system. This goal must be achieved in such a way and at such a pace that biological diversity is preserved, food production is assured and other goals of sustainable development are not jeopardised. Sweden, together with other countries, must assume responsibility for achieving this global objective.
2. CLEAN AIR The air must be clean enough not to represent a risk to human health or to animals, plants or cultural assets.
3. NATURAL ACIDIFICATION ONLY The acidifying effects of deposition and land use must not exceed the limits that can be tolerated by soil and water. In addition, deposition of acidifying

substances must not increase the rate of corrosion of technical materials located in the ground, or water main systems, archaeological objects and rock carvings.

4. A NON TOXIC ENVIRONMENT The occurrence of man-made or extracted compounds in the environment must not represent a threat to human health or biological diversity. Concentrations of non-naturally occurring substances will be close to zero and their impacts on human health and on ecosystems will be negligible. Concentrations of naturally occuring substances will be close to background levels.
5. A PROTECTIVE OZONE LAYER The ozone layer must be replenished so as to provide long-term protection against harmful UV radiation.
6. A SAFE RADIATION ENVIRONMENT Human health and biological diversity must be protected against the harmful effects of radiation.
7. ZERO EUTROPHICATION Nutrient levels in soil and water must not be such that they adversely affect human health, the conditions for biological diversity or the possibility of varied use of land and water.
8. FLOURISHING LAKES AND STREAMS Lakes and watercourses must be ecologically sustainable and their variety of habitats must be preserved. Natural productive capacity, biological diversity, cultural heritage assets and the ecological and water-conserving function of the landscape must be preserved, at the same time as recreational assets are safeguarded.
9. GOOD QUALITY GROUNDWATER Ground water must provide a safe and sustainable supply of drinking water and contribute to viable habitats for flora and fauna in lakes and watercourses.
10. A BALANCED MARINE ENVIRONMENT, FLOURISHING COASTAL AREAS AND ARCHIPELAGOS The North Sea and the Baltic Sea must have a sustainable productive capacity, and biological diversity must be preserved. Coasts and archipelagos must be characterized by a high degree of biological diversity and a wealth of recreational, natural and cultural assets. Industry, recreation and other utilization of the seas, coasts and archipelagos must be compatible with the promotion of sustainable development. Particularly valuable areas must be protected against encroachment and other disturbance.
11. THRIVING WETLANDS The ecological and water conserving function of wetlands in the landscape must be maintained and valuable wetlands preserved for the future.
12. SUSTAINABLE FORESTS The value of forests and forest land for biological production must be protected, at the same time as biological diversity and cultural heritage and recreational assets are safeguarded.
13. A VARIED AGRICULTURAL LANDSCAPE The value of the farmed landscape and agricultural land for biological production and food production must be protected, at the same time as biological diversity and cultural heritage assets are preserved and strengthened.
14. A MAGNIFICENT MOUNTAIN LANDSCAPE The pristine character of the mountain environment must be largely preserved, in terms of biological diversity, recreational value, and natural and cultural assets. Activities in mountain areas must respect these values and assets, with a view to promoting sustainable development. Particularly valuable areas must be protected from encroachment and other disturbance.
15. A GOOD BUILT ENVIRONMENT Cities, towns and other built-up areas must provide a good, healthy living environment and contribute to a good regional and global environment. Natural and cultural assets must be protected and developed. Buildings and amenities must be located and designed in accordance with sound environmental principles and in such a way as to promote sustainable management of land, water and other resources.
16. A RICH DIVERSITY OF PLANT AND ANIMAL LIFE Biological diversity must be preserved and used sustainably for the benefit of present and future generations. Species habitats and ecosystems and their functions and processes must be safeguarded. Species must be able to survive in long-term viable populations with sufficient genetic variation. Finally, people must have access to a good natural and cultural environment rich in biological diversity, as a basis for health, quality of life and well-being.

CONCLUSIONS

- Soil has an integral part to play in the global environmental sustainability challenges of food security, water security, energy security, climate stability, biodiversity, and ecosystem services. Indeed, soil has the same existential status as these issues and should be highlighted and treated similarly.
- There is an imperative for a concept of soil that is similar to food, water and energy security. We have proffered the term soil security.
- The concept of soil security is multi-dimensional. It recognizes capability, condition, capital, connectivity and codification of soil entities and encompasses the social, economic and biophysical sciences.
- Soil security is a wider, more integrative, concept than ‘soil quality’, ‘soil health’ or ‘soil protection’.

- There is a persuasive need for developing a thorough risk-based framework for assessing soil security locally, regionally, nationally and globally using the dimensions of capability, condition, capital, connectivity and codification.

Finally, soil security should be risk based in the sense that it should recognize and utilize the uncertainties in the assessment of each of the dimensions and their combination.

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A NOTE ON A BASIC APPLICATION OF THE SECOND-ORDER VARIATIONAL CALCULUS METHOD IN THE NON-EQUILIBRIUM THERMODYNAMICS

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Received: November 2016

Abstract

Relevance of the Riccati - type differential equation is indicated in the second-order variational calculus procedures in the case of the non-equilibrium thermodynamics, too. Then, the second-order variation procedure is applied for the case of the Fourier-type partial differential equation in linear approximation, and the adequate Riccati - type differential equation derived in this manner is also solved. Finally, the function of deviation from the stationary solution is also represented and discussed in detail.

INTRODUCTION

The mathematical modelling of distributed parameter complex systems plays nowadays a role of increasing importance in understanding of numerous crucial problems related to global energetic supply, dynamics of energetic systems in order to make them sustainable. Such modelling methods are frequently based on thermodynamics, whose methods must therefore be permanently re-examined and improved. It will be assumed throughout this study, that none of the essential physical properties of the macroscopic dissipative continua can adequately be described without tools of the non-equilibrium thermodynamics [1] and from the formalism of this powerful and very general discipline, relevance of the so-called Governing Principle of Dissipative Processes (usually abbreviated as GPDP), established [2] and discussed in detail in several works of Gyarmati and his co-workers, will be applied. Among the most significant results emanating from numerous applications of this principle (without pretension to give a complete overview), the successful description of the convective instability flows resulting in Rayleigh - Bénard-type dissipative structures [5] and thermodynamic waves [6] must be particularly pointed out. This is a principle (sometimes also called Onsager-Gyarmati's principle in the literature e.g. [5]), from which the well-known principle of minimum entropy production directly follows [5]. In its most general form, it can be represented as:

$$\delta\int_{t_1}^{t_2} L\,dt = \delta\int_{t_1}^{t_2}\int_{V} L_{df}\,dV\,dt = 0, \qquad (1)$$

where the Lagrange density function L_{df} generally depends on the intensive thermodynamic parameters Γ_i and f is the number of thermodynamic degrees of freedom of a given macroscopic dissipative system being examined as and the following supplementary variation conditions are also assumed to be valid [2]:

$$\delta\Gamma_i\left(\vec{r}_1,t_1\right)=\delta\Gamma_i\left(\vec{r}_1,t_2\right)=0,\quad \left(1\le i\le f\right),\delta t=0, \qquad (2)$$

for a given position vector and initial- (t_1) and final time moments (t_2), among which a transport process being examined takes place. Essentially, this variation principle is a direct manifestation of the extremal value of the local-type Onsager – Machlup (OM-) function, defined by

$$o \equiv \sigma - (\Psi + \Phi), \qquad (3)$$

where by the bilinear expression (with respect to the flux components J_i, and the thermodynamic force components $X_i = \nabla \Gamma_i$) the entropy production function $\sigma\left(\vec{J}, \vec{X}\right) \equiv \sum_{i=1}^{f} J_i X_i$ is defined, while the vector-scalar functions described by formulae $\Psi \equiv \frac{1}{2}\sum_{i=1}^{f}\sum_{k=1}^{f} L_{ik} X_i X_k$, and $\Phi \equiv \frac{1}{2}\sum_{i=1}^{f}\sum_{k=1}^{f} R_{ik} J_i J_k$ are the local dissipation potentials corresponding to the thermodynamic force-, and flux-representation, respectively. The symbols L_{ik} and R_{ik} denote the relevant conductivity-and resistance matrix elements. Then, the most general concrete form of (1) is given by $\delta \int_V o dV = 0$, known as the global OM -function [6,7], and detailed and refined examinations of this formalism also represent an open research domain from the point of view of the physical kinetics, too, e.g. [8].

