

31ST SEGH 2015

INTERNATIONAL CONFERENCE OF
THE SOCIETY FOR ENVIRONMENTAL
GEOCHEMISTRY AND HEALTH



BOOK OF ABSTRACTS

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Book of Abstracts

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FOREWORD

Dear SEGH Members and the participants of the 31st European Conference of the Society for Environmental Geochemistry and Health (SEGH).

First of all, I would like to thank all delegates who have come to Bratislava, and especially to those who have supported their participation with a presentation, either as a lecture or poster.

Our association – SEGH – brings together experts from two seemingly very different scientific disciplines, geology and medicine, especially public health. Both of these disciplines join mainly the environmental geologists, geochemists, doctors, hygienists, epidemiologists and toxicologists, who preferably examine the impact of the geological environment, mainly contaminated geological components (groundwater, soils, etc.), on the human health.

We believe that the Society for Environmental Geochemistry and Health, the State Geological Institute of Dionýz Štúr and the project team of the GEOHEALTH project have prepared a high quality professional programme and appropriate conditions for the exchange of expert knowledge and scientific experience among the conference participants.

I would like to express my thanks to all authors of the contributions, reviewers and all others, who contributed to the 31st SEGH conference scientific programme.

Finally, I hope that you enjoy your stay in Bratislava. I wish you a pleasant and fruitful conference.

Stanislav Rapant

(Chairman)

Keynote speakers



Associated Professor Stanislav Rapant, D.Sc.

Senior geochemist, State Geological institute of Dionýz Štúr, Mlynská dolina 1, 817 04 Bratislava, Slovak Republic

Stanislav is Associated Professor, D.Sc., working as senior geochemist at State Geological Institute of Dionýz Štúr, Bratislava, Slovak Republic. He has over 35 year experience in environmental geochemistry. In the last 15 years he has been dealing with the research in the field of medical geology and geochemistry and was in charge of several medical-geochemical projects performed at regional level in the Slovak Republic. Recently, he is a project manager of two projects financed under the EU Life+ programme – GEOHEALTH (LIFE10 ENV/SK/086, <http://www.geology.sk/geohealth/?lang=en>) and LIFE FOR KRUPINA (LIFE12 ENV/SK/094, www.geology.sk/lifeforkrupina). Both projects are highly innovative and bring new methodological approaches for analysis of a geological environment and human health relationship.

The 31st SEGH Conference in 2015 will be held in Bratislava, the Slovak Republic also on the occasion of the final implementation of the project **GEOHEALTH (LIFE10 ENV/SK/086)** that financially supports this event.

Project GEOHEALTH aims to analyse and reduce negative impact of geological environment on the health status of residents of the Slovak Republic. The background project information and presentation of its partial results and outputs is published on the project website <http://www.geology.sk/geohealth/?lang=en>. So far, project team members have actively presented the project results on the following international forums: Aveiro, Portugal 2012 (ISEG), Toulouse, France (SEGH 2013) and Newcastle-upon-Tyne, UK (SEGH 2014). The presentation of Geohealth project results will take place in the scientific programme of the SEGH conference in 2015, including methodology for compilation of datasets of environmental and health indicators from national databases and registries, neural network analysis of environmental and health data, definition of optimum range of chemical concentrations in groundwater and soils in relation to human health.

GEOHEALTH project background information

The main project objective is to link the information on the health status of Slovak residents (health indicators) with the data on geochemical background (environmental indicators) in order to analyse a relationship between geological environment and human health in the Slovak Republic. The dataset of health indicators was compiled based on ICD registry, 10th revision and WHO methodology and consists of health indicators characterizing various causes of deaths at a municipality level (2,883 municipalities in total). The main emphasis is particularly laid on the most common causes of deaths in our country including cardiovascular and oncological diseases (about 75% of all death causes). Other causes of deaths – e.g. diseases of gastrointestinal tract, respiratory diseases and diseases of endocrine system – are also subject to our analysis. The dataset of environmental indicators was compiled at the same municipal level and based on all available geochemical data obtained within the environmental-geochemical mapping programme in the Slovak Republic including groundwater and soils. The compiled datasets of health and environmental indicators provide unified information on health status and geochemical background for the whole Slovak territory at a municipality level. We have created a model of more than 5.5 million of Slovak inhabitants in order to analyse the associations between geochemical environment and human health. Except for standard statistical methods of data analysis (linear, Spearman correlations), we have also used a method of artificial intelligence – neural networks. So far, we have not processed all the data but we have achieved some partial results of our study. These results point out to the fact that there are macro-elements (mainly Ca, Mg, Ca+Mg, Na, K) which report the most significant and decisive influence on human health status

of residents. The influence of potentially toxic elements such as As, Pb, Hg, Cu, Cd and others is of a much lower significance than we have supposed earlier. The most common causes of deaths – cardiovascular and oncological diseases – are very closely associated with chemical contents of Ca and Mg in groundwater/drinking water as well as in soils. The municipalities with Ca and Mg deficit in geochemical environment (geochemical background – silicate volcanic, granitic and metamorphic rocks) are characterized by higher occurrence of deaths due to cardiovascular and oncological diseases (often more than 50%) on the contrary to the municipalities with higher contents of both chemical elements in groundwater and soils (geochemical background – carbonates, flysch sediments). In addition, the mean life expectancy of residents living in carbonate geological environment is significantly higher (about 2 – 4 years) than of those living in silicate geological environment.

Project partial results were published as original scientific papers in international magazines and are available together with the information on project progress at <http://www.geology.sk/geohealth/?lang=en>.



Professor Andrew S Hursthouse

Professor of Environmental Geochemistry, Assistant Dean, Research & Enterprise, School of Science & Sport, University of the West of Scotland, Paisley Campus, Paisley PA1 2BE, UK

Andrew is Professor of Environmental Geochemistry at the University of the West of Scotland. He has over 25 years experience in the assessment and management of pollutant mobility in diverse environments including air, land and sediment contamination and in the bioaccumulation in aquatic and terrestrial systems. He has researched metal mobility in the long term management of wastes from nuclear and metals manufacturing and investigated the impact of regulatory systems including soils policy at the UK national and EU level. More recent projects have included assessment of land quality in urban environments for risk assessment and urban planning and in the evaluation of dispersal mechanisms for pesticides in agroforestry. Human interaction with soils in urban agriculture from a social and risk assessment perspective has become an important issue for urban managers. The work of an EU wide COST Action network in this field brings together a wide range of stakeholders. His presentation will cover some of the primary research undertaken by groups across Europe, to develop an understanding of human behaviour at allotment sites – an important point of tension in our expanding urban ecosystems.



Professor Andy Cundy

Professor of Geoscience (Applied Geochemistry), School of Environment and Technology, University of Brighton, Lewes Road, Brighton BN2 4GJ, UK

Andy is Professor of Applied Geochemistry at the University of Brighton, UK, and has over 20 years research and consultancy experience in environmental geochemistry, and contaminated land and water management. Recently, his work has focused on the development and practical application of more effective land and water remediation methods, including the use of plant-based (phyto-management) methods which can offer lower deployment costs and combine site risk management with wider sustainability benefits. Andy's presentation will discuss this phyto-management or "green" remediation approach by drawing on examples from the USA and Europe which illustrate its practical risk management capabilities and the potential wider environmental, economic and social benefits that can be realised. Results from the recent EU GREENLAND project, which was designed to research and overcome the barriers to practical phyto-management application, will be discussed and evaluated to examine how the wider, more effective application of "green" remediation strategies can be realised in the future.



Dr. František Kožíšek

Senior researcher in water hygiene, Head of Department of Water Hygiene of Centre of Environmental Health, National Institute of Public Health, Prague, Czech Republic

Frantisek Kožíšek, M.D., PhD., graduated from Medical Faculty of Charles University in Prague in 1987 – as medical doctor with specialization on public health. He has been working at the National Institute of Public Health (NIPH) in Prague, Czech Republic, as researcher and consultant in water hygiene (water and health) since 1990. Currently he is senior researcher and head of the Department of Water Hygiene of Centre of Environmental Health (NIPH). Health risk assessment and legislation relating to drinking and bathing water are main subjects of his work. The specialty in his research is area of so called “biological value of drinking water”, which is focused on nutrients in drinking water and definition of good drinking water which would contribute to human health only in a positive way. He is Czech representative in several committees and expert groups by the European Commission like Article 12 Drinking Water Directive Committee, Expert Group on drinking water, or Expert Group on construction products in contact with drinking water. He is involved in various national and international research projects and teaches environmental health at the Charles University (3rd Medical Faculty) and at the Institute of Postgradual Education in Health Services.



Professor Taicheng An

Professor of Environmental Science and Engineering, Guangzhou Institute of Geochemistry, Chinese Academy of Science, Vice-director of Guangdong Key Laboratory of Environmental Resources Utilization and Protection, China

Dr. Taicheng An was born in Gansu, China, in 1972. He received his B.S. in Chemistry from Northwest Normal University in 1996, and his Ph.D degree in 2002 from Zhongshan University, China. Now, he is a professor of Environmental Science and Engineering at Guangzhou Institute of Geochemistry, Chinese Academy of Science, and vice-director of Guangdong Key Laboratory of Environmental Resources Utilization and Protection, China. His research interests include: 1. The transportation mechanisms, fate prediction and health effect of emerging organic contaminants, for example EDCs, PPCPs and BFRs, etc, in the environment, especially the identification of intermediates and their potential decontamination mechanisms in the natural or simulated systems; 2. Characterization, optimization and application of novel environmental friendly materials as well as natural mineral resources in environmental remediation; 3. Applications of various advanced oxidation processes (AOPs), especially heterogeneous photocatalysis for the degradation of organic pollutants and inactivation of pathogens in water and air. He has been published more than 200 peer-reviewed professional papers (including 160 SCI papers) in reputation journals, such as *ES&T* and *Water Res*. He is also the holder of total 44 patents including 36 issued. He is the winner of National Natural Science Funds for Distinguished Young Scholars in China, and the excellent Young Scientist Award from many reputation Societies, like Scientific Committee on Problems of the Environment (SCOPE) in 2011, Chinese Society for Mineralogy, Petrology and Geochemistry (Defen Hou Award) and Chinese Society for Environmental Sciences in 2010. Now, he is also served as editorial aboard of *Environmental Geochemistry and Health* (SCI), *Atmospheric pollution Research* (SCI) and *Recent Patents on Engineering* (EI).



Dr. Mark Cave

Senior researcher in analytical chemistry/geochemistry, British Geological Survey, Environmental Science Centre, Nottingham

Dr. Mark Cave (BSc, ARCS, PhD, MSc, CSci, MRSC, CChem) is a principal scientist at the British Geological Survey. He is an analytical chemist/geochemist with extensive experience in the analysis and interpretation of environmental chemical data with particular reference to geochemistry and human health. He also has an MSc in Applied Statistics (2008). He has at least 80 refereed external publications (h index = 19) and 80 internal BGS reports on analytical method development and data interpretation in environmental applications using multivariate statistical methods. He has developed a novel sequential extraction methodology for identification of the solid phase speciation of potentially harmful elements in soils and sediments using a chemometric modelling technique. He is chairman of BARGE (Bioaccessibility Research Group of Europe), working to develop harmonised protocols for bioaccessibility testing and the production of a soil reference material for in-vitro bioaccessibility measurements. He has specific experience on working on the occurrence and bioaccessibility of polycyclic aromatic hydrocarbons in soils. He has wide experience in investigating the geological controls on the bioaccessibility of naturally occurring arsenic in the UK. Extensive experience in working on the interpretation of geochemical data sets with reference to geogenic and anthropogenic influences. Recently completed projects include work for DEFRA to determine the Normal Background Concentration of Contaminants in Soils in the UK and a Tellus Border Project (EU INTEREGG IVA-funded) to determine sources of diffuse pollution, in soil chemistry data from Ireland. Dr. Cave is a member of the Royal Society of Chemistry, Chartered Chemist and Chartered Scientist, editor of the newsletter and committee member of the International Medical Geology Association and a member of the Society of Environmental Geochemistry and Health.



Dr. Alex G Stewart

Medical Consultant in Health Protection and Public Health, Public Health England, Liverpool UK

Alex is a Public Health doctor working in Public Health England (previously the Health Protection Agency), based in Liverpool. He has been interested in environmental interactions with health for over 40 years. He has 30 years active involvement in research and development around iodine deficiency, and over 15 years involvement with the characterisation, investigation, environmental management and public engagement relating to pollution issues of air, land and water and their effect on health and disease. He has worked and consulted in the UK, Pakistan, China and Morocco on these issues. In his current employment he has responsibility for the development of an Environmental Public Health Service that provides a safe and secure response to local and national environmental issues that affect the health of the 2.6 million people of Cheshire and Merseyside in NW England. His vision for this service extends beyond the standard environmental issues such as chemical spills and flooding to environmental links to wider health issues such as obesity, lung and heart disease. His talk will examine trace and essential elements and chemicals, their dietary deficiency and resulting disorders, the constraints of differing paradigms and cultural approaches to the issues, and explore the strengths of multi-disciplinary approaches to resolving problems and improving health.

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Topic 1

Health aspects of contamination of geological environment – waters, soils, sediments, air, food chain, urban environment
(risk assessment, risk management, legislative background, analytical procedures, monitoring)

Oral Presentation Abstracts – Keynote lectures

The impact of geological environment on health status of residents of the Slovak Republic

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In relation to biota or the human health, the chemical elements present in the environment can be either in deficiency or in excess. Each chemical element can be either a drug or a poison, depending only on its dosage (Paracelsus). The analysis of the relationship between the geological environment and the health status of the population in the Slovak Republic represents the main scope of the project GEOHEALTH. The most important phase of our work represented the compilation of the set of environmental indicators (chemical elements in the groundwater and in the soil) and health indicators (the health status and demographic developments) for each of the 2,883 municipalities in the Slovak Republic. Thus we obtained the databases, enabling us to search for response of the geological environment on human health. We could assess the impact of the diversity of geological environment on human health, to process the health risk assessment, to assess the impact of the geological environment contamination on human health, and using a non-traditional mathematical method - the neural networks - to determine the most influential chemical elements of the geological environment, having the greatest impact on human health. Finally we can process the environmental and health regionalization of the territory of the Slovak Republic. The topics solved in the GEOHEALTH project are really extensive. Partial project results have been already published in international journals from which the most important abstracts are listed below.

Rapant, S., Cvečková, Veronika, Dietzová, Z., Fajčíková, K., Hiller, E., Finkelman, R.B., Škultétyová, S., 2014: The potential impact of geological environment on health status of residents of the Slovak Republic. *Environmental Geochemistry and Health*, 36, 543-561

In order to assess the potential impact of the geological environment on the health of the population of the Slovak Republic, the geological environment was divided into eight major units: Paleozoic, Crystalline, Carbonatic Mesozoic and basal Paleogen, Carbonatic-silicate Mesozoic and Paleogene, Paleogene Flysch, Neovolcanics, Neogene and Quaternary sediments. Based on these geological units, the databases of environmental indicators (chemical elements/parameters in groundwater and soils) and health indicators (concerning health status and demographic development of the population) were compiled. The geological environment of the Neogene volcanics (andesites and basalts) has been clearly documented as having the least favourable impact on the health of Slovak population, while Paleogene Flysch geological environment (sandstones, shales, claystones) has the most favorable impact. The most significant differences between these two geological environments were observed especially for the following health indicators: SMRI6364 (cerebral infarction and strokes) more than 70%, SMRK (digestive system) 55%, REI (circulatory system) and REE (endocrine and metabolic system) almost 40%, REC (malignant neoplasms) more than 30%. These results can likely be associated with deficit contents of Ca and Mg in groundwater from the Neogene volcanics that are only about half the level of Ca and Mg in groundwater of the Paleogene sediments.

Fajčíková K., Cvečková V., Stewart A., Rapant S., 2014: Health risk estimates for groundwater and soil contamination in the Slovak Republic: a convenient tool for identification and mapping of risk areas. *Environmental Geochemistry and Health*, 36 (5), 973-986

We undertook a quantitative estimation of health risks to residents living in the Slovak Republic and exposed to contaminated groundwater (ingestion by adult population) and/or soils (ingestion by adult and child population). Potential risk areas were mapped to give a visual presentation at basic administrative units of the country (municipalities, districts, regions) for easy discussion with policy and decision makers. The health risk estimates were calculated by US EPA methods, applying threshold values for chronic risk and non-threshold values for cancer risk. The potential health risk was evaluated for As, Ba, Cd, Cu, F, Hg, Mn, NO₃⁻, Pb, Sb, Se and Zn for groundwater and As, B, Ba, Be, Cd, Cu, F, Hg, Mn, Mo, Ni, Pb, Sb, Se and Zn for soils. An increased health risk was identified mainly in historical mining areas highly contaminated by geogenic-anthropogenic sources (ore deposit occurrence, mining, metallurgy). Arsenic and antimony were the most significant elements in relation to health risks from groundwater and soil contamination in the Slovak Republic contributing a significant part of total chronic risk levels. Health risk estimation for soil contamination has highlighted the significance of exposure through soil ingestion in children. Increased cancer risks from groundwater and soil contamination by arsenic was noted in several municipalities and districts throughout the country in areas with significantly high arsenic levels in the environment. This approach to health risk estimations and visualization represents a fast, clear and convenient tool for delineation of risk areas at national and local levels.

Rapant S., Cvečková V., Fajčíková K., Kohút M., Sedláková D., 2014: Historical Mining Areas and Their Influence on Human Health. *European Journal for Biomedical Informatics*. 10/2014; 10(1): 24-34

Impact of potentially toxic elements (PTE) on the health status of population of the Slovak Republic has been studied in two historical mining areas with ore extraction from Middle Ages (the Middle Slovak Neovolcanics, the Slovak Ore Mts.) and one historical mining area with more than hundred years brown coal mining (Upper Nitra region). The contents of PTE were analysed in groundwater/ drinking water and soils. The health status of resident population was evaluated based on 43 health indicators classified according to the international classification of diseases (ICD, 10th revision), including mainly those indicators characterizing mortality on cardiovascular and oncological diseases. In these areas the health status of population living in municipalities with increased PTE contents (As, Pb, Zn, Cu, Cd, Hg and Sb) was compared with that in adjacent municipalities showing low PTE contents. A total of 138 contaminated and 155 non-contaminated municipalities of similar socioeconomic, natural and geochemical-geological character were compared. PTE contents in soils of polluted municipalities reported considerably increased levels – between 2 to 10 times higher in contrast to non-contaminated municipalities. On the other hand, PTE contents in groundwater were almost identical both in contaminated as well as non-contaminated areas and in majority of cases were below limit standard values for drinking water. Based on the assessment of the health status of population (using 43 health indicators), no significant difference in the health status of population in contaminated and non-contaminated municipalities has been reported.

Rapant S., Fajčíková K., Cvečková V., Ďurža A., Stehlíková B., Sedláková D., Ženišová Z., 2015: Chemical composition of groundwater and relative mortality for cardiovascular diseases in the Slovak Republic. *Environmental Geochemistry and Health* 04/2015, published online (DOI 10.1007/s10653-015-9700-5)

The study deals with the analysis of relationship between chemical composition of the groundwater / drinking water and the data on relative mortality for cardiovascular diseases (Rel) in the Slovak Republic. Primary data consist of the Slovak national database of groundwater analyses (20,339 chemical analyses, 34 chemical elements/compounds) and data on Rel collected for the 10 years period (1994-2003). The chemical and health data were unified in the same form and expressed as the mean values for each of 2,883 municipalities within the Slovak Republic for further analysis. Artificial neural network was used as mathematic method for model data analysis. The most significant chemical elements having influence on Rel were identified together with their limit values (maximal acceptable, minimal necessary and optimal). Based on the results of calculations, made through the neural networks, the following ten chemical elements/parameters in the groundwater were defined as the most significant for Rel: Ca+Mg (mmol l⁻¹), Ca, Mg, TDS, Cl, HCO₃⁻, SO₄⁻², NO₃⁻, SiO₂ and PO₄⁻³. The obtained results document the highest relationship between Rel and the groundwater contents of Ca+Mg (mmol l⁻¹), Ca and Mg. Following limit values were set for the most significant groundwater chemicals/parameters: Ca+Mg 4.4 – 7.6 mmol l⁻¹, Ca > 89.4 mg l⁻¹ and Mg 42–78.1 mg l⁻¹. At these concentration ranges the relative mortality for cardiovascular diseases in the Slovak Republic reaches the lowest levels. These limit values are about twice higher in comparison with the current Slovak valid guideline values for the drinking water.

