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The 15th European Meeting on Environmental Chemistry

BOOK OF ABSTRACTS

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EMEC15

BOOK OF ABSTRACTS

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ORAL PRESENTATIONS

ENVIRONMENTAL CHEMICAL PROBLEMS – MYTHS AND REALITY

Ivan Holoubek

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We are living in the chemical universe with chemicals with different physical-chemical and environmental-chemical properties and wide range of toxic characteristics likely to cause adverse human health or environmental effects. In this context, “substance” means a single chemical species, or a number of chemical species which form a specific group by virtue of (a) having similar properties and being emitted together into the environment or (b) forming a mixture normally marketed as a single product. Depends on their stability in the environment can be transported for long distance. Environmental chemicals can represent local, regional or global scale of problems.

There is out of discussion that huge amount of them have very high positive role, many of them are harmful, toxic, problematic, with high negative impact to man and environment.

We have a lot of problems with the state of our planet's environment; we have problems with chemicals on the planet. These problems require a broad and highly effective international cooperation. Despite tremendous efforts, a number of activities and projects well done, the key question is whether the effectiveness of activity of the international community would not be significantly higher. It is extremely important to have perspectives from the current economic crisis, critically evaluate the relationship between funds spent and the results obtained. It is necessary to critically evaluate the relationship between the resources embedded in the organization of conferences, expert meetings, workshops, tours (sitting time) and resolution procedure in individual countries (resolution time). How is the effectiveness of international institutions such as UN and its chemical conventions in the solution of the globe problems? How to carry the participation of representatives of each country largely funded from international resources to solve problems in these countries. It is necessary to critically assess whether it would be possible these (sitting) resources better invested in solving problems, solving specific problems in individual countries. Other issue is the effectiveness of the transfer of scientific results to the solution of the environmental problems. And where is a true round the main environmental problems?

ORGANIC INDICATORS FOR THE ANTHROPOGENIC IMPACT ON JAKARTA BAY, INDONESIA

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Jakarta is a booming coastal megacity in Indonesia with over 10 million inhabitants discharging enormous amounts of untreated wastewaters from households and industries into Jakarta Bay. The spectrum of organic contaminants occurring in surface waters and corresponding suspended particulate matter from Jakarta might be completely different from that known from industrial nations of the northern hemisphere. We aimed to identify those site specific compounds that represent the major and most harmful contamination of the cities` water resources and, therefore, applied a non-target screening which allows for the identification of a wide range of organic contaminants.

These screening analyses allowed to differentiate huge municipal sewage effluents from specific industrial emissions as well as agricultural run-off. Specific indicators are DEET and linear alkyl benzenes (LABs) appearing in high concentration in surface water or sediments, respectively (e.g. DEET concentrations reached 24 µg/L). The measured values are the highest one published for aquatic ecosystems. As main objective of this study the usefulness of the selected organic indicators to trace the distribution of anthropogenic wastewaters in tropical freshwater and coastal systems, including the long-range transport of wastewater emissions in coastal systems will be presented.

Additionally, chemical analyses of macrobenthos and fish samples from the coastal fishing ground have been conducted complimentarily to evaluate the contamination through the seafood webs. Some of the source specific indicator substances have been identified to be taken up from marine organism at high rates demonstrating the relevance of Jakarta Bay pollution for seafood quality.

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EMISSION LEVEL AND POLLUTION CHARACTERISTICS OF PLATINUM (Pt), PALLADIUM (Pd), IRIDIUM (Ir) AND RELATED ELEMENTS IN ROAD DUSTS FROM SEOUL AREA IN KOREA.