Particularly, if we apply the force representation (i.e. when all fluxes in a given non-equilibrium dissipative system have constant values), which had been more frequently applied [1] than the above discussed universal general form, the Euler-Lagrange equation corresponding to (1) will take the form:

$$\frac{\partial L_{df}}{\partial \Gamma_i} - \sum_{\alpha=1}^{3} \frac{\partial}{\partial x_\alpha} \cdot \frac{\partial L_{df}}{\partial\left(\frac{\partial \Gamma_i}{\partial x_\alpha}\right)} = 0, \qquad (4)$$

with Lagrange density function:

$$L_{df} = \rho \dot{s} - \Psi, \qquad (4')$$

where the entropy production equation given in substantial form $\rho \dot{s} + \nabla \cdot \vec{J}_s = \sigma$ has also been incorporated into the general formula (1). Accordingly, in the case of the simple, linear heat conduction (or: diffusion) partial differential equation of parabolic-type (for the sake of generality, the possible tensor character of the heat conductivity coefficient must also be taken into account), the relevant global form of the adequate thermodynamic variation principle is [9]:

$$\int_{(V)} \left[\rho T c_V \frac{\partial T}{\partial t} + \sum_{\alpha,\beta=1}^{3} \frac{\lambda_{\alpha\beta}}{2} \frac{\partial T}{\partial x_\alpha} \frac{\partial T}{\partial x_\beta} \right] dV \to \min., \qquad (5)$$

which, in agreement with the eqs. (1-4), leads to the Euler-Lagrange equation

$$\rho c_V \frac{\partial T}{\partial t} = \sum_{\alpha,\beta=1}^{3} \lambda_{\alpha\beta} \frac{\partial}{\partial x_\alpha} \frac{\partial T}{\partial x_\beta}, \qquad (6)$$

i.e. to the well-known Fourier-equation of heat conduction. It was assumed during these derivation operations, that all possible values of the heat capacity cV and elements of the conductivity matrix are of constant values, and the stationary character of the problem to be examined is maintained during the whole process being modelled by GPDP. Moreover, the heat flux is not varied, and on the boundary surface the temperature is also assumed to be of fixed value [9]. It must be pointed out, that these restrictions, usually prescribed for applications of variational methods in non-equilibrium thermodynamics are in agreement with well-elaborated variational techniques (in both local-, and global sense) widely applied in field theories, i.e. in the case of physical systems possessing infinitely many degrees of freedom [10]. They will also be taken into account at the second-order variation procedure, relevant for sufficient conditions of existence of extremals, to be presented below. The GPDP - similarly to other extremal principles elaborated in detail for macroscopic dissipative continua – even according to the most accurate and newest research results from this domain e.g. [11] – must be considered as extremal principle of a limited range of validity. Furthermore, the detailed descriptions of temporal behaviour of the entropy production function close to thermodynamic equilibrium states by common application of the methods of matrix analysis and group representation theory may also contribute to further refinements of the variational formalism of the non-equilibrium thermodynamics [12]. Finally, we would like to point out here, that the basic problem of simultaneous convection-diffusion processes represents even nowadays [13-15] an important and still completely open research within frame of the whole non-equilibrium thermodynamics, and developing of new and more accurate models of this problem represents a permanent task, whose complexity is reflected in the nonlinear character of the ODEs and partial differential equations (PDEs) to be solved. The main goal of the present study is to contribute to new refinements of the adequate mathematical formalism of this circle of problems.

RELEVANCE OF THE RICCATI-TYPE ORDINARY DIFFERENTIAL EQUATIONS AND APPLICATION OF THE SECOND-ORDER VARIATIONAL PROCEDURE

The main motivation for us here is, that it is a well-known basic fact from the variational calculus e.g. [10] that by second variation of a given functional connected to sufficient condition of the existence of extrema, a Riccati-type ODE can be derived (or a more general variant of its, given in matrix form). The second variation calculation procedure has not been applied in the case of GPDP, despite of the fact, that Riccati´s ODE appears very frequently in different areas of continuum mechanics [16]. Therefore, in the present paper we also intend to give a new-type background for these well-established results from continuum mechanics.

In order to derive the Riccati-type ODE in its most general form to be applied in hydrodynamics, we will apply in detail in this section the functional (4'), which is of very general character, as it has been emphasized. Therefore, we start from earlier results due to Verhás [9] (also summarized in [1]). However, according to the earlier mentioned limited validity characteristics of the GPDP, we consider our calculation results to be suitable for analysing the case of the already developed and stabilized fluid flow patterns, only.
The crucial part of this study is represented by the following Riccati – type differential equation (which is generally of matrix-analytical type) [10]:

$$A+div(\omega)-\langle\omega,B^{-1}\omega\rangle=0, \tag{7}$$

where ω is the function to be determined and the coefficients A and B are given by expressions:

$$\begin{aligned} A(x)&=\frac{\partial^2 L_{df}}{\partial\phi^2}\left(x,\phi(x),\nabla\phi(x)\right)-\\ &-\sum_{j=1}^{n}\partial_j\frac{\partial^2 L_{df}}{\partial p_j\partial\phi}\left(x,\phi(x),\nabla\phi(x)\right),\\ B(x)&=\left(B_{ij}(x);1\le i,j\le n\right),\\ B_{ij}(x)&=\frac{\partial^2 L_{df}}{\partial p_i\partial p_j}\left(x,\phi(x),\nabla\phi(x)\right). \end{aligned} \tag{8}$$

Then, in agreement with (1-6) (i.e. if we assume again, that all possible values of the conductivity coefficients-, and heat capacities are constants) for the case of the Fourier-equation the Riccati-type expression (7) takes the following form:

$$\frac{d\omega}{dx}=\int\frac{\omega^2 dx}{\lambda}, \tag{9}$$

(which scalar form is relevant for the simple case of isotropic heat conduction i.e. $\left(\lambda_{\alpha\beta}\right)\to\lambda=const.$), while its more general matrix form is given by:

$$div\left(\vec{\omega}\right)=\langle\vec{\omega},\left(\lambda_{\alpha\beta}\right)^{-1}\vec{\omega}\rangle, \tag{10}$$

(the symbol $\vec{\omega}$ denotes here a column-vector) and during this calculation procedure (in agreement with (4) and (8)), the independent variables of type

$p_i\leftrightarrow\frac{\partial T}{\partial x_i},(1\le i\le 3)$ have also been used.

MODELLING RESULTS

As a closing procedure, it is possible to derive (the MAPLE computer algebra program system [17] was applied here for this purpose) the general solutions of (9) as

$$\begin{aligned} x+c_2&=\pm\sqrt{\frac{3}{2}}\int\frac{d\omega}{\sqrt{\frac{\omega^3+3c_1}{\lambda}}},\\ c_1,c_2&=const., \end{aligned} \tag{11}$$

Finally, in order to avoid further treatment and application of this implicitly represented solution form, we will also exploit here some very suitable and general invariance properties of the Riccati-type ODE. Accordingly, the second-order differential equations of type (10) can be reduced [18] to the Riccati-type ODE of the form

$$v'+v^2=a(x) \tag{12}$$

Since in the case of our study, corresponding to (9), we have: the solution of (12) can be directly written as:

$$v(x)=\frac{1}{\sqrt{\lambda}}\cdot\frac{K\cdot e^{\frac{2x}{\sqrt{\lambda}}}+1}{K\cdot e^{\frac{2x}{\sqrt{\lambda}}}-1},(K=const). \tag{13}$$

where K is an integration constant, whose concrete values (together with those of the heat conductivity coefficient λ) decisively affects the shape of graphics corresponding to the final solution of the complete problem being examined, as it will be demonstrated below. Therefore, having solved the basic problem of the Riccati-type ODE, by use of (13) we get:

$$\omega(x)=e^{\int v(x)dx}=\ln\left(\frac{K\cdot e^{\frac{2x}{\sqrt{\lambda}}}-1}{\sqrt{e^{\frac{2x}{\sqrt{\lambda}}}}}\right). \tag{14}$$

Finally, the general formula of deviation [12] from the stationary solution function corresponding to the basic actual parabolic-type PDE can also be directly calculated, and we obtain:

$$h(x)\propto e^{-\lambda\int\omega(x)dx}\equiv\frac{1}{e^{\lambda\int\ln\left(\frac{K\cdot e^{\frac{2x}{\sqrt{\lambda}}}-1}{\sqrt{e^{\frac{2x}{\sqrt{\lambda}}}}}\right)dx}}, \tag{15}$$

and this type of expression is (at least according to our knowledge) – despite of the simplifying assumption about the isotropic character of the basic linear transport problem being examined - a completely new one in the classical theory of transport processes. Besides, it will also be assumed here, that both constants „λ" and „K" are explained in suitably chosen relative units. Then, using again the MAPLE computer algebra system, we obtain:

$$h(x)\propto e^{-\lambda\cdot F(x)}, \tag{16}$$

with:

$$F(x)=x\cdot\ln\left(\frac{K\cdot e^{\frac{x}{\sqrt{2}}}-1}{e^{\frac{x}{\sqrt{\lambda}}}}\right)$$
$$-\frac{1}{\sqrt{2}}\cdot\ln\left(\frac{1}{K}\right)\cdot\ln\left(K\cdot e^{x\sqrt{2}}-1\right)$$
$$+\frac{1}{\sqrt{2}}di\log\left(K\cdot e^{x\sqrt{2}}\right)+\frac{x^2}{2\sqrt{\lambda}}$$
$$+\frac{\ln\left(\frac{1}{K}\right)\cdot\ln\left(K\cdot e^{x\sqrt{2}}-1\right)}{2\sqrt{\lambda}}$$
$$-\frac{x\cdot\ln\left(1-K\cdot e^{x\sqrt{2}}\right)}{\sqrt{2\lambda}}-\frac{di\log\left(K\cdot e^{x\sqrt{2}}\right)}{2\sqrt{\lambda}}$$
$$-\frac{poly\log\left(2,K\cdot e^{x\sqrt{2}}\right)}{2\sqrt{\lambda}}, \qquad (17)$$

where the „dilog" and „polylog" functions are defined by formulae (e.g. [17]):

$$di\log(x)=\int_1^x\frac{\ln(t)\,dt}{1-t}, \qquad (18)$$

$$poly\log(a,z)=\sum_{n=1}^{+\infty}\frac{z^n}{n^a}. \qquad (19)$$

Then, the relevant graphical presentation of the formula (16) (after incorporating of (17)) can be demonstrated as it is given on the next two Figures:

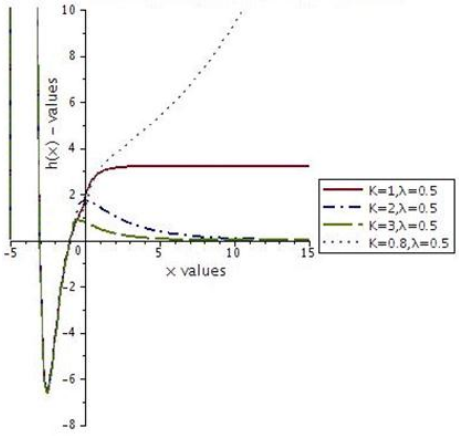

Figure 1
The value of h(x) with variation of K

All these improved and newly refined methods of the classical non-equilibrium thermodynamics may also be applied at improvements of the techniques introduced for effective modelling methods of much more complex mathematical techniques proposed for understanding and describing of some very realistic transport processes influencing the actual state of the biotope [19].