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This research has been performed within the project Geohealth (LIFE10 ENV/SK/000086) which is financially supported by the EU's funding instrument for the environment: Life+ programme and Ministry of the Environment of the Slovak Republic.

Urban allotment gardeners: a picture of European behaviour and implications for future risk assessment of urban soils.

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In the different European cities, urban allotment gardens are receiving an emerging interest from the public as well from planning authorities. Competition for land use in urban areas is high. The rising number of constructions/buildings conflicts with wide interest in the access to green space and in outdoor exercise as well as in food security, and health and well-being of the urban population. Urban allotment gardens have a particular role joining recreation, health, food security, social benefits as well as urban ecology issues over all soil and water. Allotment sites in many urban situations are old (>50 years) and a traditional feature of community activity. Others are more recently established through both urban planning and/or community demand. The responsibility for their initiation, management and design varies very widely across national and local systems. This historical context and the very dynamic urban system has resulted in the cumulative input of a variety of materials directly through use and patterns of life style and tradition, the original growth medium and from the wider urban environment. The resulting soil quality can be of concern to public health through the accumulation of potentially harmful substances to levels where risk assessment models suggest the potential for harm to humans and the wider environment, including the urban hydrological cycle. This creates a tension in some urban management system where local authorities are required to be protective of human health in the face of community demands for the protection of the allotment function for health benefit and wider ecosystem service provision.

We report on the results emerging from work undertaken by members of an EU COST ACTION (TU1201) Urban Allotment Gardens (<http://www.urbanallotments.eu/index.php>) established in 2012, running to 2016. Activities have included development of systematic questionnaire to probe the behaviour of AG and understand the different management practices and food consumption in allotment gardens. The results of surveys in a number of cities, regional variation and an understanding of human behaviour will be presented in the context of impact on exposure to potentially toxic elements. What are visit times to sites? ...are there behaviours which are likely increase or reduce exposure to soil derived contamination?what are the implications for risk assessment of site users?

Managing contaminated site risk and deriving wider sustainability benefits through “green” remediation strategies

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Historically, approaches to contaminated site risk management have focused on containment, cover and removal of contaminated soils to landfill. However, since the late 1990s there has been a move towards treatment-based remediation strategies using a range of alternative in situ and ex situ physical, chemical, biological or thermal treatment technologies. A number of these alternative technologies utilize an in situ, low-invasive/impact approach whereby plants (trees, shrubs, native grasses etc.) are used for managing site risk. Such phytoremediation (or more broadly phytomanagement) approaches can offer strong benefits in terms of deployment costs, and may provide: (i) rapid risk management via pathway control, through containment and stabilisation, coupled with a longer term removal, destruction or immobilisation/isolation of contaminants; and (ii) a range of additional benefits — economic (e.g., biomass generation), social (e.g., leisure and recreation) and environmental (e.g., CO₂ sequestration, water filtration and drainage management, restoration of plant and animal communities). Indeed, several projects have proposed the use of biomass or biofeedstocks generation from phyto-based strategies at brownfield or contaminated sites to leverage effective re-use of land that is currently economically marginal. Despite widespread use of “green” technologies such as landscaping, application of green cover, and reedbeds and constructed wetlands in remediation or industrial/urban regeneration projects, the application of phytoremediation as a practical site risk management approach is still in its relative infancy. Here, we present examples of effective phytoremediation application at heavy metal(loid) and CCl₄-contaminated sites in Europe and the USA, to highlight the risk management capability of these methods and their potential wider environmental, economic and social benefits. These sites provide evidence of the effectiveness of phyto-based strategies under varying site contexts and conditions. The European examples have been used to derive best-practice guidance and a simple MS Excel-based decision support tool for engagement with project stakeholders to promote wider, more effective application of “green” remediation strategies.

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Exposure Risks Assessment of Phthalates in Water Environment during the Photochemical Transformation: Experimental and Theoretical Studies

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Phthalates, frequently found in environmental matrixes, are typical priority control pollutants and endocrine disruptor chemicals. Moreover, it is noteworthy most organic contaminants in waters have potential to form more toxic by-products during photochemical transformation, posing an increased risk to aquatic ecosystems and human health. However, the transformation, fate and exposure risk of products during photochemical transformation of phthalates has not yet been concerned although this information is very necessary for human health and environmental protection.

This talk will introduce state-of-the-art research activities in the field, focusing on the experimental and theoretical investigation of •OH-initiated photochemical transformation of four model phthalates, including dimethyl- (DMP), diethyl- (DEP), dipropyl- (DPP) and dibutyl- (DBP) phthalate. Using quantum chemical calculation, all possible pathways of four phthalates were modelled during •OH-initiated photochemical transformation in waters. The results showed that four phthalates were degraded via •OH-addition and H-transfer pathways. Furthermore, kinetics analysis revealed with increasing alkyl chain length of phthalates, the susceptibility of phthalates to photochemical transformation increases under the same environmental conditions. The •OH-addition products were mainly formed during photochemical transformation of DMP, while H-transfer products were predominant for DEP, DPP and DBP. Furthermore, the radiolysis experiments and HPLC analysis were used to elucidate the mechanisms and transformation products of DMP in waters. The experimental results are well agreed with theoretical findings above mentioned, further confirming the reliability of theoretical approach.

Based on the ecological structure–activity relationships and estrogenic activity calculation, the exposure risks assessment of four phthalates and their transformation products were performed theoretically. With compared of the original phthalates, several transformation products particular •OH-addition products have found to be more harmful to aquatic organisms and human health. For instance, ortho-OH-phthalates have greater aquatic toxicity, and meta-OH-phthalates exhibit higher estrogenic activity. Also, the adverse effect of H-transfer products still cannot be ignored although they are less harmful than •OH-addition products. Therefore, special attention should be paid to photochemical transformation products of phthalates, particularly for those that exhibit higher estrogenic activity than the parent phthalates to human.

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Topic 1

Health aspects of contamination of geological environment – waters, soils, sediments, air, food chain, urban environment
(risk assessment, risk management, legislative background, analytical procedures, monitoring)

Oral Presentation Abstracts – Plenary lectures

Potentially Toxic Trace Element Contamination of the Little Akaki River of Addis Ababa, Ethiopia

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In this study, river water samples taken from 26 different locations along the course of the Little Akaka River in Addis Ababa were analyzed to determine potentially toxic trace element concentrations. The mean concentrations in $\mu\text{g L}^{-1}$ for Mn 1540.04, Fe 1075.92, B 383.04, Sr 336.75, Ba 132.17, Cr 67.04, Sb 42.80, Zn 25.50, Ni 6.66, Cu 5.61, V 4.87, Pb 3.13, Co 2.62, As 1.46, Cd 0.06 and Hg <0.05. Overall metal concentration were in the order Mn > Fe > B > Sr > Ba > Cr > Sb > Zn > Ni > Cu > V > Pb > Co > As > Cd > Hg. A strong positive correlation was observed between Cu-Pb, Cu-Zn, Zn-Fe, Cu-Cd, Cd-Fe, Cd-Pb, Pb-Zn, Cu-Fe, Co-Fe, Co-Pb, Ni-Zn, Fe-Pb and Mn-Ba. The concentrations of Cr, Mn, Sb, B and Pb exceeded the permissible limits of the Ethiopian, European Community and WHO for drinking water quality guidelines. Fe and Sr exceed the permissible limits of the Ethiopian drinking water guideline and Sr exceeds permitted by WHO. The concentration of Cr, Zn, Cu and Pb exceed the annual average thresholds for surface waters set in SI 272 of 2009 EQS guideline. The concentration of Cr, Mn and Sr were also higher concentration than the international guidelines value for irrigation water. The pollution of the river water is increasing alarmingly and poses serious threat to human health. It is, thus, necessary to take serious and essential measures from the concerned bodies. Adoption of adequate measures to remove the heavy metal load from the industrial waste water and upgrading of sewage treatment plants are suggested to avoid further deterioration of the river water quality.

Assessment of the seasonal variations of potentially toxic elements (PTEs) from circum-neutral mine waters

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Surface water vulnerability to pollution through weathering of metal-enriched mine wastes has significant ecological effects on catchment systems in many regions world-wide. This study focused on the impact of historic variations in seasonal climatic factors on release of PTEs from mineral phases in mining region in Leadhills and Wanlockhead, south of Scotland. The source was sulfidic Pb-Zn ore previously mined for galena and sphalerite within brecciated fault mineral veins cutting through Ordovician-Silurian sedimentary rocks. Rock debris containing primary and secondary minerals exposed to weathering for over eighty years was identified to actively impacting on local aquatic based on initial monitoring and assessment by local environmental regulator (Scottish Environmental Protection Agency). A key aim of the study was to examine mineral geochemistry within the mining influenced catchments and develop an understanding of mineral systems controlling PTE solubility (particularly Pb, Cd, Zn, Cu, Fe), and assess impact on risk assessment protocols. Field sampling were conducted at six sites over a year (and randomly from extra fourteen). Surface water – groundwater beneath mine workings debris was characterised (ICPMS/AES, GFAAS, XRD and SEM-EDS).

The results showed seasonal climatic effects on mine workings drive overall release of PTE into surface water. The water pH is strongly buffered by weathering of carbonates (dolomites ($\text{CaMg}(\text{CO}_3)_2$) and calcites (CaCO_3)) from slightly acidic to mildly alkaline (6.3 to 7.6), (redox E_h in the range -35 to 25mV), and contributing to the removal of hardness in the water under aerobic conditions. Cadmium for most sites were lower than annual environmental quality standards maximum allowable concentration (EQS MAC); diss Cd (0.109 – 2.78 mg/l), and tot Cd (0.142 – 3.27 mg/l). Pb and Zn for the sites were slightly greater than EQS MAC, diss Pb (4.28 – 25.2 mg/l); tot Pb (11.8 – 36.1 mg/l); diss Zn (9.61 – 274 mg/l), and tot Zn (13.8 – 306 mg/l). The secondary minerals precipitated on prediction with geochemical models (PHREEQC/GWB) indicate Cu/Al/Fe species in oxides, hydroxides and iron-rich minerals mainly goethite (FeOOH), hematite (Fe_2O_3) and magnetite (Fe_3O_4). There is a strong correlation on PTE concentrations through time greatly impacted by precipitation of secondary minerals in the catchment system.

Occurrence of Pharmaceuticals and Personal Care Products in the Jiulong River Watershed in the Southeast China

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In the past decades, great concerns have been raised about the potential adverse effects of pharmaceuticals and personal care products (PPCPs) on ecosystems. Up to date, only limited studies investigated PPCPs in surface waters in China with strong regional bias. Jiulong River is the second longest river of the Fujian Province in the southeastern part of China. The watershed area is 14,741 km² with two major prongs (North River and West River), and the population is more than 8 million. In this study, 31 samples were collected along Jiulong River and its estuary in the wet, normal and dry seasons. 23 classes of 51 PPCPs were analyzed using solid phase extraction liquid chromatography triple quadrupole mass spectrometry. The seasonal and spatial variations of PPCPs were investigated. In addition, selected PPCPs were used as chemical markers to assess the sewage contamination in Jiulong River and its estuary. The results showed that PPCPs were ubiquitous in all the samples. For both Jiulong River and its estuary, nine PPCPs were detected with 100% detection frequencies, including ketoprofen, diclofenac, caffeine, bisphenol A, methyl paraben, propyl paraben, triclosan, triclocarban and metoprolol, among which bisphenol A and caffeine accounted for more than 60% in concentrations. Seasonal and spatial variations were observed in occurrence and concentrations of PPCPs, and the variations were different for different PPCPs. Specifically, PPCPs generally had higher concentrations in dry season than normal season and wet season, while certain PPCPs, such as UV filters, showed higher concentrations in wet season, which were presumed to relate to their usage patterns. The concentrations of PPCPs were significantly correlated to several parameters of the surface water. In the estuary, most PPCPs were negatively correlated to the salinity. The ratios of easily removed markers and conservative markers were used to identify the contribution of raw or treated sewage input in the studied surface water. From our result, Jiulong River and its estuary were likely polluted by potential discharge of raw sewage.

Ecotoxic metals in water columns of anchialine caves along Eastern Adriatic coast (Croatia)

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Anchialine environment is described as a tidally-influenced subterranean estuary located within crevicular and cavernous karst and volcanic terrains that extends inland to the limit of seawater penetration. The anchialine habitat supports a diverse biotic assemblage predominantly comprising stygobiotic species of marine origin, many of which are members of higher taxa that are endemic to anchialine ecosystems, distinct from those in contiguous limnic and marine waters. Many anchialine caves are located along world coasts. Their uniqueness is characterized accumulations of fresh water above stratified water column with sharp halocline and underground communication with sea through the porous carbonate rocks. They have been widely recognized as significant aquatic environments due their combination of subterranean estuary and deep sea environments. Until now, almost 100 anchialine caves have been registered along the Croatian coast and on the numerous islands. The fresh water layer at such caves represented a significant resource of potable water for the ancient inhabitants of the Eastern Adriatic coast. Today with ongoing global warming and changes of precipitation this fresh water layer in anchialine cave may reclaim importance. During 10 years water columns were sampled for ecotoxic metals analysis in 7 anchialine caves (Urinjska špilja, Špilja pod Orjakom, Čapljina, Vodena jama, Živa voda, Lenga & Bječajka). Concentrations of total and dissolved trace metals (Hg, Cd, Pb, Cu, Zn, Ni and Co) and their distribution through the water column were determined. All analyses were performed in Laboratory of Physical Chemistry of Traces (Ruđer Bošković Institute, Zagreb) by using highly precise and reproducible methods. Despite absence of the anthropogenic influence, a quite high concentrations ecotoxic metals in some caves were found: Hg up to 3.7 µg/L, Cd up to 0.3 µg/L, Cu up to 28 µg/L, Zn up to 9.6 µg/L. Contrarily, water column in a cave located in industrial area (Urinjska špilja) is characterised by extremely low concentrations ecotoxic metal. Those indicate importance of researches in zone between sea and costal aquifers, in order to identify the main biogeochemical processes controlling transport and fate of trace metals and associated elements. The easiest access to this zone is through anchialine caves.

Assessment of Metal Accumulation and Ecological risk in Marmara Ereğlisi shelf northern Marmara Sea, Turkey

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The Marmara Ereğlisi is located on the north coast of the Marmara Sea and has been affected by domestic, industrial and agricultural pollution. The study of coastal sediments provides useful information in marine, environmental and geochemical research about marine pollution history. The aim of this study is to contribute to the ecological conditions of Marmara Ereğlisi in terms sediment quality, pollution history and eco-toxicological risk using sediment quality guidelines (SQGs, Effect Range-Low ERL and Effect Range-Medium ERM) values and enrichment factors (EFs). For this purpose, 3 sediment core samples were collected and investigated by analysing grain size and potential harmful element (Al, As, Cr, Cu, Hg, Ni, Pb, V and Zn) content. Sediment samples were analysed for metals using ICP-MS after a total digestion. We used SQGs and EF for assessment of the sediment quality and ecotoxicological risk. For EF calculations, average values of each element for the unpolluted part of the cores below 30 cm are used as the background values. Grain size distributions of core sediments were analysed using laser granulometry.

The core sediments contain sand, silt and clay size fractions with the average values of 17%, 36% and 47%, respectively. The average concentrations of metals measured in mg kg⁻¹ were; 20,304 for Al, 5 for As, 65 for Cr, 10 for Cu, 0.15 for Hg, 41 for Ni, 20 for Pb, 41 for V and 49 for Zn. The results of EF reveal that the upper part of core sediments were not polluted for As, Cr, Cu, Ni and V, moderately polluted in Pb and Zn and highly polluted in Hg. The largest pollution values for Hg, Pb and Zn were found in the upper part of cores with a decrease toward the bottom. These results show the increasing effect of extensive and diversified agricultural and domestic wastes in recent times. The metal concentrations of Cu, Pb, and Zn were below ERL, suggesting minimal toxicological effect on benthic organisms, whereas some sediment samples having values between ERL and ERM for As (2.5%), Cr (14%), Hg (21%) and Ni (95%) present a some toxicological risk for benthic life.

What drives bioaccessibility? A multi-technique approach to investigate the Pb-phases which control the overall solubility of Pb in topsoil & metaliferrous wastes

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Lead exposure can produce detrimental health effects at all life stages. Outcomes considered “causal,” “suggestive,” or “likely causal” include IQ decrements, low birth weight, cardiovascular disease mortality, and reduced glomerular filtration rate. High Pb soils pose a particular risk for all age ranges because of the greater potential exposure risk (via ingestion) for non-pediatric populations. However, it is recognized that bioavailability should be the guidance for risk assessment as not all forms of ingested Pb are mobilized in the gastrointestinal (GI) tract. Oral bioaccessibility protocols seek to model extraction during the passage through the human GI system and the solid phase partitioning/mineralogical form of the contaminant has a large influence on its bioaccessibility.

Here we report on a study to evaluate which Pb phases control the overall Pb solubility in samples from Mitrovica, northern Kosovo. The Pb mineral phases were determined by X-ray diffraction. Computer Controlled Scanning Electron Microscopy (CCSEM), coupled with energy dispersive X-ray spectroscopy (EDS), was utilized to identify specific Pb-particle associations (phases) in the samples (with approximately 4,000 particles analyzed per sample). Lead solubility was investigated at the bulk sample level by the Unified BARGE method (UBM), and by chemometric analysis of sequential extraction data (CISED). At the individual particle level, Pb solubility was investigated by Differential Individual Particle Analysis (DIPA). DIPA involves the collection of particle-by-particle information (elemental and morphological) on the particles in their original form, followed by removal from the SEM for chemical treatment of the sample *in situ*, followed by particle relocation and subsequent analysis of differential changes.

The samples investigated had Pb levels ranging from 54 – 47,260 mg/kg, and *in vitro* oral Pb bioaccessibilities of between 1.2 and 92%. Initial results indicate Pb-particle classes that vary in form (morphology/habit), composition (separate phase vs. homogenous composition), amount of Pb present & acid solubility. Across the suite of samples Pb-particles with Fe associations were less soluble than Pb-particles with Ca associations. Other Pb-particle associations that are sample specific (e.g. Mn associations) were also found to be important in controlling Pb solubility.

Bioaccessibility method for prediction of relative bioavailability of arsenic in contaminated soils

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Accurate assessment of human health risks from exposure to arsenic contaminated soils depends on estimating its bioavailability. U.S. Environmental Protection Agency (USEPA) guidance describes the need for development of soil arsenic bioavailability methods and data to improve the accuracy of human exposure and risk calculations at arsenic contaminated sites. Even small adjustments in soil arsenic bioavailability estimates can significantly affect estimated risk and cleanup goals, and methods are needed to provide inexpensive, accurate, and reliable data that can be applied to cleanups of arsenic-contaminated sites. In this study, we evaluated 5 commonly employed in vitro bioaccessibility (IVBA) methods to determine the bioaccessibility of arsenic in 40 contaminated soils from the United States and Australia. A wide variety of soils were used in this study, including NIST standard reference materials, railway corridors, cattle tick dip and gossan sites, and residential areas affected by mining or smelting. The 5 commonly employed in vitro gastric and/or intestinal values were compared with in vivo mouse relative arsenic bioavailability (RBA) to determine which methodologies best correlated with the in vivo data. Arsenic bioaccessibility using a simplified gastric method was highly correlated with the in vivo assay results ($R^2=0.92$). As part of our study, we built upon a previously published linear regression model to predict arsenic RBA in mice using an IVBA assay and to develop a more robust model across multiple soil types, arsenic contaminant sources, and arsenic concentrations. We validated the predictive capability of this model using an independent set of arsenic contaminated soils. Validation of model performance using data independent to those used to construct the model is imperative for IVBA data to be used routinely for incorporation into human health risk assessments. Additionally, arsenic speciation in soils was examined using the Materials Research Collaborative Access Team's (MRCAT) beamline, Argonne National Laboratory (ANL). AsV species were the dominant arsenic forms in most test soils and in SRMs while other soils had appreciable levels of AsIII sulfide or ore species. The in vivo-in vitro correlation and independent data validation presented provide critical verification necessary for regulatory acceptance in human health risk assessment.