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The emission level and pollution characteristics of platinum (Pt) in dust, soils, and tree barks collected from Seoul area was published for the first time in Korea [1]. The previous study confirmed that an important source of Pt in roadside environment is automobile catalytic converter, and that it indicates a tendency to increase Pt levels in road dusts and soils along with traffic volume. The study also suggested that not only traffic volume but also driving style have a great influence on Pt levels in road dusts. In this study previous 35 dust samples from Seoul area and newly collected 8 dusts from Seoul downtown were reanalyzed by ICP-MS and ICP-OES to determine Pt, Pd, Ir and related elements. The concentration levels of Pt, Pd and Ir in reanalyzed 35 dusts were in the range of 0 – 444 (76) ng/g, 172 – 1.215 (609) ng/g and 0.8 – 7.4 (2.9) ng/g, respectively. The level of Pt, Pd and Ir in new 8 dusts ranged 25.6 - 98.5 (65.6) ng/g, 30.6 – 147.9 (101.7) ng/g and 2.1 - 5.5 (3.2) ng/g, respectively. The background of suburb control site was 3.3 Pt ng/g, 220 Pd ng/g and 1.6 Ir ng/g. Palladium also shows similar distribution trend with Pt, and remarkably high concentration of Pd in dust was found in the heavy traffic areas, whereas Ir shows no correlation with Pt and Pd. The traffic-related elements, mostly heavy metals, such as Cr, Cu, Mo, Ni, Pb, Sb and Zn were enriched in road dusts with high Pt level. Closely correlated elements with Pt and Pd in dust were Be, Cr, Cu, Fe, Mo, Ni, Au, Hg and Bi.

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COMPLEX ASSESSMENT OF EXPOSURE OF HUMAN POPULATION TO POLYCYCLIC AROMATIC HYDROCARBONS IN TWO REGIONS OF THE CZECH REPUBLIC

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants, some of them being carcinogenic/mutagenic (in addition to benzo[a]pyrene other 15 chemicals of this group). Humans are exposed to PAHs in various ways, typically, diet represents their main source. In case of infants, human breast milk has to be taken into consideration; however, in areas with high atmospheric pollution (due to intensive anthropogenic activities) the intake via inhalation may become more significant.

Within this study, which is a part of the project concerned with the impact of atmospheric carcinogens / mutagens on the genetic damage of newborns, we assessed the levels of PAHs both in air (sampled by HiVol samplers of PM 2.5) and in one week diet of pregnant women, residents of two areas of the Czech Republic differing in atmospheric contamination. Samples were collected during two periods (i) summer/autumn 2013 and (ii) winter 2014. The newly optimized and validated analytical methods for the determination of PAHs using gas chromatography in combination with tandem mass spectrometry (GC-MS/MS) were applied for examination of both types of samples. The levels of 24 targeted PAHs in the diets were very low, in most cases below 0.1 ng/g. No significant differences between the localities and/or individual women's diet were identified. Regarding the atmospheric contamination in the highly industrialized locality (Ostrava region) more than ten times higher concentrations were determined and also significant differences during the monitored period have been identified. Finally, the contribution diet and inhalation to the overall exposure to PAHs during respective period in monitored locality were calculated.

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NEW GENERATION ANTIBIOTICS FROM AMPHIBIANS

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Amphibians are one of the oldest species on the Earth. Surprisingly they have neither teeth, nor claws. Their only protection tool is skin secretion. Antibacterial peptides secreted by amphibians in response for the outer impulse may have antibacterial, antifungal, antiviral, and anticancer activities. They can inhibit NO formation or induce insulin production in an organism. Amphibians may use their peptides even fighting predators, inducing poisoning or vomiting effect. Thus the crude secretion of *Rana temporaria* completely prevented the growth of *S. aureus* at the level of nanomoles [1]. This effect is stronger than the inhibition of *E. coli* with antibiotic netilmicin sulfate. Due to wide spectrum of biological activities frog peptides are considered to be a powerful source of the new generation pharmaceuticals. An extremely important feature involves impossibility of microorganisms to develop resistance towards peptides.

The process of discovering of new natural peptides in frog secretion is quite challenging. An original prepropeptide consists of a signal peptide, an acidic spacer and a mature active peptide. The establishing of the primary structures of these species is quite difficult as they may be rather long (47 residues), contain disulfide bridge, possess several isobaric and isomeric residues and a number of Lys and Arg residues. The latter issue prevents using usual bottom-up approaches.

Studying various species of frogs inhabiting Russia we reported about 200 natural peptides in their secretions. The proposed mass spectrometric approaches involving accurate mass measurements and several methods of triggering fragmentation in MS/MS mode, allowed overcoming all the structural difficulties [3, 4]. The secretion of particular peptides was provoked by keeping the animals in the proximity of certain microorganisms.

The proposed approach based on the normalised mass defects and isotopic shifts predicts the type of activity of new peptides and serve as taxonomic markers allowing distinguishing closely related species [2, 5].