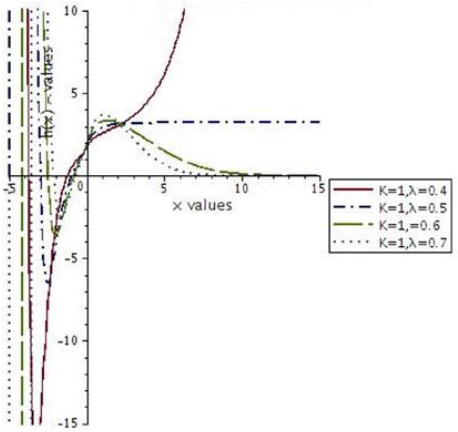

Figure 2
The value of h(x) with variation of λ

CONCLUSIONS

After a detailed analysis of the second variation procedure emanating from the Governing Principle of Dissipative Processes, a general method is proposed for detailed applications of the Riccati-type ODEs derived on the base of this variational principle of the non-equilibrium thermodynamics. A particular and simplified form of the same type ODE playing a crucial role in the most general modelling methods of the convection-diffusion processes taking place through bulk porous media is directly solved by use of the MAPLE computer algebra system, and a completely novel-type solution of very general form of this problem is presented. Finally, the function of deviation from the basic solution function of the Fourier-type heat conductivity PDE is studied in detail for the case of constant heat conductivity coefficients. A completely novel-type deviation function is derived, incorporating dilog-, and polylog-type complex functions. It is demonstrated, that application of the Riccati-type differential equations should play a crucial role in the subsequent symmetry analyses of singularity properties of solutions of these types of functions.

ACKNOWLEDGMENT

The authors are grateful to Prof. Gy. Molnárka for his help at graphical presentation of the solution formulae. They wish also to explain their gratitude to the TPF/DAAD Foundation (No. 55731) for its support during detailed studies of common convection-diffusion processes taking place in porous media.

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DETERMINE THE ADSORPTION PROPERTIES OF SEVERAL HEAVY METAL COMBINATIONS USING SPECIAL FUNGI COMPOST

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Received: November 2016

Abstract

The high heavy metal concentrations (above the limited concentrations) damage the natural waters and pollute the drinking waters also. The high concentrations in wastewaters could not treat in every wastewater yards and this is the reason the high heavy metal concentrations in the natural and drinking waters. We would like to present an alternative treating technology in this study. The heavy metal adsorption on the surface of special fungi compost is useful to treating heavy metals from wastewaters. We measured by analytical method the heavy metal adsorption properties (capacity) to determine the treating efficiency. Preparing solutions of heavy metals, the adsorptions of heavy metals on the surface of fungi compost by shaking method, the sample degradation and the analytical measurements by ICP-MS were the laboratorial experiments. We present the adsorption efficiency in all of the samples in every solution (single element content, and combined elements contents also).

INTRODUCTION

Wastewater containing copper and cadmium can be produced by several industries. The increasing awareness of accumulation of heavy metals in the environment has led to new and improved cleaning technologies. In this regard, an innovative heavy metal removal process composed of biosorption and sedimentation was developed [1].

The study of [1] covers the comparison of various types of waste biomass including bacteria, yeast fungi and activated sludge for their efficacy in the biosorption, sedimentation and desorption stages in the removal of zinc, copper and nickel ions. In the biosorption studies craned out with single metal solutions. A. nodosum, S. simosus and F. vesiculosus proved to be the best biosorbents for zinc, copper and nickel ions respectively. Overall, among the biomass tested, *A. nodosum, S. simosus, F. vesiculosus and P. chrysogenum* were found to have the highest potential for use in the heavy metal removal process [2].

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All heavy metals were detectable in the wastewater samples with a frequency of occurrence about 100% and only Pb was detected at lower frequency (90%). In a study [3] reported that the phase distribution of individual metals exhibited only little change during the treatment process with a slight progressive

increase of the dissolved phase of some metals after each treatment step. In a study [4] reported in their study that the sorption of copper and cadmium ions using activated carbon, waste materials (such as compost, cellulose pulp waste and anaerobic sludge) as sorbent. The study shows that copper being preferentially adsorbed by all materials with the exception of anaerobic sludge [5].

Compost with a smaller particle size fraction has larger surface areas and greater sorption properties than the larger particle size fraction. The aim of a study [6] research was to determine the rention capacity of compost for Cu, Zn, Ni and Cr.

Composting is a stabilization process of aerobic decomposition [7]. It leads to the development of microbial populations which causes numerous physico-chemical changes in the mixture. Composting can reduce the mixture volume by ~50%. Destroy the pathogens by the metabolic heat generated by the thermophile phase; degrade a big number of hazardous organic pollutants [8].

MATERIALS AND METHODS

B. Fungi compost samples

Fungi compost samples were used to these measurements. Fungi compost is a special compost type; it contains some important chemical and biochemical matters for fungi. The properties of fungi compost samples:

pH: 6,9
Dry matter content: 35%
N content: 0.8%
P content: 0.6%
K content: 0.9%
Ca content: 3.0%
Mg content: 0.3%

The fungi compost samples came from a small composting company (Áporka, Hungary). The sampling period was between 04/06/2015 and 16/08/2015.

C. Preparing polluted water samples

The single, double and triple combinations of heavy metals were used to preparing solutions and analytical measurements. The list of single and double heavy metal elements of prepared solutions: Mn; Cd; Mn+Cu; Mn+Cd.

All of the solutions of every single, double and triple element were prepared in each concentration (in three repeats): 250 mg/dm^3; 500 mg/dm^3; 750 mg/dm^3 and 1000 mg/dm^3 (Figure 1). All solutions were prepared with de-ionized water (18 MΩcm-1) from a Milli-Q analytical water preparing system.

The adsorptions of heavy metals on the surface of fungi compost were researched by shaking method. 10 g of fungi compost sample and 30 cm3 solution of heavy metals were taken into centrifugal tubes to the better adsorption. The shaking time was 50 min and the rotation was 480/min.

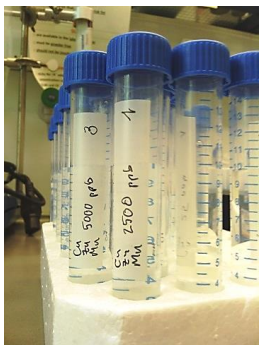

Figure 1
Preparing polluted sample solutions

D. Samples digestion

All of the samples were degrading because the organic matter content could disturb the correct measure of heavy metal content. Milestone 1200 Microwave digesting machine was used to sample digesting. 5 cm^3 HNO_3 and 1 cm^3 H_2O_2 acid reagents were added to 5 cm^3 shaken sample.

The digestion time was 24 min. After the digestion the water bath time was 30 min. The final step of the whole digestion programme was the digested sample diluting to 25 cm^3.

The setup and steps of the digestion programme:

1st step: 6 min and 250 W
2nd step: 6 min and 400 W
3rd step: 6 min and 650 W
4th step: 6 min and 250 W

E. Measurements with ICP-MS

Measure with Inductively Coupled Plasma with Mass Spectrometry (ICP-MS) is a powerful analytical method for the determination of metals e.g. Cd, Cu, Ni, Zn, and Mn [2].

The ICP-MS analytical method is sensitive and allows for the simultaneous analysis of elements and their isotopes [10]. An ICP-MS (Agilent 7500ce - Agilent Technologies, Waldbronn, Germany - equipped with autosampler) were used at the Institute of Analytical Chemistry, University of Vienna, Austria (Figure 2).

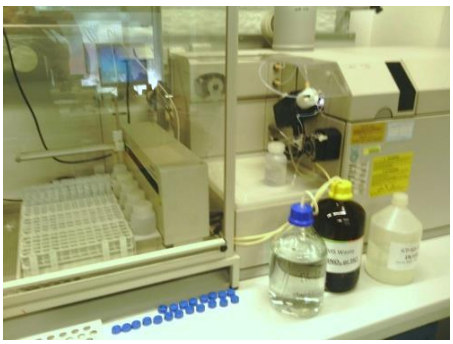

Figure 2
The used ICP-MS combined with autsampler (University of Vienna, Austria)

All of the instrumentations and parameters of the used ICP-MS listed in Table 1.