Study of mercury biogeochemical behavior in soil-plant system

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Mercury contamination of soil is a serious problem endangering environment compartments and consequently also the food chain and human health. Therefore, it is inevitable to study and understand mercury biogeochemistry, especially regarding mercury behavior in soil-plant system.

First part of our study evaluates mercury transfer, bioaccumulation and its toxicological effects in barley shoots (*Hordeum vulgare* L.) under laboratory conditions during 7-day incubation in calcareous Chernozem soil with total mercury concentration 0.061 mg.kg⁻¹ and maximum sorption capacity 13.14 mg Hg(II).g⁻¹, spiked with inorganic Hg(II) to obtain its five concentration levels in 0-130 mg.kg⁻¹ concentration range. Extremely high transfer rate of mercury into the barley shoots up to 195 mg.kg⁻¹ positively correlated with increasing Hg concentration of mercury in soil with calculated IC₅₀ value for barley shoots 184.6 mg.kg⁻¹. Determined mercury transfer from spiked soil into barley shoots was then compared to transfer from anthropogenically contaminated soils collected from former mining region in NE Slovakia where total mercury concentrations were up to 30.9 mg.kg⁻¹. Concentrations of mercury accumulated in barley shoots up to 0.07 mg.kg⁻¹ were in this case significantly lower. This indicates low mercury bioavailability in these soils tested also with several chemical and biological separation techniques including synthetically prepared rain water; 1 M MgCl₂; microbial metabolites obtained from fungal *Aspergillus clavatus*, *A. niger*, *Cladosporium* sp., *Penicillium* sp., *Trichoderma* sp. and *Alternaria alternata* species isolated from contaminated soils; 0.1 M EDTA and Diffusive Gradients in Thin-films (DGT) method. Soil mercury concentrations separated with these separation techniques were mostly in good agreement with mercury concentrations transferred from soil to barley shoots with the most suitable DGT method and fungal metabolites when assessing the mercury phytoavailability. Total mercury content seems to be in our case not suitable indicator of mercury phytoavailability and consequent transfer into the plants.

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Health risk assessment of potentially harmful elements (PHE) and micronutrients from soils and vegetables irrigated with wastewater

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In the developing world, vegetables are commonly grown in suburban areas while using untreated wastewater that contains potentially harmful elements (PHE). In Pakistan, there is no published work on the bioavailability aspect of PHE in sewage irrigated soils and/or the vegetables grown on these soils. Keeping this in view, five major industrial cities of the country were selected for assessment of the spatial distribution of risk via ingestion of vegetables grown over sewage irrigated soils. Using a mixed acid digestion-hot block method for soils and microwave-assisted acid digestion for vegetation, total metals were determined by ICP-MS. For the bio-accessible fraction of metals in soils and vegetable samples, the methodology developed by the Bio-Accessibility Research Group of Europe (BARGE) was utilised, which simulates conditions in the gastrointestinal tract to assess the human bio-accessibility of PHE by ingestion. Median concentrations of the bio-accessible fraction of PHE in selected soils were as follows (as % of total PHE contents): Cd 72; Co 16; Cr 14; Mn 29; Ni 26; Pb 55; and U 18. In vegetation samples, minimum and maximum concentrations of the bio-accessible fraction of PHE were as follows (as % of total PHE contents): Cd (50-100); Co (6-100); Cr (0-100); Mn (47-100); Ni (25-100); Pb (21-100); and U (4-100). When the vegetation was subdivided into leafy, fruiting and root vegetables, the leafy vegetables had a higher fraction (as % of total PHE) of bio-accessible PHE. Minimum and maximum levels of the bio-accessible fraction of micronutrients in vegetation samples were as follows (as % of total micronutrients composition): Cu (9.5-100); Fe (6.2-100); and Zn (69-100). Zinc had a greater better bio-accessibility compared to copper and iron in vegetation, but when subdivided into leafy, fruiting, and root vegetable sub-groups, the highest bio-accessibility was noted for root vegetables, followed by leafy vegetables for all of the PHE and micronutrients. It is concluded that rural and urban consumers who prefer root and leafy vegetables are at higher risk compared to the consumers who choose fruiting vegetables.

Organochlorine pesticides and polychlorinated biphenyls in air, grass and yak butter from Namco in the central Tibetan Plateau

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Limited studies on bioaccumulation of persistent organic pollutants (POPs) along terrestrial food chains were conducted. The food chain air–grass–yak (butter) in the pasture region of Namco in central Tibetan Plateau (TP) was chosen for study. The arithmetical mean concentrations in air of HCHs, HCB, DDTs and PCBs were 6.7, 10.3, 14.8 and 1.6 pg/m³, respectively. The concentrations of HCHs, HCB, DDTs and PCBs in grass samples were in the ranges of 1.57×10^2 – 5.88×10^2 , 50.9–84.8, 1.27×10^2 – 3.62×10^2 , and 6.4–27.3 pg/g dry weight (dw), respectively. The average concentrations of butter HCHs, HCB, DDTs and PCBs were 1.87×10^3 , 5.07×10^3 , 2.56×10^3 and 1.7×10^2 pg/g lipid, respectively. Compared with other regions, the concentrations of POPs in air, grass and butter in the TP were at the lower end of the concentrations generally found around the globe. For the compounds investigated, HCB was the main pollutant of air and butter, in line with the previous result that HCB was the most abundant compound in the air and organisms from clean environments. Besides HCB, the degradation products, i.e. β -HCH and p,p'-DDE, were the other major compounds in yak butter. Along the food chain, DDTs and high molecular weight PCB-138, 153, and 180 had higher Biological Concentration Factor (BCFs) values. The air–butter transfer factors (TFA:B) of POPs also were derived and demonstrated the practical advantage in predicting the atmospheric concentrations of OCPs and PCBs to the TP. This study sheds light on the transfer and accumulation of POPs along the terrestrial food chain of the TP.

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Mapping the spatial distribution of metal contamination and magnetic susceptibility of urban bonfire soils

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Bonfires are a major pollution source in urban soils, but there is a lack of knowledge about the impacts and spatial extent of bonfires on soil metal concentration and magnetic properties. In this study, a total of 379 soil samples were collected from a traditional bonfire site on a 1 × 1 m² grid system and analysed for total metal concentration and low frequency magnetic susceptibility ($MS\chi_{lf}$). High resolution maps of the spatial distribution of Cu, Fe, Mn, Pb, Sr, Ti, Zn and $MS\chi_{lf}$ were created and a significant relationship between each of the metals and $MS\chi_{lf}$ was revealed. Elevated levels of each metal were observed, with median and maximum values of 68 and 1117 mg kg⁻¹ for Cu, 114 and 985 mg kg⁻¹ for Pb and 561 and 21 681 mg kg⁻¹ for Zn in particular, indicating the site may pose a significant health risk. The spatial patterns were generally consistent, with Zn and Fe in particular, encompassing the position of bonfires. The spatial extent of influence of bonfires was estimated at approximately 10 meters, in line with the extent of bonfire materials. In addition, laboratory based experiments involving soil colour and the effect of temperature on $MS\chi_{lf}$ indicated that bonfires only raise soil temperatures to a maximum of 300 °C, having little effect on $MS\chi_{lf}$. The results of this study indicate the importance of metal contamination associated with bonfires in urban soils.

Mobility and speciation of potentially toxic metals in the total suspended particulate matter in Budapest, Hungary

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Knowledge on the speciation of the potentially toxic metals in the airborne particulate matter is of primary importance for the risk assessment of such materials. In this study, single and sequential chemical extractions, as well as various mineralogical analyses (XRD, SEM-EDS, TEM-EDS) were carried out to characterize the potential mobility and host phases of potentially toxic metals (primarily Pb, Zn and Cu) in total suspended particulate (TSP) matter samples from Budapest, Hungary.

Based on the enrichment factors (EF) calculated as a ratio of the metal concentration in the TSP material and the geological background materials, this material show significant enrichment in several potentially toxic metals. They are extremely contaminated by Zn and Pb (EF > 10), heavily by Cu and Mo (EF > 5), moderately by Ni (EF > 2.5) and slightly by Cr and Co (EF > 1.5).

Chemical extractions showed that highly resistant phases may host a significant portion of total metal content in the TSP material: between 27 and 64% of total Zn, 14 and 62% of total Pb and 22 and 64% of total Cu can be associated to such phases. On the other hand, up to 73%, 43% and 37% of their total Zn, Cu and Pb content may be weak acid soluble, respectively, and the water soluble fractions could be also significant for Zn (up to 30%) and Cu (up to 14%) but not for Pb (below 1%). Oxidizable metal fractions are generally of secondary importance for the studied metals suggesting the subordinate role of organic phases in metal hosting (mostly <5%).

According to the mineralogical analyses the most important chemically resistant metal bearing phase is magnetite which may compose even 10-15 wt% of the TSP material. The weak acid soluble metal fractions are shown to be associated to clay mineral surfaces for Zn and Pb, and also to metal carbonates and oxides for Zn.

Although large portion of the studied metals are hosted by resistant phases, their high concentrations and relatively high ratio in the easily soluble metal fractions pose a high risk for the human health in the urban environment.

Fractionation and mobility of heavy metals in soils of urban area of Moscow's Eastern District

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For assessment of urban soils contamination with heavy metals (HMs) their forms and mobility should be investigated. The main objective of this study is to determine fractionation of heavy metals (HMs) in urban soils of the Eastern District of Moscow where multisource pollution problems occur. 21 samples of the urban soils were collected using a regular grid with 1 km spacing and a reference sample representing background uncontaminated soils (podzoluvisols) located at the distance of 200 km to the east from the city. Each sample was digested with HF+HClO₄+aqua regia for the analysis of total HMs content and also partitioned into 5 fractions using sequential extraction procedure (Tessier et al., 1979): F1 – exchangeable (MgCl₂); F2 – bound to carbonates (CH₃COONa); F3 – bound to Fe/Mn oxides (NH₄OH·HCl+CH₃COOH); F4 – bound to organic matter (HNO₃+H₂O₂); F5 – non-silicate residual (aqua regia). The concentrations of HMs were determined using ICP-MS. The concentrations of HMs in the fraction bound to silicates (F6) were calculated as the difference between the total and F1+F2+F3+F4+F5 concentrations.

The results show that in the urban soils significant proportions of Cd, Mn, Zn are associated with Fe/Mn oxides; while lower percentage of these metals is held in other fractions. Co, Ni, As, Pb, Cr, Mo, Be, Bi, Sb are mostly bound to non-silicate residual and silicate fractions (> 60%), but the amounts of the metals associated with organic matter and Mn/Fe oxides are also high (~10-20% each). About 90% of V, Ti, Fe, Sn are found in F5 and F6. The significant proportions of W and Cu are bound to organic matter. The potential mobility factor (PMF) for each element was calculated: $PMF = (F1 + F2 + F3 + F4) \cdot 100\% / C$, where C is the total content of a HM in a sample. The results show that PMF in urban soils increases in order: Cd > Mn, Zn, W > Cu, Pb, Mo, Sr, Cr, Co, Ni, As > Be, Bi, Ag, Sb, V, Fe > Ti, Sn. Thus, very high environmental risk is associated with Cd, high risk is caused by Mn, Zn, W, and medium is formed by Cu, Pb, Mo, Sr, Cr, Co, Ni, As.

Phase and size distribution, sources and risk assessment of PAHs, NPAHs and OPAHs in a rural site of Pearl River Delta region, China

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Gaseous and particulate samples were collected in a rural site and an urban site of the Pearl River Delta (PRD) region, China. Eighteen polycyclic aromatic hydrocarbons (PAHs), twenty-nine nitrated PAHs (NPAHs) and seven oxygenated PAHs (OPAHs) were measured, and their gas-particle partitioning, size distribution, sources and risks were discussed. At the rural site, phenanthrene, 2-nitrofluoranthene and benzo[a]anthracene were the most abundant parent PAH, NPAH and OPAH, respectively. The partitioning of these compounds strongly depends on their molecular weights. The absorption model provides a better prediction of the particulate fraction of PAHs than the adsorption model, and might be applied for the discrimination of PAH derivatives sources. Molecular diagnostic ratios suggested coal combustion or biomass burning, not vehicle emission, were dominant sources. The ratios of 2-nitrofluoranthene/2-nitropyrene and 2-nitrofluoranthene/1-nitropyrene indicated that secondary formation by OH initiated reactions was the main formation pathway of NPAHs, with an average contribution of 92.6% during the sampling period, and the formation might be enhanced under haze conditions. Most of OPAHs were under the impact of regional pollution. Risk assessment showed an overall lifetime excess inhalation cancer risk of 1.12×10^{-5} in which the NPAHs taken into calculation contributed 3.5% although they only accounted for 0.7% of the 18 compound masses used in the assessment.

At the urban site, the concentrations of both parent PAHs and their derivatives showed much higher concentrations during the two hazy periods. Heavy compounds were found to be unimodally distributed, and were predominantly associated with fine particles (peaked in the size range of 0.49-0.95 μm); while light compounds exhibited a bimodal distribution, and were associated with both fine and coarse particles (a secondary peak in the size range of 7.2-10 μm). The distribution of all target compounds, especially NPAHs and OPAHs, significantly shifted toward larger size ranges (0.49-1.5 μm) under hazy conditions. Positive matrix factorization (PMF) analysis revealed that local vehicle emission was the dominant source of parent PAHs during hazy episodes, while in clear period, the atmosphere was more influenced by long-range transport of air masses from the northern China, making coal combustion being the most important source. 2-Nitrofluoranthene/1-nitropyrene (2NF/1NP) and 2NF/2NP ratios suggested that the formation of NPAHs was largely enhanced under hazy weather conditions, and the dominant formation pathway was OH initiated reactions. Risk assessment showed that the risks during the hazy periods were several times higher than clear periods, emphasizing the importance to control atmospheric pollutions.

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Variability in the transfer of potentially toxic elements (PTEs) in vegetables grown on urban allotment gardens

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Human exposure to certain PTEs contaminants may occur through the consumption of allotment- grown vegetables, if the soil on which these vegetables are grown is contaminated. In the assessment of exposure via allotment- grown vegetables, there are several important issues that need to be resolved. The aims of the research are: to investigate the degree and significance of the uptake of PTEs contaminants by allotment- grown vegetables and factors affecting them and to investigate the variability of total and bioavailability concentration of these PTEs (As, Cr, Cu, Pb, Ni, Co, Cd, Zn, Mn and V). Soil and vegetable samples were collected from allotment gardens at a site Greenock, Ayr in Scotland and some allotment gardens in Poland where contamination from lead has been identified as a major concern for human health. The soil samples were collected from 0-20cm depth using systematic sampling pattern, oven dried at 37°C, digested with aqua regia and analysed using ICP-MS in order to determine PTEs concentration. Vegetable samples were collected from the same plots, washed in distilled water and oven dried at 50°C for a period of 48hrs, digested with nitric acid and analysed using ICP-MS. The soil pseudo-total concentration across the sampling sites ranged from (9.9- 14.8 for As, 0.7- 3.5 for Cd, 492- 1204 for Pb, 104-157 for Cu, 45-98 for Ni, 413 -845 for Zn) in mg/kg, the average pH is 6.4 and LOI is 18.66%. On wet weight basis levels (mg/kg) in vegetables, Pb were in the range of 0.8- 8.62, Cu ranges between 2.92 -7.86, Cr ranges between 0.11- 2.24, As ranges between 0.76 - 1.3 and V ranges between 0.18-1.09. The result showed that the concentrations of PTEs in these vegetables were at low levels. PTEs availability to vegetables was estimated by the EDTA extraction; both correlation analysis and stepwise regression were adopted to illustrate the extractable PTEs. The results obtained show variations in PTEs in soil across the sites, the soil is slightly acidic to mildly alkaline (pH, 5.7-7.5), the high and wide concentration of lead (Pb) in the allotment garden soil, the transfer values obtained were below 1.00, indicating that the majority of the PTEs remain in soil and their uptake from soil to Vegetables at the allotment gardens are not significant.

Brominated flame retardants (BFRs) in indoor and outdoor air in a community in Guangzhou, southern China

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Brominated flame retardants (BFRs) are an important class of additives used in various products. However, their occurrence in indoor air in China is limited. In the present study, we measured and compared the BFR contamination in indoor (homes, offices, and a student dormitory) and outdoor air in a year using passive samplers in a community in Guangzhou, southern China. The concentrations of PBDEs (except for BDE209) in indoor air in the homes were mostly higher than those in the outdoor air with median indoor/outdoor (I/O) ratios of 1.2-2.1, indicating a significant emission from household products indoors especially for lower brominated PBDEs (tri- to hexa-BDEs). In addition, the indoor levels of low brominated PBDEs in houses with low air ventilation were higher than those in houses with good air ventilation. The PBDE levels in offices and dormitory were lower than those in the homes, because the quantities of furniture and household appliances were relatively smaller. Most I/O ratios were below one (median = 0.6-0.9). However, the I/O ratios of BDE209 in all the environments were below one (median = 0.24-0.70). This suggests the presence of outdoor sources in Guangzhou. This is supported by the fact that commercial deca-BDE product is still widely used in China. In the student's office (with many computers in it), the BDE209 levels were significantly than those in another office (with much fewer computers). This indicated that emission from computers is an important source of BDE209. The compositions of PBDEs differed in the indoor environments, probably due to the variations in household products in them (e.g., types, quantities, or ages). This study also indicated that although commercial penta-BDE product has been banned in China, their emission from household product remains a significant source to indoor environment and they are continuously exposed by humans.

Marine sediment geochemistry influenced by the treated city effluents discharge in the coastal zone of the Adriatic Sea (Šibenik, Croatia)

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Submerged wastewater effluent discharge in the vicinity of cities along the Adriatic Sea coast may lead to coastal marine sediment contamination by inorganic and organic pollutants, depending of sewage treatment system performance. The city of Šibenik area (Middle Eastern Adriatic coast) had faced in the past the serious problem of the eutrophication of the Krka River Estuary and coastal marine environment that had been receiving untreated industrial and domestic sewage for years. As a region is very attractive because of natural beauties, the problem was becoming more pronounced during the touristic summer period. Sewage treatment system and pipe line to outside of Krka River Estuary was constructed in 2008, and treated effluent is being released into the near shore marine environment SE of the Island of Zlarin by 5000 m long sub-marine pipe system. The investigation was undertaken to examine the metal concentrations in marine sediments influenced by the wastewater disposal system. Surface marine sediment was sampled by Veen Grab Sampler in July, 2014 from thirteen locations around the effluent discharge at the depth of the sea floor ranged from 33.4 m to 62.7 m. Samples were analysed for mineralogy, organic matter and CaCO₃ content, and major and trace element concentrations. The univariate and multivariate statistics was applied. The geochemical normalization of data was done using Al, the procedure based on calculation of the regression line of the metal on the normalizer followed by testing the ratios metal/normalizer on all data-points. Calcite is the main mineralogical component, and traces of quartz, dolomite, Mg-calcite and aragonite are present. Normalization of trace metals to Al revealed the strong significance of the regression lines only between Al/Cr ($R^2_{adj} = 0.957$), followed by Al/Pb (0.725) and Al/Zn ($R^2_{adj} = 0.863$). For Hg and Cd, regression lines were not significant. Generally, distinct anthropogenic loads of trace elements in sediment that may be related to the wastewater effluent discharge are not evident.