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DETERMINATION OF PARACETAMOL, DICLOFEANC, NAPROXEN, IBUPROFEN, AMLODIPINE AND ROSUVASTATIN IN HOSPITAL WASTE BY LIQUID-LIQUID EXTRACTION AND VALIDATED HPLC-UV METHOD

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Pharmaceutical contamination by hospital sources is a major concern to the environment as the fate of these substances in the environment is unclear. Detection of pharmaceuticals in the waste is a great challenge to the analytical and environmental scientists due to the very complexity of the waste. Lack of sophisticated instruments like LC-MS and/or HPLC-UV based analytical methods are posing greater challenge for their detection in developing countries. In addition, poor regulatory requirements allow the industrialist not to install waste water treatment plants. Therefore the pharmaceuticals enter in the wastes of developing countries in very high concentrations and they remain there as such and cause their effects. In this study, therefore a simple and reliable RP-HPLC-UV method based on liquid-liquid extraction was developed for the simultaneous determination of six commonly used pharmaceuticals viz. paracetamol, naproxen, diclofeanc, ibuprofen, rosuvastatin and amlodipine in hospital wastes of five major hospitals of Gujrat, Pakistan. The extraction and chromatographic conditions were optimized for the detection of these pharmaceuticals in waste water, sludge and solid waste originating from these hospitals. Among the three different solvents i.e. diethyl ether, n-hexane and chloroform which were used for extraction of targeted pharmaceuticals, chloroform was proved to be the best extractant. Successful separation of six pharmaceuticals was accomplished using C-18 column (250 × 4.6 mm, 5µm) and mobile phase of ammonium acetate pH 5.0 and acetonitrile in the ratio of 50:50, v/v. Method recoveries were greater than 70 % for all the pharmaceuticals in different matrices. LOQ of the method for the targeted compounds were 3 µg/L, 4 µg/L, 8 µg/L, 8 µg/L, 12 µg/L, 20 µg/L for paracetamol, rosuvastatin, naproxen, diclofenac, amlodipine and ibuprofen respectively. Analysis of real samples revealed very high concentrations of all the investigated pharmaceuticals. The highest concentration obtained was of paracetamol and it was also detected in all the five hospitals and all the sample matrices (20-696 µg/L) whereas the concentration of other pharmaceuticals were also very high although they were not detected in all the sample matrices. Concentrations of other pharmaceuticals were; Naproxen (78-220 µg/L), Diclofeanc (138-186 µg/L), Ibuprofen (26-596 µg/L), Amlodipine (70-303 µg/L) and Rosuvastatin (22-104 µg/L). The results from this study demands for installation of waste water treatment plants as well as the detection of other pharmaceuticals not only from hospital sources but also from other sources.

USE OF PASSIVE SAMPLER POCIS FOR DETERMINATION OF PHARMACEUTICAL IN WATER ENVIRONMENT

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This work is focused to use of passive samplers POCIS (Polar Organic Compound Integrative Sampler) for analysis of pharmaceuticals. As target compounds were chosen four pharmaceuticals from group of non-steroidal anti-inflammatory drugs (NSAID): ketoprofen, ibuprofen, diclofenac and naproxen, three from group of macrolide antibiotics: erythromycin, clarithromycin and roxithromycin, and caffeine. Passive samplers help to capture fluctuations of pollutant concentrations in water environment, which are not revealed by usual active sampling. Using these samplers leads to simplification analytical procedure and therefore to costs reduction. Target pharmaceuticals usually occur in water environment in trace or ultra-trace concentrations, so sometimes is almost impossible to analyze them by using conventional sampling. When passive sampling is used, samplers are deployed into a river as well for several weeks, is possible to detect also very low concentrations. For calculation Time-Weighted-Average concentrations (TWA), how is called calculated concentration of pollutant in river when is passive sampling used, is necessarily to know sampling rates for each monitored compound. This work deals with experimentally determination these sampling rates for each target pharmaceutical. POCISes were deployed to mesocosmos which was aquarium with spiked water by pharmaceuticals. Into mesocosmos continuously flowed "fresh" spiked water from reservoir. Daily were taken samples of water from aquarium and then analyzed. Subsequently were analyzed also samplers and from obtained results were calculated sampling rates for each compound. Thereafter were samplers used for monitoring pharmaceuticals in river Queich near the town Landau in Germany. For extraction of water samples from mesocosmos was used SPE (Solid Phase Extraction) method and all analysis were made by HPLC/HRMS method.