Table 1

The parameters of used ICP-MS [9]

Specifications	*Parameters of the ICP-MS*
ICP Frequency	27,12 MHz
Detection limit	Low (in ppt range)
Mass filter	Hyperbolic Quadrupole
Mass frequency	~ 3 MHz
Detector	Electron multiplier
Vacuum system	3 stage vacuum system
Pump	Rotary pump Turbo molecular pump
Autosampler type	Cetax ASX-520 (Nebraska, USA)
Maximum number of samples at one time (in the autosampler)	360 samples

RESULTS AND DISCUSSIONS

The adsorption capacity was measured in more times: in 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 and 65 min. The following diagram (Figure 3) shows the changes of adsorption capacity [%] in times [min].
The measures show the best adsorption capacity in 50 min (the capacity was 98%). The measuring in 50, 55, 60 and 65 min shows the same result.

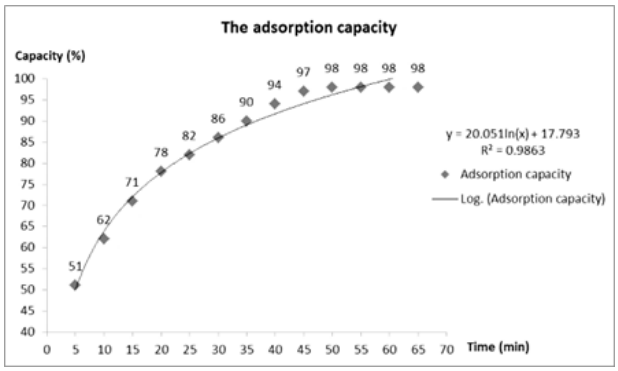

Figure 3
The adsorption efficiency changing in time

All of the samples were shaken in 50 min because of the best heavy metal adsorption. The isotope interferences are important to determine the percentages of heavy metal isotopes in samples. The following table shows the potential interferences for isotopes (listed in Table 2).

Table 2

Isotope interferences [10; 11]

Mass	Elements	Isotopic abund. (%)	Potential polyatomic interfer.	Interference isotopic abund. (%)
55	^{55}Mn	100	^{39}K^{16}O	93
			^{15}N^{40}Ar	0,4
			^{39}Ar^{16}OH	0,06
56	^{56}Fe	91,7	^{40}Ar^{16}O	99
			^{40}Ca^{16}O	97
57	^{57}Fe	2,2	^{40}Ar^{17}O	0,04
			^{40}Ar^{16}OH	99
			^{41}K^{16}O	7
58	^{58}Fe	0,28	^{40}Ar^{18}O	0,2
	^{58}Ni	68,3	^{40}Ar^{17}OH	0,04
			^{42}Ca^{16}O	0,6
			^{40}Ca^{18}O	0,2
59	^{59}Co	100	^{40}Ar^{18}OH	0,2
			^{43}Ca^{16}O	0,1
			^{23}Na^{36}Ar	0,3
63	^{63}Cu	69,2	^{23}Na^{40}Ar	99,9
64	^{64}Zn	48,6	^{24}Mg^{40}Ar	79
65	^{65}Cu	30,8	^{25}Mg^{40}Ar	10
66	^{66}Zn	27,9	^{26}Mg^{40}Ar	11
111	^{111}Cd	12,8	^{95}Mo^{16}O	16
114	^{114}Cd	28,7	^{98}Mo^{16}O	24

The solutions contain single elements were the first adsorbing test before the combinations. The Mn adsorbing was better in the higher concentrations but 500; 750 and 1000 mg/dm^3 produced the same result. The adsorbing capacity in highest concentrations could not be the limit.

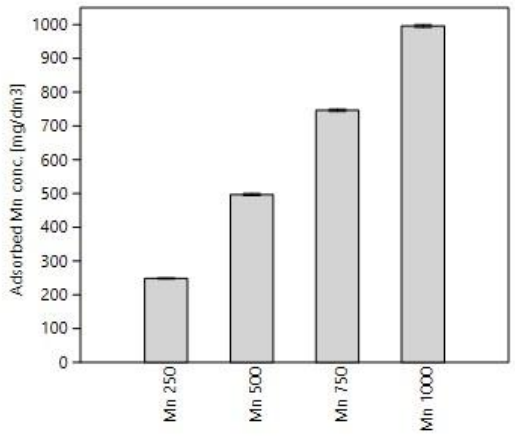

Figure 4
The adsorption of Mn

The adsorption efficiency of Cd (Figure 5.) also reached the current maximum at 1000 mg/dm^3 original Cd concentration. That means the adsorption maximum is not 1000 mg/dm^3 because the adsorption efficiency could grow more. We must determine the adsorption maximum (in the other heavy metal adsorptions also).

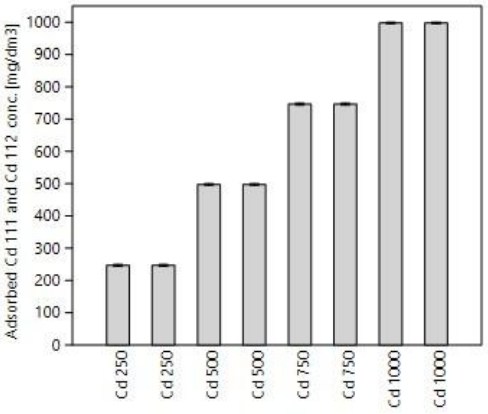

Figure 5
The adsorptions of Cd

The adsorptions of doubled heavy metal combinations show the difference between the single and the combined adsorptions. The whole heavy metal adsorption depends on the other heavy metal properties because the better adsorbing properties and the size of the molecule related to each other.
The following diagrams (Figure 6. and Figure 7.) shows the adsorptions of Mn+Cu and Mn+Cd. The adsorptions in these two combinations presented the same efficiency.

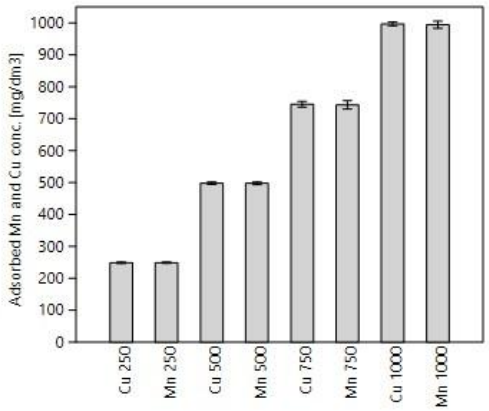

Figure 6
The adsorptions of Mn+Cu

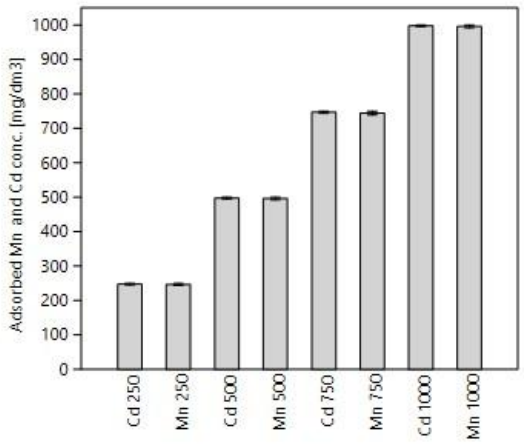

Figure 7
The adsorptions of Mn+Cd

The doubled combinations could present the habit of some heavy metals in the same time during the same adsorption experiment. We must determine the adsorption efficiency of triple heavy metal combinations and must research the adsorption in higher concentrations. That will present the whole adsorption efficiency of heavy metals.

ACKNOWLEDGMENT

This work was financed by the Balassi Institute (Budapest, Hungary) with doctoral research scholarship and the Institute of Analytical Chemistry (in University of Vienna, Austria). Á. Bálint expresses her thanks to P-MÖB-DAAD (No. 55731) for sponsorship the scientific work.
The authors would like to thanks the help and cooperation of the following people: Dr. Christopher Gerner and Dr. Samuel Meier (Institute of Analytical Chemistry, University of Vienna, Austria).

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Impacts of Global Climate Change on Health, Environment and Economy

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Received: November 2016

Abstract

This review gives the background on the gaps in our understanding of the relationship between climate change, the environment, and human health and their effects on the economic status. Also, environmental health is targeted towards preventing disease and creating health-supportive environments. There is general agreement that the global climate change is due to a wide range of natural and human factors. The impacts of global climate changes on human society and environment are found in a various ways such as extreme heat waves, rising sea-levels, changes in precipitation resulting in flooding and droughts, intense hurricanes, and degraded air quality, affect directly and indirectly the physical, social, and psychological health of humans or even impact our energy supply. Climate-related impacts are occurring across many sectors of economy, environment and natural resources, and our life styles. To prevent environmental health hazards affecting our health, it is important to be aware of the hazards and to take steps to manage the risks. This presentation also, discusses the environmental hazards which may be chemical, biological or physical in nature. While a hazard may have the potential to cause harm, the degree of harm that is likely to occur from exposure to the hazard depends on a range of factors including the characteristics of the hazard and exposed populations, the exposure conditions and duration of exposure. A risk assessment is a systematic approach for characterising the potential for harm under a certain set of conditions and time frame. The World Health Organization estimates that "more than 25% of the global burden of disease is thought to be linked to environmental factors, including chemical exposures. An estimated 3 billion people use biofuels, such as dung, brush and wood, as their main sources of energy for cooking and heating. As the global electronic waste (e-waste) stream grows, it is becoming increasingly important to understand how exposure to e-waste affects human health. Components used to make electronic devices, such as laptops, cell phones, and televisions, contain a variety of metals and chemicals that can harm health when people are exposed through handling or just living near e-waste streams. Environmental exposures pose a serious health risk to millions of children worldwide, especially to those living in low-and middle-income countries. The maintenance and improvement of environmental and public health is the main goal to meet the changes in global climates by the promotion of global cooperation among environmental health research institutes; promotion of global awareness of emerging issue in environmental health; and supporting the education and training efforts in environmental and occupational health sciences are needed to safe our environment.