Wastewater Emission and Management in Shanghai since 1980's

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Shanghai is one of the largest cities in the world. The permanent residents in Shanghai were 23.8043 million at the end of 2012. In 1981-2012, the general urban wastewater in Shanghai was between 1.775-2.42 billion tons. The urban wastewater includes the industrial wastewater and the living wastewater.

The industrial wastewater emissions was more than 1.4 billion tons before 1988, after the year, it was declining year by year, to about 649 million tons at 2002, a low value in the past 30 years, less than 50% of the 1980s. The percentage of industrial wastewater in the total urban wastewater discharge is falling from 76.9% in 1981 to under 30% in recent years. The living wastewater emissions increased from 424 million tons in 1981 to 1.697 billion tons in 2012. There is a relationship between the living wastewater increasing and the increasing of the permanent residents in Shanghai. At the same time, since 1981, the living wastewater emissions per capita per day were significantly increased; at the early 1980s, the wastewater emission per capita per day was near 100 kg (liter), increased 220 kg (liter) to the year of 2000, and dropped to around 190 kg (liter) in recent years.

From 1995, the treatment and management of urban wastewater was continuing to intensify in Shanghai. There were 17 plants for the city sewage treatment, 146.65 million tons of wastewater was treated, it was 6.35% of the total urban wastewater in 1995; the plants for the sewage treatment increased to 53 in 2012, and the treating wastewater capacity was 2.00685 billion tons, to 85.62% of the total urban wastewater in 2012.

Comparing the social-economic development and management of wastewater discharge in Shanghai, it can be seen that the wastewater emissions increasing amplitude was far less than the size of population growth and economic growth.

Heavy metal stabilization in EAFD using magnesia and Sorel cements

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Electric arc furnace dust (EAFD) is a by-product of steel production in scrap recycling facilities. About 30,000–40,000 tonnes of EAFD are produced annually in Greece only, nothing that EAFD is classified as an environmentally hazardous waste in most regions of the world. It contains considerable quantities of Zn and Fe, as well as significant amounts of Ca, Mn, Pb and Si. Several hydrometallurgical and pyrometallurgical techniques have been developed, some of them at industrial scale, for EAFD's treatment and recovery of metals' content, such as Zn, Pb and Fe. However, such plants have not been constructed in Greece since the annual produced volume is not considered sufficient to allow a profitable operation. Thus, almost the entire quantity of EAFD produced in Greece is either transported abroad, or temporarily deposited at industrial sites, which poses significant environmental risks. Therefore, there is a strong demand for an efficient process that can allow the safe disposal of EAFD in appropriate sites using an environmentally sound and low cost treatment method. A very encouraging approach, which aims to reduce the environmental and health impact of EAFD is stabilization/solidification using MgO. Stabilization of solid wastes converts hazardous substances to more stable chemical forms, which are much less soluble, mobile and/or toxic. An alternative use of MgO and Sorel cements in EAFD stabilization/solidification was studied in this work. MgO reacts with solutions of various magnesium salts, as well as phosphate salts, to form strong bonding phases, e.g. the reaction of MgO with MgCl₂, resulting to the formation of a mixture of magnesium oxychloride (MOC) phases, known as Sorel cement. EAFD treatment using MgO was found to reduce significantly the leaching of heavy metals, providing an economically viable solution. MgO is acting also as a buffering agent within the pH 9.0–10.5 range, minimizing heavy metals solubility and thus, avoiding the re-dissolution that occurs in higher pH values, when using as alkaline additives, e.g. lime or sodium hydroxide. Conclusively, MgO was found to be suitable for heavy metal stabilization, when disposing EAFD wastes.

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Pollution profiles and risk assessment of PBDEs, phenolic brominated flame retardants and bisphenol A in water and sediments from a typical electronic waste dismantling region

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Recently, electronic waste (e-waste) is becoming a global problem. Millions of tons of e-waste are recycled in developing countries using underdeveloped dismantling approaches, which could release various hazardous organics into the environment. Brominated flame retardants (BFRs), are among the organics receiving the most attention currently. Notable progress has been made in detecting these contaminants around the world (?). Nevertheless, little is known about the levels and toxicities of phenolic BFRs, including tetrabromobisphenol A (TBBPA), pentabromophenol, 2,4,6-tribromophenol, and bisphenol A (BPA), in the river water and sediment within a known e-waste dismantling region.

Given this background, this research investigated pollution profiles of phenolic BFRs, BPA, and polybrominated diphenyl ether (PBDEs) in river near an e-waste dismantling region. Eco-toxicities on fish, daphnia and green algae at three different trophic levels, and the endocrine-disrupting activities of TBBPA and BPA were also evaluated. Results showed that various persistent organics, including PBDEs, tribromophenol, pentabromophenol, TBBPA, and BPA were widely spread in the water and sediment across our surveyed region. Dismantling of e-waste has become a source of these toxic and persistent chemicals. In sediment, Σ_{19} PBDEs ranged from nd to 5.6×10^3 ng g⁻¹, while BDE-209 was the predominant congener, with a range of nd to 3.5×10^3 ng g⁻¹. Tri- to hepta-BDEs concentrations were significantly ($p < 0.01$) correlated with each other except for BDE-71 and BDE-183, and octa- to nona-BDEs concentrations were significantly ($p < 0.05$) correlated with each other except for BDE-208. BDE-209 was not significantly correlated with tri- to nona-BDEs. In water, Σ_{19} PBDEs (except BDE-209, which is below the detection limit) ranged from 0.31 to 8.9×10^2 ng L⁻¹. 2,4,6-tribromophenol, pentabromophenol, TBBPA, and BPA concentrations ranged from nd to 3.2×10^2 , nd to 37, nd to 9.2×10^2 and nd to 8.6×10^2 ng L⁻¹, respectively. Furthermore, estrogenic activity assessment showed that no estrogenic risk was expected from water and sediment based on TBBPA and BPA estrogenic activity, while eco-toxicity assessment at three representative trophic levels showed that different risks were found at most sampling sites. Monitoring these compounds over time will help researchers better understand the usage, emission, toxicity, transformation, and effective decontamination of these pollutants.

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Recent development of novel Zr-oxide based binding gels in diffusive gradients in thin films (DGT) for measurements of bioavailable chemicals in the environment

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The technology of diffusive gradients in thin films (DGT), as a passive sampling method, has received increasing attention for its applications in measurements of bioavailable chemicals (both cations and anions) in soils, waters, and sediments. It has significant advantages over traditional methods: in situ measurement, time averaged concentrations and high spatial resolution. The advantages of DGT significantly promote the collection of “true” information of the bioavailable or labile forms of chemicals in the environment.

This presentation provides a summary of recent development of a new DGT variant using Zr-oxide based binding gels. The Zr-oxide DGT was developed in 2010. It has relatively high capacity for measurements of oxyanions (P, As, Cr, Se, Sb, Mo and W), with 50 and 5~29 times of those of the commonly used ferrihydrite DGT for measurements of P and As, respectively. It is easy to provide high-resolution (sub-millimetre), two-dimensional spatial information of P using a gel coloration procedure, while this technique has been successfully applied to in situ monitoring labile P in a large eutrophic Lake Taihu in China. Simultaneous measurements of cations and anions, such as P and S, P and Fe, As and Fe, and As, Fe and P, have been successful achieved through development of several types of mixed binding gels based on the Zr-oxide gel. More functions are being extended with this technique for measurements of other analytes.

In situ monitoring of labile phosphorus and its mobility in sediments with Zr-oxide based DGT techniques

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Understanding the labile status of phosphorus (P) in sediments is crucial for the management of a eutrophic lake, but it is hindered by a lack of *in situ* data particularly on a catchment scale. The technique of diffusive gradients in thin films (DGT) provides *in situ*, dynamical, and high-resolution measurements of labile P in sediments.

In this study, we characterized for the first time *in situ* the labile P in sediments at a two-dimensional (2D), submillimeter resolution with Zr-oxide DGT in a large-lake. The partitioning of horizontal heterogeneity of labile P showed a likely active layer at the depths of 0-30 mm. Results of the apparent diffusion flux of P across the sediment-water interface (SWI) showed that the sediments tended to be a source and a sink of overlying water P in the algal- and macrophyte-dominated regions, respectively. The DGT-labile P in the 0-30 mm active layer showed a better correlation with overlying water P than the labile P measured by *ex situ* chemical extraction methods, implying that DGT is a more reliable approach in monitoring of the labile P in sediments in the field.

Another Zr-oxide based DGT (ZrO-Chelex DGT) was further employed to *in situ* collect the labile Fe and P being weakly absorbed onto sediment solids in Lake Taihu. The measurement recorded a coincident distribution between them at the one- and two- dimensional, 1.0 mm spatial resolution, which was a result of the reduction of oxyhydroxides Fe(III) and a simultaneous release of Fe(II) and P as theoretically predicted. Therefore, it provided a strong evidence for the theory of the Fe redox-driven mobilization of P in sediments.

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Photodegradation of Phenanthrene on Cations-Modified Clays under Visible Light

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Polycyclic aromatic hydrocarbons (PAHs), mainly produced via fossil fuel deposit and incomplete combustion, have been recognized as one class of primary contaminants in naturally hydrophobic phases such as soil and sediment. Due to their potential damaging to human health and ecosystem, transformation and mobility of PAHs in soil environment have attracted great attention. It is confirmed that the photolysis of organic compounds adsorbed on clay minerals is more efficient than that occurring on other minerals such as aluminum hydroxide, iron oxide (ferrihydrite), and manganese dioxide.

In the present study, anthracene and phenanthrene were employed as molecule probes to explore the potential photocatalysis effect of various clay minerals in the soil under visible-light irradiation. Among three types of Fe(III)-modified clays, Fe(III)-smectite shows the highest photodegradation rate followed by Fe(III)-vermiculite and Fe(III)-kaolinite. The photoactivity order is consistent with the iron content contained in the three clays, suggesting that Fe(III) plays an important role in photocatalytic degradation of phenanthrene. To further inspect the effect of Fe(III), additional four types of cations were paralleled. As a result, the photodegradation rates of phenanthrene follow the order: $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Cu}^{2+} \gg \text{Ca}^{2+} > \text{K}^+ > \text{Na}^+$, which is consistent with the binding energy of cation- π interactions between PAHs and exchangeable cations. The result suggests that PAHs photolysis rate depends on cation- π interactions on clay surfaces. Moreover, phthalates, 9, 10-phenanthrenequinone and alkanolic acids were identified by GC/MS analyses as the main intermediate compounds, and the organic compounds were mineralized finally.

The present work provides valuable insights into understanding the transformation and fate of PAHs in the natural soil environment and sheds light on the development of technologies for contaminated land remediation.

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Treatment of air and water by nanostructured photocatalysts under solar light

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During the past 20 years, the average growth rate of China's GDP reached 9.5% but the extensive growth mode depleted large amounts of resources and brought high pollutant emissions. So, China is faced with many problems in land use, air quality and water conservation, etc. Especially, global warming from the fossil fuel greenhouse gases which contribute to the climate changes is becoming a major concern. To keep Chinese sustainable development, the environmental problems have to be solved through clean methods. For fully taking the advantage of solar light to address environment issues, it requires new initiatives to harvest incident photons with high efficiency.

Nanoscience and nanotechnology and their merger with other science may contribute to the development of a more efficient and sustainable environment system. The important functions of nanostructured architectures for environmental pollution control will be demonstrated and exemplified by using normal semiconductors such as Cu₂O, CdS, TiO₂ and their hybrids with carbon nanotubes and other semiconductors. The relationship between structure and property of these materials for organic pollutant degradation, CO₂ conversion to organic fuel under simulated solar light will be discussed. Density functional theory calculations are also related to the design of new materials based on electronic structure interaction. Finally, the following conclusions will be reached.

The photocatalytic activity for Cu₂O under solar light is related to the preparation method and morphology. Through doping and hybrid, its stability and activity for organic pollutant degradation can be improved. The photocatalytic mechanism working for Cu₂O is quite different from that for TiO₂. The photo-generated electron in conduction band leads to the high negative potential, which could be used as O₂ cathode for photoelectrocatalysis. The in-situ produced H₂O₂ together with Fe²⁺ under visible light as a simple and cheap photo-Fenton technology is promising for environmental pollution control.

Different conductive type of Cu₂O film on Cu foil leads to different CO₂ conversion efficiency in photochemical, electrochemical and photoelectrochemical system, respectively. The best yield for CO₂ reduction is obtained in the photoelectrochemical system. The presence of Cu₂O thin film on Cu substrate contributes a higher selectivity for C₂H₄ production than blank Cu. Additionally, CO₂ conversion efficiency over Cu/Cu₂O (p-type) is much higher than that over Cu/Cu₂O (n-type) with similar morphology. The morphology of Cu₂O has an effect on CO₂ reduction activity in the photoelectrochemical system as well.

Carbon nanotubes can be used to facilitate the degradation efficiency of organic pollutant and reduction activity of CO₂ over carbon nanotubes/semiconductor hybrid photocatalysts.

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Evaluation of the efficacy of Different Types of Periphytic Biofilms for Enhanced Decolorization and Biodegradation of Dyes

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Synthetic dyes have a wide application in various industries such as food, pharmaceutical, textile, cosmetic and paper industries and pose a threat to environmental safety. Recently implementation of microbial biomass is becoming a prominent technology to treat various dyes replacing former treatment processes. Microbial consortiums have already been proved more efficient as compared to single strains. The aim of our study was to use three different kinds of periphytic biofilms collected from Xuan Wu lake, Located in Nanjing, China, to assess its potential for enhanced decolorization and detoxification of 4 dyes of different nature i. e. amaranth (azo dye), Brilliant Blue FCF (disodium salt), Crystal violet (triphenyl methane dye) and Methyl orange (azo dye). In the present study, we investigated various physicochemical parameters such as agitation, temperature, pH, biomass concentration, initial dye concentration for maximum degradation of dyes. The degradation was possible through a broad pH (2–12) and temperature (10–45°C) range. Optimum conditions for decolorization were pH 7 and temperature 25–35°C. An increase in periphytic biomass enhanced the degradation of dyes. Cytotoxicity and phytotoxicity studies carried out before and after decolorization dyes revealed the nontoxic nature of the biotreated sample. Biodegradation was confirmed by analysing the product using UV–vis, and FTIR. The results have indicated a higher degradation efficacy of periphytic biofilms in distilled water and low requirement of environmental factors for dye removal proves biodegradation by biofilms a valuable treatment process. It also suggests that these biofilms have the potential to be used at commercial levels to degrade various kinds of dyes.

Direct Rapid Analysis of 21 Antibiotics in the Surface Water of Urban River, Shenzhen, China Using Ultrahigh Performance Liquid Chromatography – tandem Mass Spectrometry with SPE Pre-concentration

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Antibiotics are extensively and world-widely used as therapies for pathogenic infection, which made great contribution to human health as well as agricultural growth. Nevertheless, the abuse of antibiotics has caused lots of environmental problems at the same time, such as water pollution and the emerging of antibiotic resistant bacteria. Antibiotics have entered the water environment in the forms of prototype or metabolites in urine or feces, with the concentrations of $\sim\mu\text{g/L}$ or $\sim\text{ng/L}$, and caused potential harm to both human health and ecological environment. Therefore, it is necessary to establish a robust and sensitive analytic method to determine multiple antibiotics simultaneously by ultrahigh performance liquid chromatography – tandem mass spectrometry (UPLC - MS/MS) in urban rivers.

In this study, UHPLC – MS/MS was utilized to develop a rapid, sensitive and reliable method with solid phase extraction (SPE) pre-concentration for trace analysis of 21 pharmaceuticals antibiotics in surface water of urban river in Shenzhen, China. Detection parameters for UHPLC – MS/MS analysis were optimized, including sample pH, eluent, mobile phase (solvent and additive), column temperature, and flow rate. Under the optimal conditions, all analytes were well separated and detected within 10.0 min by UHPLC – MS/MS. The recoveries of 21 antibiotics were in range of 69~115% and 62~113% in pure water and surface water, respectively. The detection limits (LODs) for the target compounds were in the range of 0.02~2.27 ng/ in surface water. The analysis of the urban river samples in Shenzhen China revealed the occurrence of 21 classes of antibiotics including sulfadiazine, sulfamethoxazole, sulfamethazine, sulfamerazine, sulfachinoxalin, sulfanilamide, sulfathiazole, sulfacetamide, sulfapyridine, sulfachlorpyridazine, sulfisoxazole, levofloxacin, enoxacin, enrofloxacin, nadifloxacin, ciprofloxacin, norfloxacin, lomefloxacin, erythromycin, roxithromycin and chloramphenicol. Their concentrations ranged from 3.9 to 2,554.7 ng/L. The most frequently detected antibiotics were found to be sulfonamides and fluoroquinolones in surface water. The concentrations of antibiotics from samples collected in March were higher than those collected in July, 2013. The highest total concentration of 21 antibiotics in water samples were 2,554.7 and 1,948.0 ng/L in March and July 2013, respectively. The results provided basic data for evaluating the health and ecological risk of antibiotics in these areas.

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Stress of Five Heavy Metals on the Resistance of Isolates from Swine Wastewater to Four Antibiotics

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Co-existence of heavy metals and antibiotics becomes increasingly common in environmental pollution. To investigate the stress of heavy metals on microbial resistance to antibiotics, fifty-six strains of bacteria were initially isolated from some swine water in Guangzhou city, based on their resistance to four antibiotics (Cefradine, Norfloxacin, Amoxicillin, Tetracycline) and five heavy metals (Pb^{2+} , Cr (VI), Hg^{2+} , Cu^{2+} , Zn^{2+}), a Gram-negative isolate, *Pseudomonas putida* XX6, was selected to study the detail stress rules of heavy metals on its resistance to antibiotics. The antibiotics incidences of these isolates were in the order of Norfloxacin > Amoxicillin > Cefradine > Tetracycline, and that of *Pseudomonas putida* XX6 was Cefradine>Amoxicillin \approx Tetracycline>Norfloxacin. The addition of heavy metals made all isolates' resistance to antibiotics decrease, and Cr (VI) impacted their resistance to Norfloxacin most obviously. If heavy metals concentration was the most important factor affecting the resistance of *P. putida* XX6 to the antibiotics? There was a positive correlation between the bacterial resistances to antibiotics and low concentration heavy metals (no more than 0.01 mg/mL of Pb^{2+} or Cu^{2+} or Zn^{2+} , 0.2 mg/mL of Cr(VI) or Hg^{2+}), and the correlation turned to negative with the concentrations of heavy metals increasing. But the bacterial resistance to Amoxicillin or Cefradine remained irrelevant to the concentrations of Cr (VI) or Pb^{2+} . Results showed that the combined effect of antibiotics and heavy metals could alter their individual effect on bio-toxicity as well as on the biological removal capability of pollutants.

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Gene response of CYP314, CYP360A and GST and whole-organism changes in *Daphnia magna* exposed to Ibuprofen

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As emerging environmental contaminants, the fate and ecological impact of non-steroid anti-inflammatory drugs (NSAIDs) in aquatic environment has gained increasingly widespread concern over the past years. However, the knowledge about toxic mechanism of NSAIDs to aquatic invertebrate remains still not enough. In the present study, we investigated the gene response of CYP314, CYP360A and GST and whole-organism changes in *Daphnia magna* exposed to environmental relevant concentration ibuprofen (IBU). It was indicated that the effects of chronic IBU exposure on the growth and reproduction of *D. magna* cannot be ignored. Results suggested that some intrinsic relationship may exist between the expression alteration of CYP314, CYP360A and GST genes and the reproduction performance of *D. magna* under IBU exposure. Overall, the antioxidases were generally induced upon IBU exposure compared to control. Significant induction occurred in short-term exposure of IBU for SOD, GST and CAT, but inhibition came after prolonged exposure. MDA content reached a maximum when GST and CAT dropped to a lower level. APND and ERND related to CYPs were extensively activated, while EROD showed a general decline with prolonged IBU exposure after its induction of 6 h. CYP360A8 gene response exhibited a high similarity with ERND, suggesting that a similar detoxification role exists in *D. magna* for CYP360A, much like the role of CYP 3A in mammals. The reduction in the gene expression of CYP314 may be partially related to the molting inhibition of *D. magna*, but further investigation is needed to verify this hypothesis. In summary, the integrated approach combining the response in genes level with the performance in whole organism can help to elucidate the toxic effects of IBU and provide more insights into exact toxic mechanism of ibuprofen in aquatic organisms.