Keywords: *Global climate change; health; environment; economy*

INTRODUCTION

The World Health Organisation defines environmental health as addressing physical, chemical, and biological factors external to a person, and related factors which impact on behaviour. The issue of global climate change, the role of human activity in such change, and the potential impact of climate change on the health of environment and human populations is a great global public interest (Figure 1).

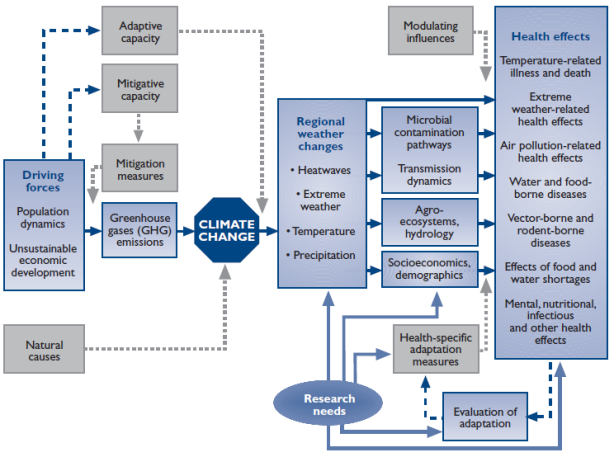

Figure 1
Climate change and health: pathway from driving forces, through exposures to potential health impacts. [1].

Global climate change poses the threat of serious social upheaval, population displacement, economic hardships, and environmental degradation. Human health could be influenced by increased variability and sustained changes in temperature, rainfall patterns, and storm severity, frequency of flooding or droughts, and rising sea levels (Figure 2).

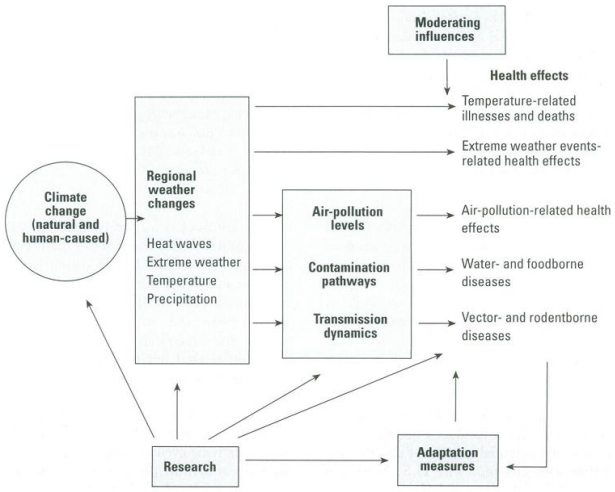

Figure 2
Potential health effects of climate variability and change [1].

Figure 2 shows the moderating influences include nonclimate factors that affect climate-related health outcomes, such as population growth and demographic change, standards of living, access to health care, improvements in health care, and public health infrastructure. Figure 3 shows the potential effect of climate change.

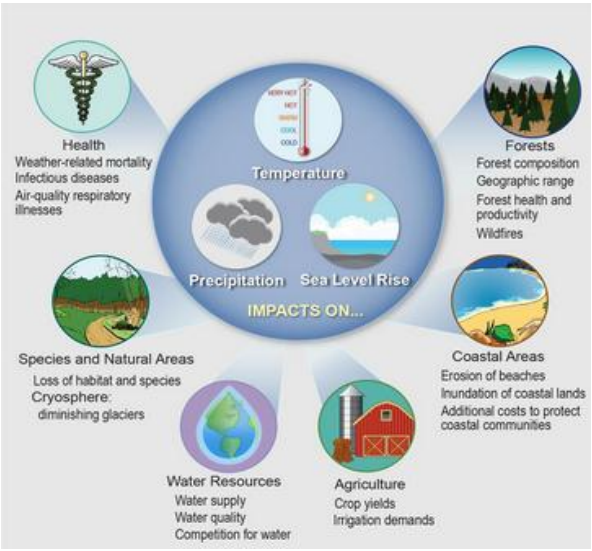

Figure 3
The relationship between climatic change and the human activities in different economic fields

Environmental monitoring in its widest sense is central, including not only the measurement of the levels of atmospheric gases and physical properties (notably temperature) that has long constituted traditional environmental monitoring but also the determination of indices that reflect the effects of relevant atmospheric changes (including changes in ecological systems, effects on populations, etc.), many of which lie outside the natural sciences.

In turn, these global environmental changes are the result of a complex set of drivers. These include: population change (population growth, movement and rapid urbanization); unsustainable economic development (manifested in current production and consumption patterns); energy, agricultural and transport policies; and the current state of science and technology.

Economic and technological developments have contributed to a remarkable improvement in the global health status since the industrial revolution. The unwanted side effect of this development has been a range of harmful changes to the environment, initially at local level but now extending to the global scale. Many of these largescale environmental changes threaten ecosystems and human health. Indeed, scientists are concerned that current levels and types of human economic activities may be impairing the planet's life-support systems at a global level. Various global environmental threats have been followed by concerted actions in the form of international conventions, global assessments and global agendas for action, with the support of many nations. Some have been more successful than others; some need more time to reach consensus. All have a sense of urgency and need commitment by governments and people, at all levels.

Important Concepts

Weather is the state of the atmosphere at any given time and place. Most of the weather that affects people, agriculture, and ecosystems takes place in the lower layer of the atmosphere. Familiar aspects of weather include temperature, precipitation, clouds, and wind that people experience throughout the course of a day. Severe weather conditions include hurricanes, tornadoes, blizzards, and droughts.

Climate is the long-term average of the weather in a given place. While the weather can change in minutes or hours, a change in climate is something that develops over longer periods of decades to centuries. Climate is defined not only by average temperature and precipitation but also by the type, frequency, duration, and intensity of weather events such as heat waves, cold spells, storms, floods, and droughts.

It may be helpful to think about the difference between weather and climate with an analogy: weather influences what clothes you wear on a given

day, while the climate where you live influences the entire wardrobe you buy.

The impact of globalization on the built environment is a transnational interconnection in every aspect of economy, society, culture and spatial developments. In response to the needs of the economic and industrial developments, this interconnectedness changes interactions between the people, the urban and the natural landscape. These changes not only include the transformation of people's attitudes toward lives, but also comprise the alteration in physical environments. Either types of change, whether physically or sensationally, are closely related to the lifestyle of local residents, the construction of the living space, and the attitude toward the man-made environment.

There is a growing recognition of the link between climate change and human health and wellbeing. It is true that if human reduced their CO_2 emissions tomorrow, the effects of past emissions will still lead to increased temperatures. Once climate change was discussed in terms of sea-levels and ice caps, now it has become one of the most significant challenges to public health we have ever faced, putting at risk the very pillars of life: clean water, sanitation, air quality and food. It is a challenge to us as individuals but also to environmental health practitioners (EHPs) who have a key role both in adaptation and mitigation of climate change. At the very least EHPs have a key role in increasing the human resilience to the effects of climate change. Climate change mitigation strategies are almost synonymous with health improvement, whether through improved housing, active transport, changes to patterns of food consumption or economic localisation. Environmental health is targeted towards preventing disease and creating health-supportive environments. Economic development has been a key priority and strategic goal around the world. However the economy and the environment are interdependent – as has been recognised in the principles of sustainable development.

What is climate change?

Climates around the world are changing as a result of rising global temperatures. There may still be disagreement about what has caused this phenomenon, but there is little doubt about its effect on our weather and ecosystems.

What causes it?

Certain gases in the earth's atmosphere trap heat like a blanket. This is necessary for life on earth because without it the earth would be 30°C cooler. But modern lifestyles have increased the amount of these so called 'greenhouse gases' in the atmosphere. Among the most significant of the greenhouse gases are water vapour, methane (CH_4) and carbon dioxide (CO_2). There's now 35% more carbon dioxide in the atmosphere than at any time in the last 650,000 years

How does it affect us?