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Topic 1

Health aspects of contamination of geological environment – waters, soils, sediments, air, food chain, urban environment
(risk assessment, risk management, legislative background, analytical procedures, monitoring)

Poster Presentation abstracts

WATER-M – Unified Intelligent Water Management

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Water is a finite resource that should be carefully managed. However, more than 50% of the world population is living on areas with a water sustainability problem. The Water-M project is geared to enable the creation of new products and services to build a unified water business model with the core of early warning tools, real time acquisition and processing platforms and services for water suppliers and water consumers. Water-M project deals with the interoperability, real-time, big data and heterogeneous data challenges to find solutions towards a Smart Water Network.

Objectives of the project include definition of a unified smart operation for water supply. This is achieved via shared development and demonstration actions with several water supply stakeholders; water utilities, research institutes, technology solution providers and responsible authorities. The solutions, which are not nowadays widely used in enhancing water safety and supply efficiency, include e.g. adding distributed intelligence via real-time platforms, XTPP and large storage and data processing technologies. The provision and validation of novel monitoring and sensing solutions for detecting possible harmful compounds and residues form a remarkable part in enhancing water safety and quality. Providing new added value services and information for smart water networks to both suppliers and customers pave the way for new business and operation model, which allows citizens and different kind of interest groups to understand and participate on remaining and enhancing a high-quality water supply system.

The Conclusions and the Results of the project are based on following topics:

- 1) Implementing a smart monitoring and early warning tools for failure detection, diagnosis, water outages and harmful compound detection.
- 2) Providing a unified Water Information Model for exploiting data from the water grids and support decision making to increase reliability operation.
- 3) Achieving high levels of water supply efficiency by e.g. more efficient leak detection and supply network monitoring.

The Water-M project is carried out as a part of European ITEA2-programme. It includes industry-led consortiums from Finland, France, Turkey and Romania and is carried out by 15 companies, 5 research institutes and one governmental authority. The project is running until DEC 2016.

Monitoring of contamination sites in Slovakia – data for identification of threats to human health

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Since 2012, the State Geological Institute of Dionýz Štúr implements the project named „Monitoring of contaminated sites of selected areas of the Slovak Republic“. The aim of the project is the design and implementation of monitoring systems for selected 161 contaminated sites in Slovakia. The project meets the program objectives of the Government of the Slovak Republic, which are defined in the document „National Contaminated Sites Remediation Program 2010-2015“. The project activities are in accordance with standard practices in the EU, in accordance with the Water Framework Directive and respective Daughter Directive on the protection of groundwater. These directives constitute the basic legislative framework for the implementation of this project.

Contaminated sites pose a risk of contamination of groundwater and rock environment. They represent primarily large industrial areas, settlement agglomerations, landfills, mining industry, manufacture of paper and paper pulp processing, metallurgical production etc. Within the project activities, it is important to identify contaminants in order to verify that plumes from contaminated sites do not expand, deteriorate the chemical status and whether they pose a risk to environment and even to the human health. Nowadays, a huge amount of environmental samples is collected and analysed to identify the quality of groundwater, surface water, soils, stream sediments, including borehole core samples as well. The new information is transformed into conceptual models for each contaminated site individually to identify possible contaminant linkages and potential risks to environment and human health. Preliminary results of risk assessment roughly divide the contaminated sites into three categories: 1) sites where no further action is probably needed and monitoring will stop soon, 2) sites with potential risk to environment and human health and further information is necessary to establish what further action is appropriate and 3) sites where more information is needed to assess level of risk. Key outputs from this stage of the project will be finalized in final report in December 2015, including 1) contamination level and extent, 2) trends in contamination and 3) development of the conceptual model, the evaluation of the potential risks and the proposals for further decision making process.

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Traditional Practicing with Arsenic Rich Water in Fisheries leads to Health Hazards in West Bengal and North-Eastern States of India

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The supply of good quality food is main necessity for economic and social health of urban and rural population throughout the globe. This study comes to know the severity of As in the west Bengal and north-eastern states of the India. Over the 75% large population of India lives in villages and associated with farming and its related work. Arsenic contamination in ground water is major growing threat to worldwide drinking water resources. High contamination of As in water have been reported in many parts of the world (Chandrasekharam et al., 2001; Smedley and Kinniburgh, 2002; Farooq et al., 2010). West Bengal is the densest populated area of India, fish and rice are the staple food in West Bengal and as well as in north-eastern states of India. For the fulfil demand of fish large population of the area are using fisheries as the business. In context to West Bengal and North-eastern states of India, arsenic in food chain is emerging menace. In these areas ground water is rich in arsenic, several fold higher concentrations prescribed by WHO (10 µg/L) permissible limits have been reported. Over the 36 million people in Bengal delta are at risk due to drinking of As contaminated water (Nordstrom, 2002). To investigate the extent of arsenic contamination, 26 water samples were collected on a random basis. Analysis for all major (cations) and trace elements was done by ICP-AES (Perkin-Elmer, France). Sulfate (SO₄²⁻) concentrations were measured by spectrophotometer (Shimadzu UV-Visible spectrophotometer 160), alkalinity by titration and chloride (Cl⁻) by Expandable Ionanalyzer 940A with a combination electrode Orion ionplus 9817 BN. More than fifty percent samples showing higher concentration of arsenic with 535 µg/L was registered from Ngangkha Lawai Mamang Leikai area of Bishnupur district which is fifty fold of the WHO limit. Continuous traditional practicing (As rich water pond) and untreated arsenic rich water in fisheries may leads to health hazards. A sustainable development in aquaculture should comprise of various fields including environmental, social, cultural and economic aspects. A scientific study has to be needed for the overcome on this problem and rain harvested water may be used for reduce the arsenic problems in fisheries and health hazards.

Arsenic Concentration in Groundwater and Soil Profile of Thoubal District, Manipur India

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The supply of good quality food is main necessity for economic and social health of urban and rural population throughout the globe. This study comes to know the severity of As in parts of Manipur north-eastern state of the India. Over the 75% large population of India lives in villages and associated with farming and its related work. Arsenic contamination in ground water is major growing threat to worldwide drinking water resources. For the better understating of arsenic contamination in the groundwater of Thoubal district a systematic study has thus been undertaken to assess the groundwater quality of Thoubal district of Manipur. A detailed field work conducted for collection of the water and soil samples to know the hydrological condition in the area. The water and soil samples were analyzed by ICP-IES in the laboratory. Selected certified reference materials have been repeatedly analyzed to control the quality of the analysis. The maximum 76 µg/l with average of 33 µg/l arsenic was registered in groundwater whereas surface water remains below detective limit. Soil samples at every 10 inches interval were collected and homogenised to ensure representative sampling and soil profile was carefully noted while sampling. The maximum of 24 mg/kg with average of 18 mg/kg concentration of arsenic has been registered. The presence of As free water on the surface and contaminated groundwater at deeper levels indicates the existence and operation of As release mechanism within the aquifer sediments. It is advisable that the surface water sources to be evaluated for the biological content and if found safe should be recommended to until a network to supply safe drinking water is put in place. The rate of increase in As concentration in the groundwater and its mobilization under non-reductive condition needs to be further investigated for better understanding of the processes involved in As mobilization. A scientific study has to be needed for the overcome on this problem and rain harvested water may be used for reduce the arsenic problems in the area.

Environmental monitoring in the Suape Port and Industrial Complex, Pernambuco, Brazil: ecotoxicological aspects and heavy metals content in sediments

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A monitoring program to verify the environmental impact of a petrochemical and shipyard industries in the Suape Port and Industrial Complex bay area has been started in 2011. Seven sampling sites were selected in the bay area in order to carry out the monitoring program. The main objective of this program is to evaluate the influence of the aforementioned industries in the water and bottom sediment quality. In order to achieve this objective, toxicity tests and chemical analyses were carried out in the seven selected sampling sites in the Suape bay. The toxicity in the water was investigated using bioassays with the embryonic development of the *Lytechinus variegatus* sea urchin whereas for the sediments the bioassays were done using the copepod harpactoid *Tisbe biminiensis*. The analyzed parameters were compared to the controls by the use of statistical tests to detect significant reduction. During the 2 year period (2011-2012) some monitoring stations presented chronic or sub lethal toxicity, but there was not observed a regular pattern in the toxicity in the studied area, neither spatial nor temporal that could be related to the petrochemical and shipyard industries. Bottom sediments were sampled to monitor the metal load discharged into the bay area. Br, Co, Mn, Sb, Ti and Zn were the chemical elements selected to monitor the potential metal load discharged into the bay area. Regarding the metal load it is observed an increase of the metal content when compared to the data published in 2003. However, the values are still below the limits established by Brazilian regulations and most of them are below the upper crust median value.

Characteristics of metal-bearing particles in attic and household dust from Pb mining and smelting area (Žerjav, Slovenia)

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The environment in the study area of Žerjav (NNE Slovenia) is heavily burdened with Pb, Zn and Cd, due to past mining, primary Pb smelting and present-day Pb recycling. The results of investigation of solid particles deposited in snow indicated prevalent influence of present-day Pb recycling on recent metal pollution in the area. Objectives of present study were to assess relation between recent and past airborne metal pollution and characterise particles that potentially influence human health.

Attic and household dust samples were collected at two locations in Žerjav. Samples were dry-sieved to a fraction < 0.125 mm. Chemical analysis was performed at AcmeLabs by aqua regia digestion ICP-MS and ICP-ES and fusion ICP-MS. Solid particles were characterised by their elemental composition and morphology using a JEOL JSM 6490LV SEM, coupled with an Oxford INCA Energy EDS system at 20 kV accelerating voltage and 60 s spectrum acquisition time. Mineral equivalents were assessed from atomic proportions of constituent elements, acquired by semi-quantitative analysis.

Contents of Pb and Sb in attic dust exceed the New Dutchlist intervention values for soils by 135 and 55 times, respectively. Values are also exceeded for Cd, Zn, As, Cu and Tl. In household dust, contents of Pb, Sb and Zn exceed soil intervention values by 4 times for Pb and 2 times for Sb and Zn. SEM/EDS analysis showed that the attic dust mostly consists of Ca-sulphates (31%), while metal-bearing particles occupy 22% of the sample. According to their morphology, chemical and mineral composition, 50% of all metal-bearing particles (Cu-bearing anglesite and Zn-sulphate) most probably originate from primary Pb smelting, 27% of metal-bearing particles (pure anglesite, sphalerite, and Zn-, Cu-, Sn-bearing Fe-oxyhydroxy sulphates) result from mining activities and weathering of ore outcrops, while 23%, mostly Pb-K sulphate, Sb-, Sn-, Cl-bearing anglesite, and Pb-Sb-Sn-oxides and sulphates, emanate from present-day Pb recycling. In the household dust, C-bearing particles (55%) prevail, while metal-bearing particles represent 4% of the sample. 77% of metal-bearing particles (Pb-, Zn-bearing Fe-oxyhydroxides and barite), originate from mining activities and ore outcrop weathering, 20% from primary Pb smelting and only 3% from present-day Pb recycling.

Assessment of the environmental conditions of the Calore river basin (south Italy): a stream sediment approach

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The investigated area is located in Campania region (Italy) and it extends for about 3058 Km². It is drained by the Calore River, a tributary of the Volturno: the biggest south-Italian river. The aim of the study is to determine the geographic distribution of concentration values for each element, therefore, to provide reliable analytical data to allow a quantitative assessment of the metal pollution threat to ecosystem and human health. For this purpose, 562 stream sediment samples were collected at a sampling density of 1 site per 5 Km². All samples were air-dried, sieved to < 100 mesh fraction and analyzed for 37 elements after an aqua regia extraction by a combination of ICP-AES and ICP-MS. Statistical analyses were performed to show the single element distribution and the distribution of elemental association factor scores resulting from R-mode factor analyses. Maps showing elements distributions have been obtained using GeoDAS and ArcGIS software. Multifractal inverse distance weighted is the used interpolation method. In some areas, especially residential areas, a strong heavy metal contamination (Pb, Zn, Cu, Sb, Ag, Au, Hg) was identified likely due to both motor vehicles and industrial plants. The enrichment factor of these elements is 3 - 4 time higher than the background values. The four-factor model, accounting for 79.48 % of data variability, has been deemed appropriate for stream sediments of the Calore river. The element association of Factor 1 (Al, Fe, K, Na, As, Cd, La, Pb, Th, Tl, U) is controlled by the presence of sediments developed from pyroclastics and alkaline volcanic lithologies covering the south-west area of the basin. The factor scores association F2 (Co, Cr, Mn, Ni) is certainly related to the presence of manganese oxides, specifically, the highest factor score values are found in correspondence of the sedimentary lithologies in the northern part of the basin. The factor scores associations F3 (Cu, Pb, Sb, Zn) and F4 (Ag, Au, Hg) can be explained by elements introduced into the environment by human activities. The highest F3 and F4 factor scores are generally concentrated in correspondence with main road junctions, urban settlements and industrial areas.

Complex mineralogical study of metal sorption onto soil mineral phases

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Soil mineral phases play a significant role in controlling trace metals mobility in soils through sorption processes. We combined batch cadmium, copper, lead and zinc sorption experiments on six soil samples with contrasting characteristics in their pH, TOC, CEC and clay content/mineralogy with the mineralogical analyses of the solid phase by transmission electron microscopy, X-ray diffractometry and infrared spectroscopy. Metals' selection was carried out on the basis of their environmental and agricultural importance. Our aim was to study the metal sorption capacity of soil mineral phases and to evaluate the effect of presence of mineral phases affecting the sorption capacity of soil particles.

Copper and lead were characterized by higher and stronger sorption when compared to cadmium and zinc. Only the former two metals showed significant differences in their sorbed metal amounts on the studied samples and soil mineral particles due to the competitive situation.

Cadmium, copper and zinc sorbed mostly on soil mineral constituents, whereas lead was preferentially associated to organic matter. Additionally, the competitive situation resulted in increase of the role of iron oxide phases in lead sorption. Among soil mineral phases, highest metal amounts were immobilized on the swelling clay mineral particles, but iron oxides may also have similarly high sorption capacity for lead. The close association of iron oxides and clay minerals (probably in form of coatings) resulted in significant change in their sorption capacities for all the studied metals. Alkaline conditions due to the carbonate content resulted in both increased role of precipitation for lead and copper and in an elevated sorption capacity for the latter by discrete mineral particles that were not found for cadmium, lead and zinc.

Using such kind of complex mineralogical analysis of the soil, the sorption characteristics of metals onto soil mineral phases could be supported by more detailed data. When the methods used in this study are combined, they become an extremely powerful means of obtaining a more complete insight into soil-metal interaction.

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Response of the edible herb *Centaurea raphanina* to elevated heavy metal concentrations in soil of the protected forest area in Lavrion Greece

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The consumption of herbs and green vegetables growing wild is very common in the Mediterranean and particularly the Greek traditional diet. In this study the widely consumed plant *Centaurea raphanina*- common name "alibarbaron", a perennial, endemic plant of Greece, is examined in terms of heavy metal concentrations in aerial and sub- aerial parts of plants growing wild in the wider area of Lavrion, Greece. Lavrion has a long history of mining and metallurgy of mixed sulphide deposits that left behind a legacy of severe soil contamination.

The aerial parts, the roots and adjacent soil were collected during the flowering season from three distinct areas within the area of National Forest Reserve of Sounion, south of Lavrion city. The specific sampling locations were selected on the basis of a published soil geochemical map. Soil contamination varied with respect to heavy metals over a factor of 2 to 40 between the three sampling areas. Eight composite plant and soil samples were collected from each area. Plant roots were separated from aerial parts in the laboratory, thoroughly washed by deionized water and air dried in room temperature. All plant samples were ground in an agate mill and concentrations of heavy metals (Pb, Zn, Cu, Cd, Cr, Ni, Mn, Fe) were measured by atomic absorption spectroscopy (AAS) following microwave digestion by HNO₃/ H₂O₂, 6:1 v/v. Heavy metal concentrations in the soil samples were measured by AAS following *aqua regia* digestion of the <100 µm grain size fraction.

A significantly different uptake of heavy metals in the aerial parts of *C. raphanina* was observed between the 3 sampling areas depending on soil contamination level. Concentrations in the edible part of the plant reached 880 mg/kg Pb, 1320 mg/kg Zn, 9 mg/kg Cu and 27 mg/kg Cd. Observed correlations between concentrations in soil and leaves were positive for Pb, Zn and Cd but negative for Cu. Data also indicate a control mechanism of metal uptake by the studied plant species under stress conditions. Overall the study makes an interesting case for exploring the plant response to elevated concentrations of heavy metals in soil and provides useful information for assessing potential risk by *C. raphanina* consumption in the area.

Traffic related metals in road deposited sediment and topsoil as a source of environment pollution

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The purpose of this research was to extend the current knowledge on traffic related pollution. Human and environment exposures to particles emitted from motor vehicles include complex mixtures of metals from tires, parts wear: systems brakes, clutch plates, the erosion of the active layer of the catalyst and re-suspended road dust. The main goal is to characterize road-specific metals bounded in road deposited sediment, roadside topsoil and parking lot sediment. While a lot of work has been dedicated to the determination of metals, research on the transformation in environment is still insufficient. Samples were taken in Krakow that is a very important transportation hub in southern Poland, characterized by a very high traffic, congestion and is a significant tourist destination due to its cultural heritage. Detailed morphology and chemical composition of solid phase based on mineralogical and geochemical research is necessary to evaluate their harmfulness and mobility. Metals contents (14 elements) and their chemical forms (BCR procedure) in size classified road deposited sediment; roadside topsoil and parking lot sediment were determined by ICP-MS, ICP-OAS and AAS. Based on results, it was found that traffic seems to be the significant sources of metals. Samples taken on approx. 1m from curb were characterized by a high contamination compared to the soil collected approx. 50m from the curb on the meadow. Studies have shown that Zn content was an average 20.2 and for Cu -124 mg/kg in topsoil samples taken from Blonia meadow. In samples taken 1 m from curb, was detected an average approx. 46 mg/kg of Cu and in case of Zn - 166 mg/kg. In case of road deposited sediment results showed 2 fold higher concentrations than in soil samples taken at a distance of 1 m from the curb and about 4 fold higher compare to samples taken from the meadow. It was also confirmed that metals are mainly found in the fraction below 63 μm , which is very important from the point of view of traffic related metals. Obtained results make considerable impact on research in environmental monitoring as well as an attempt to analyses of ecological risk assessment.

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Application of biometeorological forecasts for urban areas in LIFE-APIS/PL project – first approach

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In September 2013 University of Wrocław in cooperation with Voivodeship Inspectorate of Environmental Protection in Wrocław has started a project “Air Pollution and biometeorological forecast and Information System” (LIFE-APIS/PL) for Lower Silesia (Poland). One of the project objectives is to develop a warning system for adverse biometeorological conditions. This problem is particularly important in the cities, where urban heat island causes increased exposure to heat stress among residents. WRF model has been used as a tool for forecasting biometeorological conditions. It provides spatial information about meteorological parameters, permitting calculation of biometeorological indicators such as UTCI and HSI. Spatial resolution of the model for Lower Silesia is set to 4 km. Reference data for Wrocław (main city of the region), are results of measurements from Wrocław University Meteorological Observatory and results of periodic measurements conducted within the city. The model is tested based on current forecasts and reanalyses for periods representing characteristic weather situations (heat waves, cold waves), for which verification data are available. Reanalyses used in presented study have been developed within the project BLOWRF. Obtained results indicate that currently used spatial resolution of the model gives acceptable results for Wrocław area. It allows to capture differentiation between city centre and peripheral areas of the city. This may be illustrated by data obtained from reanalyses for heat wave episode from 07 – 17.07.2010. Spatial distribution of modelled temperature data for this situation showed a clear thermal privilege of the city centre. It was noticeable especially at night, when the differences between the temperature of the rasters representing the centre and the surroundings were to 5°C. Results of in situ measurements carried out in Wrocław University meteorological observatory and in the Wrocław Old Town showed analogous differentiation. This was reflected in the diversity of biometeorological indices such as UTCI and HSI. While in the peripheral areas thermoneutral conditions were detected at night, in the centre of Wrocław unfavourable conditions persisted, causing constant heat stress.