On a global scale, climate change is affecting the abundance of flora and fauna and survival chances of many endangered species, raising sea levels, melting the polar ice caps and underground permafrost and devastating agriculture. Climate affects our health in two ways – directly, for instance through increased exposure or physical injury as a result of storms or floods. Or indirectly by altering ecosystems which can interrupt the supply of water and food or by fostering disease. Some of the key health dangers from climate change include:

- Infectious diseases: vector borne, waterborne and food related
- Death from extremes of temperature
- Malnutrition and global food supply shortages due to crop failure
- Trauma and mental health problems caused by extreme weather
- Illness related to poor air quality and pollution
- Cancer and cataracts caused by ozone depletion

The following are some of the anticipated or likely increased threats to health and wellbeing in the British Isles as a result of climate change. These have been predicted based on current evidence and modelling. They are grouped under three main headings in terms of the anticipated or predicted impact:

- Increasing temperatures
- Increasing rainfall
- Global issues

Climate Change: An Issue of Environmental Health and Social Equity

At the core of climate change is the increase in average global temperatures. Global temperatures rose by three quarters of a degree centigrade (0.74°C) between 1906 and 2006 and many predict they will continue to climb. This rise in temperature has subsequently caused an increase in sea levels in the main due to thermal expansion and melting glaciers, ice caps and polar ice sheets. Scientists on the UN's Intergovernmental Panel on Climate Change (IPCC) in 2007 stated that this warming, in their opinion, was almost entirely due to human activity and they predicted that average global temperatures will rise by another 1.1 to 6.4°C by the end of this century. Climate change impacts will affect social and ecological systems in complex and broad-ranging ways as technological, economic, social and ecological changes take place across regions, groups and sectors. Many of these impacts, such as impacts on ecological

systems, have cascading effects on social, economic and health outcomes. In order to respond to climate change, more vigorous actions are required to mitigate emissions of greenhouse gases (GHGs) and to adapt to unavoidable consequences that are increasing vulnerability around the world. This training places local sustainability, its development challenges and local vulnerabilities in the context of climate changes at regional and global levels in order to understand their linkages. It is well recognized that a response strategy to climate change is an additional and new area of sustainable community development, that in addition to many other local priorities like reducing poverty, improving sanitation and safe access to fresh water, health issues and diminishing ecological resiliency.

Global issues

Five development priorities were identified at the World Summit on Sustainable Development in Johannesburg, South Africa in August 2002: (a) water, where 1.3 billion people live without clean water and 2 billion without sanitation; (b) energy, where 2 billion people live without modern energy services, including electricity; (c) health, where 1.3 billion people are exposed to dangerous levels of outdoor pollution and about 2 billion to dangerous levels of indoor air pollution, and nearly all inhabitants of the earth are at some risk of infectious diseases; (d) agriculture, where 800 million people are currently malnourished; and (e) biodiversity, where genetic, species and ecosystem-level diversity is being lost at an unprecedented rate [2].

It is also an inter- and intra-generational equity issue, since our actions today will affect future generations and countries that currently have no control over the factors that are influencing climate change. Climate change affects our environment and natural resources, and impacts our mode of life in many ways. For example:

- Warmer temperatures increase the frequency, intensity, and duration of heat waves, which can pose health risks health risks, particularly for young children and the elderly.
- Climate change can also impact human health by worsening air and water quality, increasing the spread of certain diseases, and altering the frequency or intensity of extreme weather events.
- Rising sea levels threaten coastal communities and ecosystems.
- Changes in the patterns and amount of rainfall, as well as changes in the timing and amount of stream flow, can affect water supplies and water quality and the production of hydroelectricity.
- Changing ecosystems influence geographic ranges of many plant and animal species and the timing of their lifecycle events, such as migration and reproduction.
- Increases in the frequency and intensity of extreme weather events, such as heat waves, droughts, and floods, can increase losses to property, cause costly disruptions to society, and reduce the availability and affordability of insurance.

Relationship between climate change, population, Economy and environment

- *Global Environmental Health*

Global Environmental Health may be defined as: research, education, training, and research translation directed at health problems that are related to environmental exposures and transcend national boundaries, with a goal of improving health for all people by reducing the environmental exposures that lead to avoidable disease, disabilities and deaths.

- *Climate Impacts on environment and human health*

1. Impacts from Heat Waves
2. Impacts from Extreme Weather Events
3. Impacts from Reduced Air Quality
4. Impacts from Climate-Sensitive Diseases
5. Other Health Linkages

Weather and climate play a significant role in people's health. Changes in climate affect the average weather conditions that we are accustomed to. Warmer average temperatures will likely lead to hotter days and more frequent and longer heat waves.

- *Environmental health and economic development*

A healthy population is essential for economic development. The poorest people on the Earth tend to suffer most from the health effects and exposures to environmental hazards like air pollution and impure water. In turn, disease and disability related to polluted environments slows and blocks economic development. In addition to its toll on human suffering, illness carries a significant financial burden in the form of healthcare expenditures and lost productivity (Figure 4).

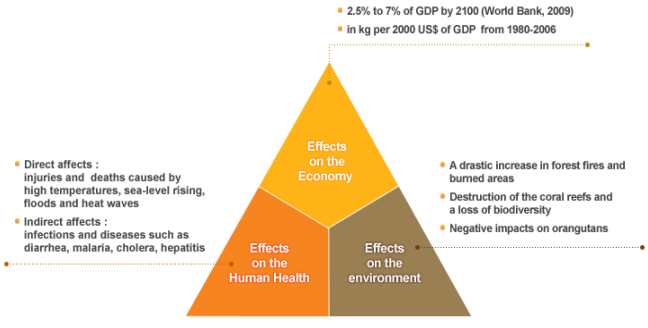

Figure 4
Effects of climate change on the Economy and Effects on the Human Health

- *Economic development and environmental health*

Economic development has led to tremendous improvements in people's well-being, but often at the expense of the environment. Industrialization has contributed to pollution of air and water, changing dietary patterns, and shifting patterns of transportation and land use. Exposures to air and water pollutants directly increase disease. Similarly, dietary changes and decreased levels of physical activity, resulting from transportation and other work and lifestyle changes, are contributing to global epidemics of obesity, diabetes, and associated diseases. Globalization and the large geographic scale over which rapid industrialization is occurring make these environmental health problems global health problems. One approach to economic analysis of climate change is cost/benefit analysis. The benefits in this case are the damages potentially averted through action to prevent climate change; the costs are the economic costs of shifting away from fossil fuel dependence, as well as other economic implications of greenhouse gas reduction.

- *Integration of environmental health and sustainable development*

Protecting and creating healthy environment is a critical component of sustainable development. Environmental health can be integrated into sustainable development by:

- Improving environmental quality for the poorest populations with the greatest burden of environmental diseases, by reducing exposures to air pollution in homes and villages from biomass burning, and providing clean water and sanitation.
- Identifying efforts to address environmental problems that can also provide health benefits. For example, creating environments that encourage biking and walking for transportation reduces greenhouse gas and toxic air pollution emissions (environmental benefit) and increases physical activity (health benefit).
- Recognizing that some policies, practices, and technologies designed to promote sustainability and economic development may have unintended adverse environmental health effects, and attempting to prevent or mitigate these before they are implemented.

- *Environmental Factors and the Burden of Disease in Developing Countries*

Many of the diseases that are most closely associated with poverty are related to the environment.

- The WHO estimates that roughly 25% of the disease burden in the developing world is due to environmental factors. [5]
- 1.9 million people primarily children, died in 2004 from inadequate access to clean water and sanitation. [4]
- 2 million people, mostly women and children, die each year from exposure to indoor air pollution from cooking with solid fuels such as wood, dung, and charcoal. [5]

Non-communicable diseases (NCDs), such as heart disease, stroke, diabetes, cancer, and chronic respiratory conditions, are of growing importance in low- and middle income countries. Many NCDs can be caused or worsened by environmental hazards, such as air pollution, toxic chemicals, and built environments that discourage physical activity. NCDs can impair economic development by pushing people into poverty, due to lost productivity and the costs of long-term therapy. In low- and middle-income countries, where people frequently pay out-of-pocket for healthcare and where healthcare systems have limited resources and capacity, NCDs take a large human and economic toll.

- 80%of all deaths due to NCDs occur in the developing world. [6]
- People in the developing world die from NCDs at a younger age than people in the developed world. -29% of all deaths from NCDs occur in individuals under the age of 60 in low- and middle-income countries. [6]

Climate Change and Human Health

A changing climate impacts our health and wellbeing. The major public health organizations of the world have said that climate change is a critical public health problem. Climate change makes many existing diseases and conditions worse, but it may also help introduce new pests and pathogens into new regions or communities. As the Earth becomes warm, oceans expand and the sea level rises, floods and droughts become more frequent and intense, and heat waves and hurricanes become more severe. The most vulnerable people are at increased risk for health effects from climate change. Climate change also stresses our health care infrastructure and delivery systems (Figure 5).

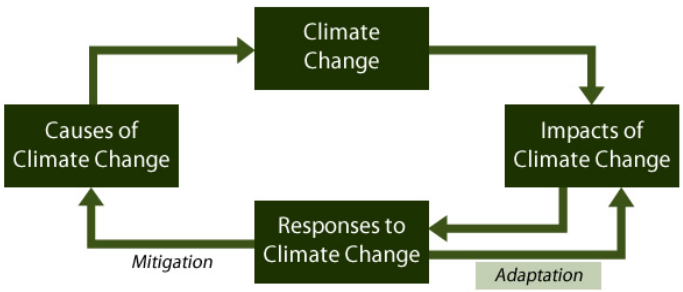

Figure 5
How People Interact with the Climate System

Changing weather patterns and extreme weather events are already a reality for communities in many developing countries. It is estimated that by 2025,

almost two thirds of the world's population are likely to experience some kind of water stress, and for one billion of them the water shortage will be severe. 2015 is a key year in the fight against climate change. In December 2015, world leaders will meet at the UN Summit (COP21) in Paris, to agree a global agreement on climate change. The world needs a strong and fair global agreement that:

1. sets legally binding targets for countries to reduce their emissions of greenhouse gases;
2. promotes the rights of those most vulnerable in the developing world, including small-scale farmers, strengthening their resilience to climate change;
3. ensures enough financial support is provided to help developing countries tackle the ongoing impacts of climate change.

Human society is structured around normal weather, with some days hotter than average and some colder. At the distant tails are extreme events such as catastrophic weather. Climate change shifts the entire distribution curve to the right: old extremes become the new normal, new extremes emerge, and the process continues until we take action (Figure 6).

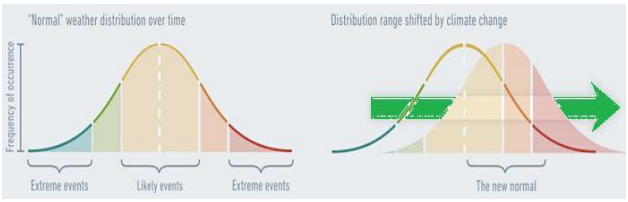

Figure 6
Extreme weather events become the new normal.

Global warming is already underway with consequences that must be faced today as well as tomorrow. Evidence of changes to the Earth's physical, chemical and biological processes is now evident on every continent. Three things are true of every hot spot:

- There is robust scientific evidence published in peer-reviewed literature showing that global warming impacts have already occurred in the area, or are projected to occur as warming trends continue.
- The location is beset by multiple stresses from other human activities that are likely to exacerbate the effects.
- The location is already having, or is projected to have, multiple climate change impacts

Solutions to Global Warming

There is no single solution to global warming, which is primarily a problem of too much heat-trapping CO_2, methane and nitrous oxide in the atmosphere. The technologies and approaches outlined below are all needed to bring down the emissions of these gases by at least 80% by mid-century. To see how they are best deployed in each region of the world, use the menu at left.

1. Boosting energy efficiency
2. Greening transportation
3. Revving up renewables
4. Phasing out fossil fuel electricity
5. Managing forests and agriculture
6. Exploring nuclear
7. Developing and deploying new low-carbon and zero-carbon technologies
8. Ensuring sustainable development

Adapting to changes already underway

As the Climate Hot Map demonstrates, the impacts of a warming world are already being felt by people around the globe. If climate change continues unchecked, these impacts are almost certain to get worse. From sea level rise to heat waves, from extreme weather to disease outbreaks, each unique challenge requires locally-suitable solutions to prepare for and respond to the impacts of global warming. Unfortunately, those who will be hit hardest and first by the impacts of a changing climate are likely to be the poor and vulnerable, especially those in the least developed countries. Developed countries must take a leadership role in providing financial and technical help for adaptation

The temporal and spatial climatic changes that will affect the biology and ecology of vectors and intermediate hosts are likely to increase the risks of disease transmission. The greatest effect of climate change on disease transmission is likely to be observed at the extremes of the range of temperatures at which transmission typically occurs.

To fully appreciate the urgency of climate change, it's important to understand the ways it affects society and the natural environment. Sea levels are rising and glaciers are shrinking; record high temperatures and severe rainstorms and droughts are becoming increasingly common. Changes in temperatures and rainfall patterns alter plant and animal behaviour and have significant implications for humans. In this section, explore the connections between the climate data and the changes happening around you in all parts of the globe, including your own backyard.

Not only are global warming-induced changes currently underway, but scientists also expect additional effects on human society and natural environments around the world. Some further warming is already unavoidable due to past heat-trapping emissions; unless we aggressively reduce today's emissions, scientists project extra warming and thus additional impacts.

Relationships between climate policy and health

There are three strong reasons for the climate policy community to consider health impacts:

1. the impacts are large, increasing and inequitably distributed;
2. the majority of people everywhere are concerned about the protection of their own and their children's health and are hence prepared to support mitigation policies; and
3. certain mitigation policies have significant positive health 'co-benefits', and these should be quantified and promoted to support mitigation arguments. There are 2 large groups of climate-exacerbated adverse health effects: the first is a direct effect, the second largely indirect.

- *The effects of heat on human health*. These direct effects are potentially magnified by climate change. A particular perspective is that heat and humidity do not only act on human physiology, but also reduce work productivity, particularly in developing countries [7]. The collection of articles on 'Heat and Health' focuses on direct human exposures to extreme heat, which will be an increasing condition in most of the world with climate change. Excessive heat exposure is a health risk for all age groups. Jendritzky and Tinz [8] showed with innovative maps the extent to which different parts of the world are now at risk and will be at greater risk in 2050. Honda and Ono [9] have developed an improved method to quantify heat-related mortality risks, and Rocklöv and Forsberg [10] compare different methods for quantifying mortality impacts during heat waves. Parsons presents practical approaches for reducing health risks during heat waves [11]. The main focus in the other articles is on the vulnerable group of adults carrying out heavy labour in hot working environments: outdoors or indoors. Kjellstrom et al. [12] describe the physiological mechanisms behind the health and productivity effects. Examples of these types of occupational health concerns are given by Lin and Chan [13], Ayyappan et al. [14] and Delgado [15]. Crowe et al. [16] discuss in detail the possibilities of investigating such concerns in Costa Rica, and Kjellstrom et al. [17] present the 'High Occupational Temperature Health and Productivity Suppression' (Hothaps) study programme, and invite interested scientists to participate. This programme will investigate global climate change impacts on heat and occupational health, a new concept publicised for the first time via this journal.
- *The effects on infectious diseases*. These are indirect effects of climate change. Using a decidedly global lens, we report on increases in various infectious diseases both in the Arctic ([18], [19], (20), [21]) and in tropical countries [22], [23], [24], [25], [26], [27] and [28]). The authors examine a wide range of diseases of parasitic, bacterial and viral origin. The focus, however, is on action for health systems: (i) assessing the dynamic, magnitude and nature of health impacts [16, 17]; (ii) identifying most vulnerable populations [14]; and (iii) contributing to the development of new tools for health systems for surveillance and early warning [15, 17] The paper by Yamamoto et al. [25] examines the link between climate change and indoor air pollution, two seemingly unrelated public health threats. Evengård and Sauerborn [26] 'connect the dots' by pointing to a set of six common scientific and policy challenges in the Arctic and the tropics with regard to climate-sensitive infectious diseases. These papers thus stress common ground in research and policy challenges in what otherwise are extremely different settings: the cold high-income countries and the warm low and middle-income countries. Byass [27] finally reviews and portrays the dearth of research on climate change and health in Africa and looks at ways of stimulating more work in this field, particularly by African scientists.

The global populations are exposed to an increasing frequency and intensity of extreme weather variability and changes temperature and precipitation. These exposures either affects health directly or are associated with a number of changes in sectors and systems such as water, agriculture, energy, etc. that are important determinants of human health. There are many other determinants of health that may or may not be affected by the changing climate, such as health care infrastructure. The observations of the last decades show that impacts vary significantly by location and by population across Europe. The actual future impacts on human health will very much depend on the character, magnitude, and rate of climate variation to which "health" is exposed and the actual sensitivity and the ability of populations, governments and health systems to cope with the consequences. Figure 7 shows the different pathways of direct and indirect exposure taken into account in this assessment. These exposures and impacts will vary over time and will change with on-going climatic changes. Also, Figure 6 shows the observed and potential health impacts of climate change. Climate and weather represent important elements of the environment where human beings continuously adapt or acclimatize themselves to maintain healthy conditions.

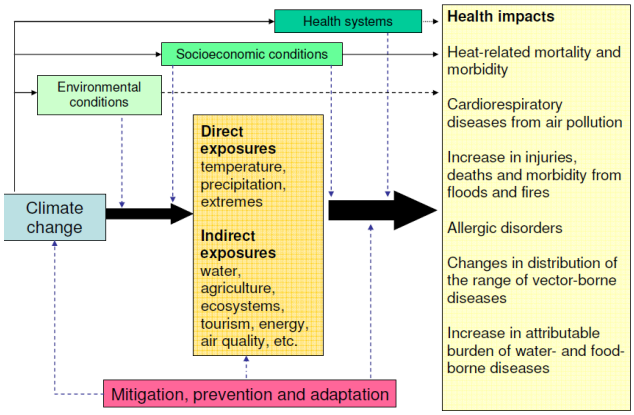

Figure 7
Direct and indirect exposure to climate change and human health **[**28**]**

The observed and projected changes in the climate system will affect the various sectors of the Earth's systems in different ways:

1. Impacts related to water;
2. Impacts on ecosystems, forests and agriculture;
3. Impacts on urban environments and socioeconomic sectors.
4. Heat and health

Steps can be taken to lessen climate change ("mitigation") and reduce its impacts on our health and the health of future generations ("adaptation"). Some of these steps can yield benefits for our health, environment, economy, and society at the same time. The federal government has called for efforts to support adaptation and mitigation of climate change to create healthier, more sustainable communities (Figure 8). The goals of the NIEHS Climate Change and Human Health Program align with these efforts.