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Air pollution and biometeorological forecast and information system – aims and objectives

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Urban air pollution is associated with significant adverse health effects due to high concentration of air pollution and bioclimatological conditions. Air pollution significantly affects quality of life. According to WHO data, the average life length in Poland is 10.7 months shorter due to air pollution. Prediction of health effects and life quality information and abatement systems require accurate forecasting of air pollution episodes and population exposure. Such system should include modelling of meteorological and biometeorological factors, emission rates and air pollution concentration. This poster presents air pollution and biometeorological forecast and information system (LIFE-APIS/PL) developed by University of Wrocław and Lower Silesian Voivodeship Inspectorate for Environmental Protection for the Lower Silesia Region. The project is co-financed by the European Commission. It started in October 2013 and will be completed at the end of September 2017. Exceedances of PM_x and O₃ target values in terms of human health protection in Lower Silesia (SW Poland) have been registered for many years. To improve that situation it is necessary to build up knowledge of the complex interactions between pollutants, weather conditions and human health and develop the integrated air quality management support systems. The LIFE-APIS/PL project will integrate set of advanced tools for emissions inventory and analyses, local and regional-scale air pollution modelling and geospatial data analysis. Information obtained as a result of modelling and forecasting can be used to support environmental management in order to improve the quality of the environment, reduce risks to human health and improve living conditions. The project will create an information and warning system for the public that includes air pollution, meteorological and biometeorological conditions. This objective will be achieved through: 1. Design and implementation of the air quality and biometeorological modelling system (WRF, WRF-Chem, ANN). 2. Design and implementation of communication system about risks (spatial and non-spatial data). 3. Design and implementation of support system for the air quality management.

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Mobile measurement station as a tool for verifying air quality modeling system in LIFE-APIS/PL Project

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LIFE-APIS/PL is a LIFE+ project realized by University of Wrocław and Voivodeship Inspectorat for Environmental Protection in Wrocław. The main aim of the project is to create an integrated system designated to provide information about threats connected with air pollution and adverse biometeorological conditions for the area of Lower Silesia. The system will be working on modern numerical models WRF and WRF-Chem, providing high resolution information about spatial distribution of meteorological conditions and air quality. The project will create an integrated and innovative supporting system for environmental management. It will combine various methods to provide achievement of best possible results in the field of modeling and forecasting of air quality and biometeorological conditions. Its activity will be supplemented with data from the Lower Silesia air quality monitoring system as well as results of in situ measurements obtained through use of an advanced mobile meteorological station, constructed on basis of a small van. The mobile meteorological station will enable complex patrol measurements of meteorological conditions as well as particulate matter concentration. The station is a prototype solution containing a meteorological station with a 10 m measurement mast (temperature and wind profile), optical dust measuring device as well as a bistatic sodar (sound detection and ranging) for 250 m high vertical profile of the atmosphere structure. The conception was based on authors' previous experience with meteorological measurements in urban areas that included especially the issues of Urban Heat Island and the structure and dynamics of atmospheric boundary layer in urban areas. The objective of the measurements is to obtain representative information on time and spatial variability of meteorological and biometeorological conditions in various landuse. It will also lead to refine the information on the spatial distribution of the analyzed parameters and provide data necessary for verification and calibration of numerical models (WRF and WRF-Chem). Furthermore the complex structure of land use and building geometry in cities cause great difficulties in modeling meteorological conditions and air quality in urban areas. Thus detailed mobile measurements make the best way to obtain precise image of spatial distribution of meteorological and air quality conditions.

Distributional characteristics of ambient fine particles (PM1.0 and PM2.5) in a roadside area of Korea

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Ambient fine particles show that motor vehicular emissions, especially diesel exhausts, usually indicate the most significant source of ultrafine (aerodynamic diameter equivalent to or < 0.1 μm) and fine particles (PM2.5) in urban areas. In this study, we undertook the measurements of about 25 elements including hazardous elements using instrumental neutron activation analysis (INAA) of PM1.0 and PM2.5 at a roadside area in Korea. For the collection of PM1.0 and PM2.5, annular denuder air sampler was equipped with a polycarbonate membrane filter. Air flow rate for the sampler was adjusted to 16.7 L/min at the beginning of sampling, and the sampler was operated continuously on a 24-hr basis. Field campaigns were carried out during 8 seasons in 2012-2014. Standard reference material (SRM) 2783 (air particulate on filter media) of the National Institute of Standards and Technology (NIST), USA was used for QC purposes. The elemental concentrations were compared statistically with the certified (or recommended) values. The deviation between the two values generally fell below 5% for many species (Ca, Co, K, Mg, Mn, Na, Sb, Sm, Ti, V, and Zn). If relative standard deviations (RSD, %) of trace elements were compared, they tended to fall below 5%. As such, the analytical results derived for most elements were fairly reliable. Based on our measurement data, we tried to figure out distribution characteristics of PM1.0 and PM2.5 and the associated elements. The PM1.0 concentrations in the roadside area varied in the range of 5.0 to 63.6 $\mu\text{g}/\text{m}^3$ with average of $19.6 \pm 11.8 \mu\text{g}/\text{m}^3$ (\pm standard deviation), while the PM2.5 concentrations varied in the range of 8.2 to 78.6 $\mu\text{g}/\text{m}^3$ with average of $27.3 \pm 14.5 \mu\text{g}/\text{m}^3$. The average PM1.0 concentration constitutes approximately 72% of the average PM2.5 concentration. It was also found that the mean concentrations (ng/m^3) of hazardous elements such as As, Cr, Se, V, and Zn were much more enriched in the PM1.0 rather than in the PM2.5. In addition, more enrichment in the PM1.0 for Br and Se may indicate that PM1.0 can be a useful marker for motor vehicular emissions.

Geochemical data in urban areas: considering depth and analytical techniques

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Many attempts have been made at quantifying thresholds of potentially toxic elements (PTEs) in soil. However, the concentration of the element at a particular location is not sufficient to determine the potential risk it poses; the bioavailability of the PTE must also be considered. The Tellus soil geochemical data set consists of almost 8000 samples taken across Northern Ireland at two depths and analysed by a number of techniques. Shallow samples (0-20cm) were analysed by both inductively coupled plasma (ICP) following an aqua regia acid digestion and x-ray fluorescence (XRF), while the deep samples (35-50cm) were analysed by ICP following both an aqua regia and a 'near total' digestion. By comparing concentrations of PTEs at different depths, an understanding of their sources or availability can be gained i.e. geogenic or anthropogenic. ICP measurements depend on the acid extraction, meaning they will be relatively greater where the element exists in an extractable form in the soil, while XRF is said to measure total concentrations. Availability gives an indication of potential risks to receptors, as PTEs which are more available in the environment are more readily taken up by plants and animals.

This study compares shallow XRF concentrations with shallow and deep ICP (following aqua regia digestion) concentrations by constructing ternary plots of these three variables for a range of elements. Interesting behavioural mechanisms of PTEs in urban areas have been identified within the city of Belfast (Northern Ireland). Some deep samples show elevated concentrations of copper and nickel, as we would expect due to the proximity of the Antrim basalts to Belfast. Surprisingly, elevated concentrations of lead, tin and to a lesser extent, antimony at depth are also present at some locations. The two analytical techniques show similar concentrations for most elements in the urban samples; when compared to the spread of the remaining rural samples it is clear that the urban samples cluster together closely. Preliminary results suggest less available forms of most PTEs are found in urban areas, when compared to the remaining rural data, suggesting that the greatest risk from PTEs may not always be in urban areas.

The mineral and chemical composition of atmospheric dusts in Krakow, Poland

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In Krakow – almost a millionth urban agglomeration, the quality of air is notoriously deteriorating. The measurements of the environmental monitoring system indicate that over the last 5 years the concentration of NO₂, benzene, PM₁₀, PM_{2.5} and benzo(a)pyrene in the air many times exceeded the permissible level and posed a major threat to the health of the residents of Krakow. Therefore, in 2014, the samples of urban atmospheric dusts were collected in 3 different locations of Krakow, ie.: in the city centre; in the industrial area - Nowa Huta district and in the last location in a modern residential area - Pychowice district.

Using the instrumental methods of analysis such as XRF, FTIR and SEM-EDS, the mineralogical composition of the dust samples was specified, and by the extraction by means of a mixture of concentrated acids (HCl+HNO₃+HClO₄) the chemical composition of the analyzed material was examined.

Conducted by XRD method analysis of urban atmospheric dust samples allowed to note the existence of the following mineral phases: quartz, hydrated iron phosphate and primary soil minerals (probably phyllosilicates). What is more, frequent appearance of amorphous phases (this is most likely organic substance) was spotted as well. The absorption spectra were made by using FTIR method and characterized by the presence of bands (the number of wave approx. 2852 and 2929 cm⁻¹) derived from hydrocarbon materials - bond CH₂ and CH₃.

The presence of such mineral phases as calcite, anhydrite, gypsum and clay minerals was also observed. SEM-EDS analysis confirmed the presence of a semi-crystalline mixture of Fe, Ca, Al and Mg oxides. The micro-concretions of oxides/hydroxides of Fe (hematite, goethite) were noted as well. The chemical analysis methods confirmed presence of Fe and Ca up to 4% of weight, Zn 0.2% and Pb up to 260 mg kg⁻¹. Unacceptably high concentrations of following elements were also found (in mg kg⁻¹): As (5-120), Ba (43-1400), Cu (24-706) and Tl (1-52).

Detected, due to conducted research, chemical and mineralogical composition of the urban industrial dust components confirmed the significant contribution of anthropogenic origin particulars (mainly industrial), which significantly affects the conditions of life of the entire biosphere in Krakow, and they especially strongly affect the human respiratory system.

Bioaccessibility of Pt, Pd and Rh from gasoline and diesel automotive catalysts

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Platinum group elements (PGEs) are rare in nature. However, their use in automotive catalysts cause anthropogenic emissions and spread in the environment. Automotive catalysts are chemically and physically stressed by fast changing oxidative/reductive conditions, high temperature and mechanical abrasion. As a result, platinum group elements (PGEs) are emitted with exhaust gases in particulate form to the environment. In addition, they can be mobile and accumulate in living organisms including human beings. In our research, we focused on bio-accessibility of PGEs from gasoline and diesel catalysts to human digestive track. We used dust from two crushed gasoline, two crushed diesel catalysts (new and aged) and certified reference material - recycled catalyst NIST 2556. While catalysts for gasoline engines contain a mixture of Pt-Pd-Rh, catalysts for diesel engines are composed only of Pt. For evaluation of bio-accessible PGEs from crushed catalysts we used standard physiologically based extraction test (PBET) that simulates, sequentially, chemical conditions in the human stomach and intestine. The experiment was carried out under predefined pH 1, 2.5 and 4 covering fasting and fed conditions at a stomach. After one hour, the stomach phase was removed and stored. The bicarbonate solution was added to attain neutral conditions of intestinal phase. Final solutions were analysed by ICP-MS. The percentage of bio-accessible PGEs from catalysts was in the following order: Pd > Rh > Pt. The Pt leaching slightly increased from stomach to intestinal phases. However the leaching of Pd and Rh slightly decreased from stomach to intestine. The bio-accessibility in the stomach is similar from pH 2.5 to 4, but increases greatly at pH 1. The solubility of PGEs in the human digestive tract may form PGEs-chloride complexes, which have toxic and allergenic effect.

Evaluation of iodine toxicity and bioaccumulation by barley (*Hordeum vulgare*) using methods of analytical geochemistry

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Iodine is an essential trace element for humans and indispensable for the proper production of hormones by the thyroid gland. There is a strong association between the occurrence of iodine deficiency disorders (IDD) and iodine levels in the environment, especially in soil and drinking water. The most important pathway which leads to natural biofortification of iodine in food chain is the soil-plant/forage-animal/human pathway. Despite iodine can be toxic for plants the first “soil to plant” transfer step is the most important for this pathway.

The aim of this work was to investigate the iodine most common forms iodide (I^-) and iodate (IO_3^-) toxicity and bioaccumulation by barley (*Hordeum vulgare*) from spiked and naturally contaminated agricultural soils and agar cultivation media using laboratory pot experiments. The amount of bioaccumulated iodine and the iodine abundance in the soil was measured by inductively coupled plasma mass spectrometry (ICP-MS) after performing single extraction with tetramethylammonium hydroxide (TMAH) and sequential extraction methods including extraction with water, $MgCl_2/NH_4OAc$, $NH_2OH.HCl$ and TMAH (at room temperature and 70°C) after 7- and 14-day cultivation period. Inhibitional and toxic effects were evaluated on the basis of quantitative (stem length, weight) and qualitative plant characteristics. Changes in chlorophyll synthesis were also measured spectrophotometrically.

Iodine in the agar medium had negative effect on the growth, weight, chlorophyll synthesis and root development of *Hordeum vulgare*. 50% inhibition occurred at concentration 2-2.5 $g.l^{-1}$ iodine in agar medium, however iodine seemed to have stimulative effect on the growth at very low concentrations. The major forms extracted from the media after cultivation were (1) water soluble, (2) exchangeable, (3) oxides, (4) organic matter-bound and (5) residual. Higher bioaccumulation rate occurred in samples grown in agar-nutrient solution cultivation medium compared to soil system, while iodide seemed to be more bioavailable compared to iodate.

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Prioritisation of Contaminated Sites

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Prioritisation of sites contaminated by previous industrial activities is essential to make the most efficient use of resources and to ensure that those sites posing the most serious threat to human health and the environment are dealt with first. Prioritisation of contaminated sites has been a requirement of the UK Contaminated Land Regime and we present an outline methodology based on lessons learnt from this.

The UK contaminated land regime uses the concept of “reasonable possibility of significant contaminant linkage”¹ as the legal test for intervention. It then places a duty on the regulator to investigate the risks, develop a management plan and apportion costs for any mitigation to the appropriate persons. The poster will explore how the significance of risks are assessed in the UK and how this could be re-calibrated for a broader international use to take account of much more serious hazards from large scale contaminating processes. Specific consideration will also be given to the recording and mapping of manufacturing locations and the ascribing of standard land use classifications. Selected standard Land Uses will then be used as a means of conceptually prioritising the risks posed by the chemicals present at such sites based on the seriousness of the health risk (potency and nature of health effect) and the most likely exposure pathway (using a combination of chemical properties, mass emission, and process controls as the key parameters). Review of chemical hazards and exposure potential enables the identification of substances of higher relative concern, thereby allowing the effective targeting of resources and effort in subsequent risk assessment and management.

¹ A contaminant linkage is used as a broad term to define the relationship between a contaminant (or group of contaminants) and exposure pathway leading to an effect on human health or the environment e.g. shallow surface soils contaminated by polyaromatic hydrocarbons (PAHs) could be considered a risk to human health by direct ingestion (and possibly also inhalation).

Topic 2-3

Deficit and/or excess of chemical elements in geological environment and their health effects
on humans, human biomonitoring

Linking of geochemical and medical data – datasets, procedures, methods

Oral Presentation Abstracts – Keynote lectures

Health and regulatory aspects of calcium and magnesium in drinking water

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Calcium (Ca) and magnesium (Mg) as major representatives of natural water constituents and its relationship to human health have been studied for more than 100 years, more extensively since 1960s, and there were thousands of studies published up to now. Surprisingly, the extensive data on its health significance available and the knowledge acquired has had currently a low effect on the regulatory field, although the World Health Organization (WHO) routinely acknowledged its importance in 1970s and 1980s, the first international regulation was set up already in 1980 in the Council Directive 80/778/EEC (≥ 60 mg/l as calcium or equivalent cations required as minimum for softened and desalinated drinking water), and many new supporting studies have been published since that time. Nevertheless, new Drinking Water Directive (98/83/EC) has been in force since 2003 and it does not present any requirement for the Ca and Mg levels or water hardness anymore. Also the WHO changed its former supporting position and its current approach is rather fuzzy and not transparent, probably due to strong press from industrial lobby groups. This situation cannot be considered as satisfactory from public health point of view as recent systematic review and meta-analysis of the most valid epidemiological studies investigating the association between cardiovascular disease and drinking water hardness brought convincing epidemiological evidence about protective role of magnesium in drinking water as a pooled odds ratio showed a statistically significant inverse association between magnesium and cardiovascular mortality (odds ratio 0.75). It means that the highest exposure category (people consuming drinking water with magnesium 8.3 – 19.4 mg/l) was significantly associated with a decreased likelihood of cardiovascular mortality (by 25%), compared with the baseline, i.e. people using water with Mg content of 2.5 – 8.2 mg/l. Protective role of water calcium towards cardiovascular disease was also confirmed by some studies, but the evidence is not such strong as for magnesium. Beside cardiovascular disease, other beneficial health outcomes relating to certain level of calcium or magnesium in drinking water are discussed as well as recommendations for actions to raise public awareness on water hardness and human health.

Reference: Catling L.A. et al. A systematic review of analytical observational studies investigating the association between cardiovascular disease and drinking water hardness. *Journal of Water and Health*, 2008, 6:433–442.

Micronutrients and health: simple or simplistic?

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Nutritionally important micronutrients include elements (e.g. iron, iodine, zinc, iron, cobalt, chromium, copper, manganese, selenium, molybdenum) and organics (e.g. vitamins A-E, folate, carotenoids). Although deficiencies of these essential components of the diet can have devastating consequences (e.g. anaemia, reduced cognition and brain development, blindness, growth retardation, infections, increased mortality) on a global scale in both children and adults, there is no easy definition of a micronutrient other than “essential chemicals needed by life in small quantities”. The upper limit of “small quantity” is open to discussion.

Fortification of foods is recognised internationally as low-cost, with effective global programmes to supplement the diet with iron, iodine and vitamin A. However, it may be too simplistic to say that iodinated salt, for example, is a simple answer to iodine deficiency, without a fuller understanding of wider cultural and behavioural issues that impact the aetiology, programme delivery and assessment of success.

There are important differences between the causes of the deficiencies: e.g. iodine (due to source of food) and iron (due to choice of food). Equally, there are noteworthy differences in approach to the disorders between different communities (expert understanding vs. lay opinion of aetiology, chemists approach to the solution vs. public health professionals, totalitarian cultural answers vs. democratic), which, if not clearly understood and examined, can lead to unforeseen consequences ranging from the misunderstanding the aetiology of the deficiencies through community resistance to evaluation of the wrong components.

As in many complex situations, no one approach, nor one perception, encompasses the whole picture. Geochemists have a role to play beyond the understanding and application of chemistry in the environment; health professionals' role is broader than the application of science to disease and patients. SEGH provides a forum for the interaction of these professionals, and others, to respond to micronutrient deficiencies, by enabling the building of effective collaborations that have practical and academic outcomes that direct policy and improve community and global health.

Examining the links between soil geochemistry and health related deprivation indices in London

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There is very clear evidence that humans are exposed to Potentially Harmful Elements (PHE) in soil (2011a) and that densely populated urban areas contain elevated concentrations of PHEs (2011b). Whilst the amount of PHE that is absorbed into the body can either be measured directly by biomarkers, or indirectly through in-vitro bioaccessibility testing, the actual effects on human health are less easily measured. This study aims to examine possible relationships between the geochemistry of the soils of London with health related deprivation indices.

London Earth is a part of the Geochemical Baseline Survey of the Environment (G-BASE) Project, the British Geological Survey's National Capability in geochemical mapping. Over 6000 soil samples were collected at a density of 4 sites per km². The <2 mm fraction from the topsoil samples (5–20 cm) were milled, pelletised and analysed by X-ray fluorescence spectrometry (XRFS) for 50 elements.