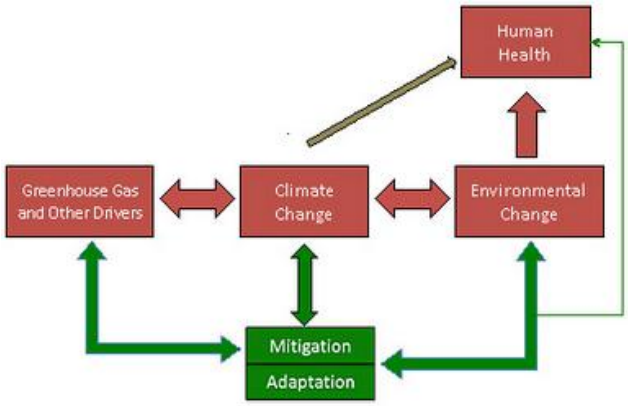

Figure 8
Changes in GHG concentrations and other drivers change the global climate altering the human.

Climate change could significantly affect vector-borne disease in humans. Temperature, precipitation, humidity, and other climatic factors are known to affect the reproduction, development, behaviour, and population dynamics of the arthropod vectors of these diseases. Climate also can affect the development of pathogens in vectors, as well as the population dynamics and ranges of the nonhuman vertebrate reservoirs of many vector-borne diseases. Whether climate changes increase or decrease the incidence of vector-borne diseases in humans will depend not only on the actual climatic conditions but also on local non-climatic epidemiologic and ecologic factors.

Strategies to Reduce the Environmental and Health Impacts of Climate Change and Variability

a) *Reduction of greenhouse gases: mitigation*

The IPCC suggests:

- changes in lifestyle towards reducing individual and collective ecologic footprints;
- upgrading energy infrastructure;
- investment into energy security;
- energy efficiency measures for vehicles, buildings and the electricity sector;
- renewable energy;
- biofuels; and
- a model shift in transport and carbon storage.

Not all of them have the same potential for GHG reduction or growth. Some of them also have possible health impacts (nuclear energy and carbon storage) but most of them combined in the long term would have multiple benefits for health.

Education and training programmes can help overcome barriers to the market acceptance of energy efficiency, particularly in combination with other measures. Changes in occupant behaviour, cultural patterns and consumer choice and use of technologies can result in considerable reduction in CO_2 emissions related to energy use in buildings. Transport Demand Management, which includes urban planning, can support greenhouse gas mitigation.

In industry, management tools that include staff training, reward systems, regular feedback and documentation of existing practices can help overcome industrial organization barriers and reduce energy use and greenhouse gas emissions. The widespread diffusion of low-C technologies may take many decades, even if early investments in these technologies are made attractive. Initial estimates show that returning global energy-related CO_2 emissions to 2005 levels by 2030 would require a large shift in the pattern of investment, although the net additional investment required ranges from negligible to 5–10%. Renewable energy generally has a positive effect on energy security, employment and on air quality. Biofuels might play an important role in addressing greenhouse gas emissions in the transport sector, depending on their production pathway. Biofuels used as gasoline and diesel fuel additives/substitutes are projected to grow to 3% of the baseline of total transport energy demand in 2030. This could increase to about 5-10%, depending on

future oil and carbon prices, improvements in vehicle efficiency and the success of technologies to utilize cellulose biomass. Modal shifts from road to rail and inland waterway shipping and from low-occupancy to high occupancy passenger transportation, as well as land use, urban planning and non-motorized transport, offer opportunities for greenhouse gas mitigation, depending on local conditions and policies. By 2030, about 30% of the projected greenhouse gas emissions in the building sector can be avoided, with net economic benefit. Energy efficient buildings, while limiting the growth of CO_2 emissions, can also improve indoor and outdoor air quality, improve social welfare and enhance energy security.

In particular, CO_2, as a naturally occurring compound or an anthropogenic emission, takes part in the so-called geochemical C cycle. The most appropriate way to treat C cycles is to view them as genuine cycles and, thus, at the systems level, subtract the fixation of CO_2 during tree growth from the CO_2 emitted during waste treatment of discarded wood and to quantify the CH_4 emitted (Figure 9). In solving the multifunctionality problem, two steps may be distinguished. The first concerns the modeling of the product system studied in the inventory analysis. In this step, system boundaries are set, processes are described, and process flows are quantified. Multifunctionality problems can be identified and the model of the product system is drafted. The second step concerns solving the remaining multifunctionality problems. For this step, various ways of solving the multifunctionality problem have been proposed and applied, on the basis of mass, energy, economic value, avoided burdens, etc. As the GHG indicator may constitute the basis for granting subsidies to stimulate the use of bioenergy, for example, and as the method for the GHG indicator provides no guidelines on the handling of biogenic CO_2 and guidelines for solving multifunctionality problems such as with coproducts and recycling that leave room for various choices, this study analyzed whether the current GHG indicator provides results that are a robust basis for granting such subsidies.

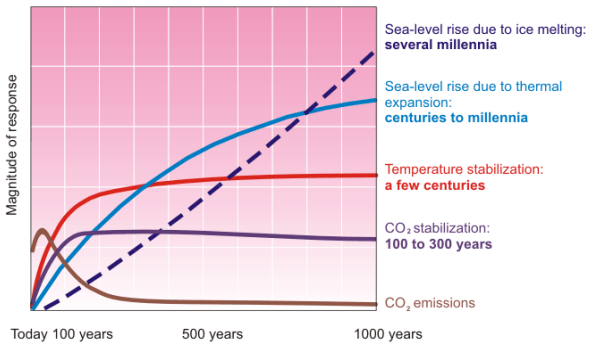

Figure 9

CO_2 concentration, temperature and sea level continue to rise long after emissions are reduced (Source: IPCC)

The economic potential in the industrial sector is predominantly located in energy intensive industries. Full use of available mitigation options is not being made in either industrialized or developing nations. Emission estimates include the six direct greenhouse gases under the Kyoto Protocol (CO_2, CH_4, NOx, hydro fluorocarbons, perfluorocarbons, sulphur hexafluoride) which contribute directly to climate change owing to their positive radioactive forcing effect, and four indirect greenhouse gases (NOx, CO, non-CH_4 volatile organic compounds, SO_2). The additional policies and measures identified in the draft national strategy affect all economic sectors and all greenhouse gases. Measures in the agricultural and forestry sectors include the implementation of programmes and initiatives aimed at increasing the quantity and improving the management of forest areas and woodlands, reclaiming abandoned territories and the protection of territories that face instability or risk of desertification. These include:

- management of existing forests;
- re-vegetation of farmlands and grazing lands;
- natural reforestation;
- afforestation and reforestation in existing woodlands, in new areas and in areas subject to risk of hydro-geological instability.
- The measures taken to reduce greenhouse gas emissions in Italy are not adequate.
- If human health were included in policy planning, the costs of greenhouse gas mitigation could be offset by the benefits it will have for human health through the reduction of air pollution.
- Integrating air pollution abatement and climate change mitigation policies offers potentially large cost reductions compared to treating those policies in isolation.
- Lessons learned in other countries showed that combined examples of measures to reduce greenhouse gas emissions and air pollution are also reducing the use of resources through energy conservation, increasing energy efficiency, fuel switching, demand management and behavioural change.

b) *Economic Analysis of Climate Change*

Scientists have modelled the effects of a projected doubling of accumulated CO_2 in the earth's atmosphere. Some of the predicted effects are:

- Loss of land area, including beaches and wetlands, to sea-level rise
- Loss of species and forest area, including coral reefs and wetlands
- Disruption of water supplies to cities and agriculture
- Health damage and deaths from heat waves and spread of tropical diseases
- Increased costs of air conditioning
- Loss of agricultural output due to drought

Some beneficial outcomes might include:

- Increased agricultural production in cold climates
- Lower heating costs
- Less deaths from exposure to cold

In addition to these effects, there are some other, less predictable but possibly more damaging effects, including:

- Disruption of weather patterns, with increased frequency of hurricanes and other extreme weather events
- A possible rapid collapse of the Greenland and West Antarctic Ice Sheets, which would raise sea levels by 12 meters or more, drowning major coastal cities
- Sudden major climate changes, such as a shift in the Atlantic Gulf Stream, which could change the climate of Europe to that of Alaska
- Positive feedback effects, such as an increased release of CO_2 from warming arctic tundra, which would speed up global warming

Economic analysis could thus justify much more aggressive climate change policy, but significant political barriers stand in the way of such policies. One positive indication for continuation and strengthening of climate policies is that public opinion broadly favors action on climate change.

CONCLUSION

- Planned adaptation to climate change, driven by the need to sustain economic development, health and well-being in the face of potentially major disruptions to critical natural systems, is essential for the world.
- It is necessary to evaluate future risks to the environmental and human health from climate change.
- It is necessary to create and enforce collaboration among health scientists and stakeholders, experts on the environment and civil protection, central and local government and health services.
- Multidisciplinary expert groups on health and the environment should be set up to contribute to the process of validation of priority action and adaptation options.
- Local case studies could be planned to assess examples of policy integration with the aim of strengthening public health and minimizing the costs of inaction.

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7th ICEEE-2016 International Conference
„Global Environmental Change and Population Health: Progress and Challenges"
November 17th - November 19th 2016
Budapest, Hungary