The Index of Multiple Deprivation 2010 (McLennan et al., 2011) is a measure of multiple deprivations. People may be deprived in one or more of the dimensions. The overall Index of Multiple Deprivation is a weighted area level aggregation of these dimensions of deprivation which are: Income, Employment, Health, Education, Barriers to Housing and Services, Crime and Living Environment.

The relationship between Health deprivation and the geochemistry of the soils has been investigated using machine learning methods including Random Forests.

Preliminary results show that Sn is a significant predictor of health deprivation exhibiting a sigmoidal dose response style of relationship. The significance of Sn as predictor of health outcomes will be discussed and how the relationship between Sn and other PHEs could be used to set soil guidance values for human health.

References

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2011b. *Mapping the Chemical Environment of Urban Areas*. (Wiley.) ISBN 978-0-470-74724-7

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Topic 2-3

Deficit and/or excess of chemical elements in geological environment and their health effects
on humans, human biomonitoring

Linking of geochemical and medical data – datasets, procedures, methods

Oral Presentation Abstracts – Plenary lectures

Major and trace elements in some bottled water brands from Khouzestan Province market, SW Iran, and accordance with national and international standards

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There is no doubt that the most essential element for life is, after air, water and life is not possible without either of these two elements. So, access to clean and healthy water has always been one of the most important challenges for human communities from a long time ago. The consumption of bottled water has recently increased in Iran, which is dominantly due to the change of consumption priority from tap water to bottled water. In this study, a total of 10 bottled waters packed in 250 ml plastic bottles from natural springs and wells were randomly purchased in Khouzestan Province market. The selected bottled water brands were analyzed for 40 parameters using ICP-OES, IC, HGAAS, spectrophotometric, titration and conductometric methods. The studied bottled waters are classified as Ca-Mg-HCO₃ type according to Piper diagram, and as fresh waters with very low to low mineral concentration based on Styfzand (1986, 1993) classification. Major and trace element concentrations differ among the analyzed bottled waters, reflecting the lithologic influence of the aquifers from which they are extracted. The comparison between obtained results and Iranian national standard for natural mineral water and US-EPA standard show that among analyzed parameters only the amount of nitrate in two and three samples exceeds its allowed levels according to Iranian and US-EPA standards, respectively. Since Iranian national standard defines a permissive level for total amount of nitrate and nitrite, this total amount in three samples exceeds its allowed level. All analyzed samples, however, are in accordance with WHO regulations regarding all parameters for which action levels are defined. The fact that nitrate concentrations in some bottled water brands are above the standard levels has no a geologic reason, but it is due to human activities, especially the use of nitrate-bearing chemical fertilizers. The high level of nitrate is a threat for human health, because it causes methaemoglobinaemia disease in babies. On the other hand, nitrate reacts with amines to produce nitrosamine which is a carcinogenic agent.

Exposure, remediation and health impact of groundwater arsenic

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Arsenic (As) poses a severe threat to human health through exposure pathways mainly including water and diet. To systematically understand the health risks induced by As ingestion, we explored water and diet contributions to As exposure, and compared As in biomarkers and the arsenicosis in a geogenic As area in China. In this study, high percentages of water (77% of n=131 total samples), vegetables (92%, n=120), cereals (32%, n=25), urine (70%, n=99), nails (76%, n=176), and hair (62%, n=61) contained As higher than the acceptable levels. Dietary As contributed 92% of the average daily dose (ADD) when the water As concentration was less than 10 µg/L, for which 5 out of 30 examined participants were diagnosed with arsenicosis symptoms. The distinct positive correlation between ADD and As concentrations in urine, nails, and hair suggests different applicability for these biomarkers. Synchrotron-based µ-XRF analysis demonstrated that As is mainly associated with sulfur in nails and hair. Nails, rather than hair and urine, could be used as a proper biomarker for arsenicosis.

As a cost-effective and user-friendly technique, adsorptive filtration is widely used in fixed bed columns without chemical addition. To provide a practical solution to geogenic As groundwater, we developed regenerable TiO₂ adsorbent and explored the molecular-level As removal mechanisms and the health impact of As removal. Two household filters loaded with 110 g TiO₂ in the on-off operational mode can provide 6-L/day As-safe drinking water up to 288 and 600 days from the groundwater containing 700 µg/L As and 217 µg/L As, respectively. Integration of batch experiments and column tests was successfully achieved by using PHREEQC incorporating a CD-MUSIC model and one-dimensional reactive transport block. The treated groundwater was supplied to the local residents and the total As concentrations in their urine samples decreased from the range 972-1980 µg/L to 31.7-73.3 µg/L after drinking the treated groundwater. Our study provides a complete example for geogenic As exposure, removal mechanism, and the health impact.

Toenail and hair biomarkers of past exposure to inorganic arsenic from Private Water Supplies in Cornwall, UK

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Chronic exposure to inorganic arsenic (As) is an established cause of numerous detrimental health impacts including cancers of the lung, bladder and skin. Cornwall, UK received previous attention due to mineralised geological domains and a history of mining resulting in the dispersion of refined, high-As mine tailings. Soil and dusts have formed the focus of previous studies but there has been recent concern over groundwater pumped from private water supplies (PWS) for drinking water as a potential exposure route. A survey of 512 Cornish households of PWS users conducted by the British Geological Survey and Public Health England found that 5 % of drinking water samples exceeded the UK As Prescribed Concentration or Value (PCV) (10 µg/L). The current study revisited homes selected to maximise contrast in As exposure and used non-invasive toenail and hair (and urine – presented at SEGH 2014) biomonitoring which reflects uptake from up to a few months before sampling to (1) quantify past exposure to inorganic As, (2) assess the importance of PWS as the exposure route.

Following ethical approval (University of Manchester: Ref 13068, NRES: Ref 13/EE/0234) toenail ($n=204$) and hair ($n=184$) samples were obtained from volunteers, all of whom reported using their PWS for drinking. Samples were cleaned to remove exogenous As before a mixed acid digestion in a microwave assisted reaction system (MARS). Digests were analysed for total As by inductively coupled plasma mass spectrometry (ICP-MS) - also used to quantify total As in PWS drinking water samples.

Results will be presented on the distribution of drinking water, toenail and hair total As concentrations and compared to previous findings (e.g. Button et al. 2009). Correlation analysis between drinking water and toenail/hair biomarker As concentrations will provide an indication of the value of these biomarkers as indicators of past exposure to As from PWS.

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Soil Geochemistry and impacts on human health

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The soil plays a basic role for humans as fulfil many functions not only just a medium to grow plants. Soil functions as a filtering, buffering, storage, and transformation system which protects water, plants, air and humans. Soil is effective in these functions only as long as its capacity and its biological activity factors are preserved. Most of the plants nutrients come from the soil. Therefore, soils that provide a healthy, nutrient rich growth medium for plants will result in quality plant products required for human and animal life. Critical to human health is to achieve adequate, safe, and nutritious food that is economically assessable and socially acceptable.

There is a long history documenting that human health is affected by the health of the soil. Despite this connection there has not been a great amount of attention focused on this area when compared to many other fields of scientific and medical study. In spite of fact that many disciplines are involved in soils and human health research (e.g., soil science, the medical professions, geography, anthropology, biology, agronomy, sociology, etc.), not all of these disciplines work together. Looking to the future, complex interdisciplinary research is needed related to the soils and human health issue. Soil can influence the human health in many ways. Soil is a key component in transition of risk elements from soil into human body. The ability to produce healthy crops in sufficient amounts depends on soil properties and conditions. Soil degradation, decreases crop production and threatens food security. The soil geochemistry which studies these topics can contribute for improving our understanding of links between soil properties and human health. This contribution is to bring several examples of the case study in Slovakia to document the behaviour of chemical elements depending on physical and chemical properties of soil (pH, redox, antagonism). In a scientific world where the overall trend is narrow specialization, soil geochemical studies present a significant challenge in further prospect. To the soil geochemistry, related to human health, should be given more importance than it currently receives.

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Highly Efficient Removal of Tl(I) ions by Fe@Fe₂O₃ Core-Shell Nanowires: Process and mechanism studies

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Thallium (Tl) is a highly toxic heavy metal, which is more toxic to mammals than cadmium, lead, copper or zinc. It exists in two oxidation states, Tl(I) and Tl(III), with Tl(I) as the predominant one in aquatic systems. Recent studies on Tl pollution indicated that Tl was an emerging pollutant in the environment of China due to the increasing awareness of its high risk to human health. The well-known mechanism of Tl toxicity is related to the interference with the vital potassium-dependent processes, substitution of potassium in the (Na⁺/K⁺)-ATPase. The maximum contaminant levels of Tl set by the USEPA are 2 µg/L in drinking water and 140 µg/L in wastewater, respectively. Therefore, it is necessary to develop effective method for removing Tl from environment.

A novel nanoscale zero-valent iron, Fe@Fe₂O₃ core-shell nanowires (FCNs) was synthesized and employed for effective removal of Tl(I). A batch technique was adopted to investigate the removal efficiency of FCNs toward Tl(I) under various environmental conditions. The as-prepared and Tl(I)-loaded FCNs were examined by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) analysis, in order to clarify the possible removal mechanisms of Tl(I).

Sorption of Tl(I) on FCNs was strongly dependent on ionic strength but not on pH. The Tl(I) sorption reaches equilibrium within 180 min, and follows the pseudo-second-order rate equation, and fits the Langmuir model. The XPS characterization results suggested that the possible Tl(I) removal mechanism involved the dominant Tl(I) sorption, followed by the partial transformation of Tl(I) into Tl₂O, precipitating on the surface of FCNs without any redox reaction taking place. These results suggest that FCNs may be a promising candidate for the removal of Tl(I) from aqueous solution.

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Geologic/edaphic constraints to bioavailable selenium (Se) a contributing factor to epidemic 2014 Ebola Virus Disease (EVD)

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The 2014 Ebola virus disease (EVD) epidemic in West Africa has a hemorrhagic fever fatality rate of ~70% and has claimed >9000 human lives. Genomic assays (Gire et al. 2014) of the current mutating RNA Ebola virus (EBOV) indicate this strain branched in 2004 from its 1976 origin in the Democratic Republic of Congo (formerly Zaire), though the virulent EBOV protein 35 (VP35) appears substantially unchanged subsequent to its 1976 origin. Host deficiency in micronutrient Se, a physiologic antioxidant, could be a contributing factor in the 2014 EVD epidemic. Method: Hypothesis is based on literature reported data. Previous research (Beck et al. >1995; Broome et al. 2004) determined that individuals simultaneously deficient in Se and infected with benign strains of Coxsackievirus B3 (Keshan Disease, KD), influenza A virus (IAV) H3N2, or an oral live attenuated poliovirus used as vaccine developed impaired immunity against these RNA viruses; also, each virus type rapidly mutated to non-stochastic, replicatable, long-lived, virulent forms in the Se-deficient host (blood plasma <1.2 $\mu\text{Mol Se}$) – viral mutation rates under host Se-deficient oxidative conditions were orders of magnitude faster than RNA virus mutations in the ambient environment. Immunocompetence of the Se-deficient host improved with dietary-Se supplementation, and viral mutations slowed. Overlay of Oldfield's World Atlas of Se (2002) with origins of contemporary novel virulent RNA proteins indicated IAV H5N1 and SARS coronavirus evolved in Se-poor regions in China; HIV-1 and EBOV, in Cameroon and DRC, respectively (Harthill 2011). Data from KD regions indicate low pH/ high OM sequester soil Se (Fordyce et al. 2000; Johnson et al. 2000; Wang and Gao 2001); poor diets provide $\approx 10 \mu\text{g Se/day}$ (US DRI for adults is $55 \mu\text{g Se/day}$) yielding blood levels $\sim 0.28 \mu\text{Mol Se}$, <20% the US average blood value (Xia et al. 2005; Levander 1986). Soils data for central/west Africa suggest bioavailable Se could be bound by volcanic Mn/Al hydroxides and clays (Malisa 2001) or depleted; mean blood value is $\approx 0.60 \mu\text{Mol Se}$. Conclusion: While virulence (VP35) of the 2014 EVD epidemic evolved in 1976, the effects of prolonged human Se-deficient hyperoxidative conditions on EVD are not known.

Topic 2-3

Deficit and/or excess of chemical elements in geological environment and their health effects
on humans, human biomonitoring

Linking of geochemical and medical data – datasets, procedures, methods

Poster Presentation Abstracts

The elimination of negative impact of geological compound of the environment on health status of residents in the Krupina district, the Slovak Republic

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Beneficiary organizations: State Geological Institute of D. Štúr, Krupina city

Geological setting of the Slovak Republic is very diverse. It is reflected in varied geochemical background, emitting chemical elements of different composition into other compounds of the environment, into drinking water and the food chain. They have either a positive or negative impact on human health. The district of Krupina is located among Neogene volcanics. In previous researches, such geological environment was determined as the most unfavourable. The environment of volcanic bodies does not emit into the food chain and drinking water sufficient amount of chemical elements necessary for human health. It relates mainly to deficient contents of Ca, Mg, and the water hardness. This is probably reflected in finding that the health state of population in the district of Krupina is one of the most unfavourable throughout the whole Slovakia. It is characterized mainly by increased incidence of cardiovascular and oncological diseases. The main objective of the project is to improve the health state of the population of the Krupina district. A simple technological measure will increase the content of Ca, Mg and further elements in selected local sources of drinking water. This approach will provide sufficient quantity of necessary chemical elements for human health. The target objective will be reached by solving of following partial goals:

- compilation of data set of environmental indicators (chemical elements/components) for two main compartments of geological environment (groundwater/drinking water and soils) and data set of health indicators (indicators of demographic growth and health state of population), and their linking through statistical analysis,
- analysis of chemical contents of critical elements (e.g. Ca, Mg, Se, Zn) in biological materials (urine, hair, nail) to confirm close relationship between geological environment and health state of residents,
- the evaluation of life style and health-care accessibility on health state of residents,
- environmental-health analysis of Krupina district and definition of limit values for drinking (ground) water and soils, maximum acceptable and minimum content levels necessary for human organism based on health effects of evaluated critical elements,
- elaboration of set of measurements to minimize negative influence of geological environment in Krupina district and their implementation into practice (mainly educative and training activities, legislative measurements and particular technological actions).

Implementation of these objectives and measures for improvement of water and soil quality in the Krupina district will lead to the improvement of the health state of the resident population.

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The potential impact of geological environment on health status of residents of the Slovak Republic

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In order to assess the potential impact of the geological environment on the health of the population of the Slovak Republic, the geological environment was divided into eight major units: Paleozoic, Crystalline, Carbonatic Mesozoic and basal Paleogen, Carbonatic-silicate Mesozoic and Paleogene, Paleogene Flysch, Neovolcanics, Neogene and Quaternary sediments. Based on these geological units, the databases of environmental indicators (chemical elements/parameters in groundwater and soils) and health indicators (concerning health status and demographic development of the population) were compiled. The geological environment of the Neogene volcanics (andesites and basalts) has been clearly documented as having the least favourable impact on the health of Slovak population, while Paleogene Flysch geological environment (sandstones, shales, claystones) has the most favorable impact. The most significant differences between these two geological environments were observed especially for the following health indicators: SMRI6364 (cerebral infarction and strokes) more than 70%, SMRK (digestive system) 55%, REI (circulatory system) and REE (endocrine and metabolic system) almost 40%, REC (malignant neoplasms) more than 30%. These results can likely be associated with deficit contents of Ca and Mg in groundwater from the Neogene volcanics that are only about half the level of Ca and Mg in groundwater of the Paleogene sediments.

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Historical Mining Areas and Their Influence on Human Health

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Impact of potentially toxic elements (PTE) on the health status of population of the Slovak Republic has been studied in two historical mining areas with ore extraction from Middle Ages (the Middle Slovak Neovolcanics, the Slovak Ore Mts.) and one historical mining area with more than hundred years brown coal mining (Upper Nitra region). The contents of PTE were analysed in groundwater/ drinking water and soils. The health status of resident population was evaluated based on 43 health indicators classified according to the international classification of diseases (ICD, 10th revision), including mainly those indicators characterizing mortality on cardiovascular and oncological diseases. In these areas the health status of population living in municipalities with increased PTE contents (As, Pb, Zn, Cu, Cd, Hg and Sb) was compared with that in adjacent municipalities showing low PTE contents. A total of 138 contaminated and 155 non-contaminated municipalities of similar socioeconomic, natural and geochemical-geological character were compared. PTE contents in soils of polluted municipalities reported considerably increased levels – between 2 to 10 times higher in contrast to non-contaminated municipalities. On the other hand, PTE contents in groundwater were almost identical both in contaminated as well as non-contaminated areas and in majority of cases were below limit standard values for drinking water. Based on the assessment of the health status of population (using 43 health indicators), no significant difference in the health status of population in contaminated and non-contaminated municipalities has been reported.

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Mercury enrichments in Slovenian soils

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Regional geochemical survey was conducted in years 1990-1993 covering the entire territory of Slovenia. Soil sampling was performed in a 5x5 km grid with randomly selected starting point to assure systematic sampling (Andjelov, 1994). A total of 817 top-soil samples were collected. In 2012 the stored soil samples were taken out of depot at Geological Survey of Slovenia and prepared for analysis of Hg concentration. The main objective was to produce geochemical map of Hg distribution for identification of regional differences and environmental implications caused by anthropogenic activities.

Mercury concentrations were determined by ICP-MS, after digestion of a sample aliquot with aqua regia, at ACME laboratories (Canada). The shipment of samples, replicates and reference materials to the laboratory was carried out in a random succession. Objectivity was assured through the use of neutral laboratory numbers. Accuracy was verified against standard materials. Geochemical map of Hg distribution was generated.

The determined Hg concentrations range between 0.012–5.293 mg/kg with the median of 0.106 mg/kg. Geochemical map of Hg distribution revealed a significant mercury anomaly localized in western part of Slovenia where the world's second largest mercury mine deposit (Idrija) is situated. In Idrija mercury ore was excavated and processed for nearly 500 years, until 1995. We divided data to western and eastern part of Slovenia and realized that there is an important difference in basic statistics. Hg median for western part is 0.151 mg/kg (0.016–5.293 mg/kg) and for eastern part 0.083 mg/kg (0.012–3.936 mg/kg). This proves important large scale impacts of ore processing in Idrija area. The determined Hg median for both parts is higher than the Hg median for European soils.

Some other anthropogenic influences are observed in the Hg distribution map. Typically for urban soils, Hg is enriched in soils of Ljubljana city. An influence of polymetallic mine in Litija is also clearly expressed, while some other anthropogenic sources like coal-fired power plants near Velenje and Trbovlje are not observed in map of Hg distribution.

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Developmental disorders in the population of children as a consequence of selected neurotoxic substances in environment of Silesian District, Poland

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The participation of the lead compounds in the formation of neurodevelopmental disorders in children is proven, however sudden increase the number of developmental disorders in children in recent years, is not adequate to the changes in the environment such as reduction of the concentration of lead (Pb) in the environment. At the same time increased environmental burden by persistent organic pollutants as polychlorinated biphenyls (PCB), which are characterized by high neurotoxicity has been observed.

The study was undertaken to investigate the hypothesis that the high coefficients of developmental disorders and psychomotor developmental disorders in the population of children are associated both, with lead and polychlorinated biphenyls, which are present as environmental pollutants in the place of their residence.

On the basis of the raw data on developmental disorders and psychomotor developmental disorders in children in 19 selected Silesian cities, the coefficients were calculated (per 100 000 children) for the years 2004-2010. The environmental burden was estimated on the basis of annual average concentrations of Pb in the Silesian cities in 1989-2008. For the estimation of environmental exposure to PCBs in the cities of the Silesian, the concentrations of PCBs, which were analyzed in the samples of PM10 collected at three locations in two seasons (winter, summer), were used. The relationships between the incidences of developmental disorders and psychomotor developmental disorders in children and environmental burden by Pb and PCBs were performed.

Significant differences in the incidence of developmental disorders and psychomotor developmental disorders in children between the Silesian cities were indicated. The relation between lead concentrations and developmental disorders in children in cities was not found.

The correlation between developmental disorders and psychomotor developmental disorders and the environmental burden by PCBs has been found.

Research indicates that the main neurotoxic factor affecting the incidence of developmental disorders in children is PCB.

Stillbirths and low birth weight among newborns as a consequence of air quality in Silesian District, Poland

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The research indicated that environmental pollutants, including common air pollutants, such as: benzo(a)pyrene, particulate matter PM₁₀, SO₂, NO and NO₂, have an influence on an occurrence of stillbirths and births of newborns with low birth weight (LBW).

Objective of this study was to check the relation between the commonly present air pollutants in Poland and the number of stillbirths and births of newborns with LBW.

The rate of stillbirths and the rate of newborns with LBW were calculated for the years 2002 - 2010 on the basis of annual and monthly number of cases in Poland. The relation between a frequency of an occurrence of births of newborns with LBW and the exposure of mother-to-be to benzo(a)pyrene, PM₁₀, SO₂, NO₂, NO in the air during the pregnancy and its particular trimesters, as well as to BaP&SO₂, PM₁₀&SO₂, PM₁₀&NO₂, PM₁₀&NO during the period of one, two and three years before newborn's birth were checked in four biggest Silesian cities by using the function of linear regression and of multiple regression.

The relationship between a frequency of births of newborns with LBW and women's exposure to benzo(a)pyrene and PM₁₀ during the period of one year, two years and three years before newborns' birth was proved. The analysis of the exposure to mixture of benzo(a)pyrene, PM₁₀ and selected gaseous air pollutants proved a strengthening role of SO₂ (in case of BaP&SO₂ and PM₁₀&SO₂), NO₂ and NO (in case of PM₁₀&NO₂ and PM₁₀&NO) in relations to LBW. In the study, an influence of benzo(a)pyrene and PM₁₀ on the number of stillbirths was not proved as well as a relation between pregnant women's exposure to selected air pollutants in particular trimesters of pregnancy and a frequency of births of newborns with LBW.

Exposure of the pregnant women to benzo(a)pyrene and PM₁₀ during the period of one year, two years and three years before child's birth increases a number of births of newborns with LBW. A number of births of newborn's with LBW is dependent on simultaneous exposure of their mothers to the mixture of typical pollutants such as: PM₁₀, SO₂, NO₂ and NO.

Contamination of the soil cover with heavy metals and metalloids and population health in the crop of non-ferrous metals (Zakamensk, Buryat Republic)

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Increasing consumption of mineral resources has a negative impact on the environments. In 70 years of exploitation, the Dzhidinsk enterprise on mining sulfide-tungsten and molybdenum ores has shaped a natural-technogenic complex (200 km²) with nearly 44.5 million tons of tailings. It contains Pb, Zn, F, Mo, W, Be, Bi, As, etc. The aim of our study is soil cover state estimation as an indicator of environmental pollution and medical-demographic situation evaluation in the Zakamensk city.

The soil-geochemical survey of Zakamensk was performed in summer 2012. Soil samples (129, including 24 of background soils) were analyzed for 18 heavy metals and metalloids (HMs) contents belonging to the I–III hazard classes; the contents of Be, Sn, Cs and Bi were determined by ICP-MS (Elan-6100 and Optima-4300 spectrometers, Perkin Elmer, USA). The geochemical transformation of urban soils was estimated with enrichment ($EF=C_a/C_b$) and dispersion ($ED=C_b/C_a$) factors, where C_a is the element concentration in urban soil samples, and C_b is its concentration in the background soils, that were only calculated for the soils developing from the same parent materials. The eco-geochemical assessment of urban soils was based on the coefficient showing the concentration of particular elements relative to the maximum permissible concentrations $K_o = C_a/MPC$ and the integral index of the environmental contamination (IEC) with a set of elements.

For Zakamensk, W, Bi, Cd, Pb, and Mo are priority pollutants. It occurs because of priority of physical and chemical tailings weathering and by including waste products from mining in the construction of buildings, playgrounds, and roads. The strongest impact are experiencing soil industrial zone, where the pollutants are: $Bi_{23,6}W_{21,0}Cd_{10,8}Be_{8,1}Pb_{8,0}Mo_{6,9}Sb_{6,6}$ (superscript - Kc value). Soils of residential high-storey blocks are polluted by $W_{6,0}Bi_{5,2}Cd_{4,8}Pb_{2,6}Be_{2,5}Zn_{2,4}Cu_{1,5}$. Soils in the village residential and recreation area on the left bank of the Modonkul River are clean, far from tailings. Concentrations of most elements, except ore elements and their associates ($Bi_{3,1}W_{2,0}Mo_{1,8}$) and typical urban pollutants ($Pb_{2,0}Zn_{1,3}$) are close to background values. Average IEC value in the city is 93, which indicates very dangerous ecological situation; about 50% of the city has $IEC > 128$. The concentrations of Pb, Sb, Cd, and As in the soils of the industrial zone exceed the MPC values by 1.7–7.8 times.

The spatio-temporal analysis of the children under the age of 14 health status demonstrated that Zakamensk district is characterized by increased rates of endocrine system (increased concentrations of Co, Pb in soil) and skin (increased concentration of As in soil) diseases. The incidence rate of these diseases is above the average incidence rates for Russia and in the Buryat Republic. The high rate of perinatal mortality (more than 10 deaths per 1000 live births) in the city indicates the adverse environmental conditions and the lack of adequate health care.

Fast and simple screening for the simultaneous analysis of seven metabolites derived from five volatile organic compounds in human urine using on-line solid-phase extraction coupled with liquid chromatography-tandem mass spectrometry

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Recently, the International Agency for Research on cancer classified outdoor air pollution and particulate matter from outdoor air pollution as carcinogenic to humans (IARC Group 1), based on sufficient evidence of carcinogenicity in humans and experimental animals and strong mechanistic evidence. In particular, a wide variety of volatile organic compounds (VOCs) are volatilized or released into the atmosphere and can become ubiquitous, as they originate from many different natural and anthropogenic sources, such as paints, pesticides, vehicle exhausts, cooking fumes, and tobacco smoke. Humans may be exposed to VOCs through inhalation, ingestion, or dermal contact, which may increase the risk of leukemia, birth defects, neurocognitive impairment, and cancer. Therefore, the focus of this study was the development of a simple, effective and rapid sample preparation method for the simultaneous determination of seven metabolites (6 mercaptic acids + t,t-muconic acid) derived from five VOCs (acrylamide, 1,3-butadiene, acrylonitrile, benzene, and xylene) in human urine by using automated on-line solid-phase extraction (SPE) coupled with liquid chromatography–electrospray tandem mass spectrometry (LC–MS/MS). Negative electrospray ionization tandem mass spectrometry was utilized for quantification. The coefficients of correlation (r^2) for the calibration curves were greater than 0.995. Reproducibility was assessed by the precision and accuracy of intra-day and inter-day precision, which showed results for coefficient of variation (CV) that were low 0.9 to 6.6% and 3.7 to 8.5%, respectively, and results for recovery that ranged from 90.8 to 108.9% and 92.1 to 107.7%, respectively. The limits of detection (LOD) and limits of quantification (LOQ) were determined to within 0.010 to 0.769 ng mL⁻¹ and 0.033 to 2.564 ng mL⁻¹ in this study. To the best of our knowledge, this is the first study to provide simple, small injection volumes (40 μ L) and a rapid LC-MS/MS method combined with an on-line SPE step for the simultaneous detection, identification, and quantification of seven metabolites derived from five VOCs in human urine for evaluation of the future risk of human exposure to volatile organic compounds.

Contents of calcium, magnesium and carbonates in soil and mortality for cardiovascular diseases in Slovak Republic

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The study deals with the analysis of relationship between chemical contents of Ca, Mg and carbonates in soils and the data on relative mortality for cardiovascular diseases (REI), indirect standardized mortality ratio (SMRI) and potential years of life lost for cardiovascular diseases (PYLLI) in the Slovak Republic. Data include 10,738 chemical analyses of soils for 34 chemical element/compounds, excerpted from Slovak national databases for soils. Data of mortality were collected for period 1994-2003. The statistical method of data correlations was used based on calculation of mean values (health and chemical data) for each of 2,883 municipalities. Linear regression and Spearman correlation were used as mathematic methods for modelling of relation data analysis. Based on the results of calculations counted by both of mathematic methods, contents of calcium, magnesium and carbonates in soil were defined as a significant parameter for REI, SMRI and PYLLI.

The obtained correlation coefficients are suggestive of necessary chemical parameters for better health status in case of mortality to cardiovascular diseases. At these results the relative mortality and indirect standardized mortality ratio reach the highest correlation relationships with concentration of magnesium and content of carbonates in soil in the Slovak Republic. These coefficient values are the most significant among of all: for chemical parameter Mg toward REI -0.113 and SMRI -0.091; for contents of carbonates toward REI -0.207 and SMRI -0.095. No significant correlation for concentration calcium in soils was observed.

Transfer of As and Sb from soil to plant in area of abandoned Sb deposit Čučma

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Presented study shows the results of geochemical study of soil and plant samples from the locality Čučma. Main object was to evaluate soil contamination around abandoned Sb deposit. The mining area of Čučma belongs to the important ore deposit in the south part of Slovenské rudohorie Mts. The waste from mining and ore processing represent the most significant source of contamination in this area. Accumulated elements are released from old adits, tailings ponds and tailings piles and contribute to the contamination of the natural environment. The soil was sampled with a soil probe from the depth of 0 – 15 cm (A-horizon) and from the depth of 15 – 30 cm (B-horizon). The soil samples were prepared by standard methods (dried, homogenized, sieved to the ≤ 2 mm fraction). The plant samples were collected according to the biggest species abundance in the locality of the soil samples taking. Herbs were sampled as whole (*Mentha longifolia*, *Typha latifolia*, *Dryopteris filix-mas*, *Athyrium filix-femina*), only leaves were taken from woody plants (*Carpinus betulus*, *Fagus sylvatica*). The Sb concentration of studied soil samples varied from 6.9 mg.kg⁻¹ to 142.322 mg.kg⁻¹. The range of As concentration in the soil samples was 16 – 2.253 mg.kg⁻¹. All collected and analyzed soil substrates exceed background concentrations of Sb in soils of Slovakia and also exceed the permissible limit of As content in soils. The As concentration in the plant samples varied from 1.3 mg.kg⁻¹ to < 0.1 mg.kg⁻¹. The range of Sb concentration in plant samples was 0.16 – 21.94 mg.kg⁻¹. The bioaccumulation factor (BAF) was calculated to assess the uptake of element from soil and translocation to shoots. Unexpectedly, maximum BAF values were detected in localities with the least concentration of selected elements in soil. The contents of contaminants in soils and plants of locality Čučma refer to the character of the soils significantly affected by the weathering processes of rocks and associated mining activities. Low availability of elements reflects their binding to stable and less soluble secondary mineral phases present in soil substrate.

Mobilization of arsenic in technosoils under laboratory dynamic (column) conditions (studied location Zemianske Kostol'any)

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This study describes the mobilization of arsenic from technosoils in Zemianske Kostol'any under column (dynamic) conditions. Studied location is the most polluted area in Slovakia, where in 1965 a dam failure of a coal ash impoundment released 3 million m³ of power plant ash with a high content of arsenic and other potentially toxic trace elements (mercury, cadmium, copper, lead, zinc) in the surrounding environment. Instead of remediation the ash layer was covered by 40 to 100 cm of different soil types. It is important to know the processes by which the mobilization of elements depends on (environmental characteristics, physico-chemical properties, mineral composition of the ash, sediments and soils. The rate of leachability of potentially toxic elements is related to their concentration in coal and ash, depends on the conditions of coal combustion, on processes of sorption/desorption, on redox and dominantly on pH conditions of environment. The total content of arsenic in the studied samples is in the range of 1,100-1,139 ppm. From soil probes were collected two samples (ZK1, ZK2), from the following depth 30 and 60 cm. The soil samples were processed in a standard manner (drying, homogenisation and sieving into a fraction smaller than 2 mm). Column experiments were performed in two glass column. A peristaltic pump was used through the column leaching solution (demineralized water, 1mM citric acid and 0.1 M hydrochloric acid) from bottom to the top for 105 days, whereas every 35 days leaching agent was changed to compare the efficiency of solutions. Most arsenic during experiments with demineralized water released from the sample ZK2 from a depth of 60 cm (11.11 % from As_{tot} 1,100 ppm), during the experiment with citric acid from a given sample of 16.58 % As was obtained and during the experiment with hydrochloric acid from a given sample of 5.18 % was obtained. From the results obtained we can find that the strongest extractant was citric acid. This work confirms that soil microorganisms producing organic acids play an important role in the environmental fate of arsenic in soils.

Risk assessment of toxic elements leachability from soils and impoundment sediments (abandoned Sb deposit Poproč)

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Mining soils and impoundment material from the highly contaminated mining site of Poproč (Slovak Republic) were subjected to leaching experiments in order to determine the available contents of selected elements. These soils and waste are enriched in a variety of heavy metals and metalloids, mainly with As, Sb, Zn and Pb levels up to 1,463 ppm, 5,825 ppm, 1,202 ppm and 425 ppm, respectively. The extractability of selected potentially toxic trace elements was evaluated by single extraction with inorganic and organic extractants in order to simulate four types of conditions. Extraction with distilled water was used for the determination of mobile, easily-soluble fraction of elements from samples. The sequence of leaching efficiency and average extractabilities of monitored elements expressed as percentage of the total contents in samples were: Zn (8.03 %) > As (0.73 %) > Sb (0.66 %) > Pb (0.12 %). The sequence of extractability of As, Sb, Zn and Pb with the NH₄NO₃ procedure for assessment of plant-available forms was: Zn (14.56 %) > Pb (0.30 %) > As (0.13 %) > Sb (0.06 %). Extraction efficiency of distilled water was more effective for arsenic and antimony, while the extraction with ammonium nitrate solution was effective for lead and zinc. The highest extractabilities were found when organic single-extraction techniques were applied. The average bioleaching efficiency of elements with liquid Sabouraud medium was: Zn (55.71 %) > As (40.74 %) > Sb (14.38 %) > Pb (10.01 %). The addition of glucose to the liquid Sabouraud medium increased the release of elements due to activation of heterotrophic microorganisms and sequence of leaching efficiency was: Zn (64.90 %) > As (50.66 %) > Sb (14.55 %) > Pb (8.5 %). The results obtained from the experiments showed that combination of different methods of extraction (H₂O, NH₄NO₃ and bioleaching), could be used for reduction of contamination at studied site and become one of the possible alternatives of bioremediation of soils at Poproč.

Fungal transformation of antimony pre-adsorbed onto ferric and manganese oxohydroxides and oxides

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Antimony (Sb) is considered a high priority global contaminant with harmful effects on environment and human health. Furthermore, industrial antimony application is widespread, thus posing serious problem for the environment especially near mining and smelting areas. Natural antimony retention is often realized via its adsorption onto precipitated amorphous or mineral ferric and manganese oxohydroxides and oxides in sediments and waters. However, widespread fungal consortia may significantly alter antimony mobility in these systems due to their ability to produce chelating and acidic metabolites which may desorb antimony from mineral surfaces. Therefore, this phenomenon was studied under laboratory conditions during 14-day incubation of common fungus *Aspegillus niger* which produces up to 28.6 mmol.L⁻¹ and 16.1 mmol.L⁻¹ of oxalic and citric acid, respectively. Fungal activity led to efficient antimony desorption. Almost all of pre-adsorbed antimony was leached from laboratory prepared hausmannite (Mn₃O₄) and up to 60% from RTG amorphous FeOOH which crystallography was studied in more detail by Mössbauer spectroscopy. Leached antimony was available for fungal bioaccumulation and partially distributed in culture medium and fungal biomass. Here, very unique biological transformation into volatile antimony derivatives appeared. Antimony biovolatilization should be considered the main fungal detoxification mechanism in all treatments, effectively removing almost 34% and 61% of initial 2.6 mg antimony media content in presence of FeOOH and hausmannite, respectively. Results clearly indicate significant fungal contribution on antimony retention in natural geochemical barriers and that their presence should be monitored due to potential risk of antimony release.

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Potentially toxic elements in crop plants growing on geogenic polluted soils of Eastern Slovakia

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The objective of this study was to investigate the connection between the geogenic polluted soils of Eastern Slovakia (Central Carpathian Paleogene) and the concentration of potentially toxic elements in several crop species growing in this region. The contents of typical serpentine elements are highly increased in soils developed on flysch sedimentary rocks. The total amount of Cr (102 – 650), Ni (34 – 269), Co (4.1 – 24.6), V (74 – 165), Fe (30,144 – 49,518) and Mn (542 – 2,014) (all in mg.kg⁻¹) were significantly higher in these “serpentine like” soils than reference values for Slovak soils. Cr and Ni concentrations exceeded critical values for contaminated soils in most cases. Considerable amount of potentially toxic elements is uptaken by plants. In this study, samples of grains, stems, leaves and roots from mentioned area, were collected. Atomic emission and mass spectrometry with inductively coupled plasma and electrothermal atomic absorption spectrometry were used to determine element concentrations in plant samples. The levels of chromium in grains (0.2 – 11.8) were found most increased in oat (average 2.8) and rye (average 1.2) (all in mg.kg⁻¹). The highest content of nickel was found in oat grains once again (average 4.7 mg.kg⁻¹), but very high concentrations were documented also in soybean and rapeseed. Slightly elevated cobalt contents were observed in most plant samples. Concentrations of Fe, Mn or Cu in samples were comparable with background values for these elements in crops. Besides plant specification, soil physico-chemical properties play an important role in elements transfer to the crops. Our results indicated that amount of Cr and Co in soybean sample increases in the following order: root > stem > leave > grain. On the other hand, Ni content was highest in grains and decreased in order - stem > root > leave. The present study documented that several crops grown on geogenic contaminated soils show a high risk of having metals concentrations beyond the permissible limits. Consumption of contaminated plant foods from this area can be associated with some health concerns. It is really necessary to pay attention to the research of Cr and Ni effects on human health in contaminated sites.

Distributions of potentially toxic elements in soils of children urban environment in Bratislava, the capital of Slovakia

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The contamination of urban soils by potentially toxic elements (PTEs) is one of the fastest growing types of environmental contamination due to vehicle emissions, industrial discharges and other activities. The main goal in this study was to determine the concentrations of potentially toxic elements (PTEs) (namely Cu, Zn, Pb, As, Cd, Hg and Fe) in soils of kindergartens, urban parks and playgrounds in Bratislava. A total of 97 surface soil samples were taken from different land use areas in Bratislava city (Districts I. – V.) and analyzed for basic soil properties and concentrations of selected PTEs in accredited laboratory (Cu, Cd, Pb, Zn by inductively coupled plasma-atomic emission spectrometry ICP-AES; Hg by atomic absorption spectrometry AAS-AMA and As by atomic absorption spectrometry AAS with hydride generation). Based on the analysis results we found that historical and functional land use areas were the most significant factors in gradual increases of PTE concentrations because the city centre (District I.) and industrial areas (Districts II. – III.) had the highest concentration of PTEs contrary to suburban Districts IV. – V. mainly used as residential areas. This trend has been confirmed also by calculation of contamination factor and index of geoaccumulation. Elevated values of the contamination factor and the geoaccumulation index, particularly for Pb, Zn and Cd, and less for Cu and Hg, exhibited the soil samples collected from kindergartens and playgrounds located in the Districts I. – III. Significant positive correlations between these elements (Spearman $r=0.26 - 0.79$; $\alpha=0.05$), between Cu, Zn, Pb, Hg and total organic carbon content of the soils (Spearman $r=0.22 - 0.49$; $\alpha=0.05$), and between Cu, Cd, As, Fe and silt fraction (Spearman $r=0.23 - 0.44$, $\alpha=0.05$) were found.

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