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BIODEGRADATION OF OXOBIODEGRADABLE POLYMERS UNDER ENVIRONMENTAL CONDITIONS

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Oxobiodegradable polymers were developed to improve disposal of plastic waste and limit their impact on the environment. Under abiotic stresses, the molecules are oxidized and break down into small fragments that can be biodegradable. To assess the oxobiodegradability of polymer materials, a standard test method was developed using an oxidation pre-treatment and the inoculation with a pure microorganism strain [1]. This test showed that under controlled conditions, oxidized fragments of polyethylene [2] and polypropylene [3] films containing pro-oxidant additives become readily biodegradable. Under environmental conditions, a large number of microorganisms can use a wide range of substrate as nutrients. This complex system can trigger co-metabolic biodegradation of contaminant or competition for substrate that can impact the rate of polymer degradation. To improve the standard test method and bring it closer to environmental conditions, the influence of different source of microorganisms and nutrients on the rate of polymer degradation was assessed. The biodegradability of high-density polyethylene films (HDPE), containing pro-oxidant additives (manganese + iron salts) was studied using the standard test method [1]. Photo and thermal oxidation pre-treatment, corresponding to about three years of outdoor weathering, was monitored by FTIR measurements. The oxidized samples were then inoculated with identified microbial strains in a controlled mineral medium containing the polymer as sole carbon source and incubated up to 180 days. The metabolic activity of the microorganisms was determined by measuring the adenosine triphosphate (ATP) and the adenosine diphosphate (ADP) content. This sensitive and quantitative measurement reflects the energetic metabolism state of the cells and indicates if microorganisms use polymer fragments as a substrate. A bacterium strain (*Rhodochoccus rhodochrous* ATCC 29672) producing bio-surfactant and a fungal strain (*Phanerocaete chrysosporium* ATCC 34541) producing exo-enzymes (peroxidases) were grown separately and in co-cultivation to detect synergistic or antagonistic activities that can modulate the efficiency of biodegradation.

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DEVELOPING POLYMER-CLAY COMPOSITE SORBENTS FOR THE REMOVAL OF EMERGING ORGANIC POLLUTANTS FROM WATER

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Efficient composite sorbents were designed and their performance as sorbent materials in filtration columns was compared to that of granular active carbon (GAC). Polymer-clay composites based on the adsorption of protonated poly-4-vinylpyridine-co-styrene (HPVPcoS) and of polymethyl-4-vinylpyridine-co-styrene (QPVPcoS) to (MMT) montmorillonite were developed. The removal of emerging micro-pollutants, including pharmaceuticals, along with the removal of "classic" pollutants, such as herbicides, was explored. The composites were characterized by adsorption isotherms, SEM, TGA, FTIR, XRD and zeta potential measurements. Zeta potential of the clay decreased (less negative) with an increase in polycation loading and charge reversal was reached even at low polymer loadings. Zeta potential of QPVPcoS was higher than that of HPVPcoS and the composites of the former polymer exhibited higher zeta potentials (same polymer loading). Polymer intercalation in the clay platelets was obtained from XRD measurements. Two modes of polymer adsorption with two onset temperatures higher than the onset temperature of the polymers were suggested by TGA measurements of the composites. Simazine removal was significantly higher by the HPVPcoS-MMT composite due to the formation of hydrogen binding in addition to pi-pi interaction between the pollutant and polymer. While, the removal of the anionic persistent pharmaceutical, diclofenac, was higher by the QPVPcoS composite due to electrostatic interactions along with pi-pi ones. The adsorption kinetics of diclofenac and of simazine to the QPVPcoS- and HPVPcoS-MMT composites, respectively, was substantially faster than to GAC. Equilibrium was reached within 10 minutes for the composites, whereas, on GAC it was reached only after 2-3 hours. Finally, the removal efficiency of diclofenac and of simazine by filtration columns of QPVPcoS-MMT and HPVPcoS-MMT, respectively, was studied and compared to the filtration by GAC columns. In both cases the filtration by the composite columns was more efficient than by the GAC filters.

WASTEFFECT: THE LIFE CYCLE OF EMERGING CONTAMINANTS IN WASTE

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Waste treatment has become a dynamic sector. With the increase of population worldwide, and therefore waste generated, many countries have shifted from landfilling to recycling and incineration, including Norway. Parallel to these developments are increasing regulations regarding contaminants and emerging contaminants. As waste can be a major source of contaminants into the environment, questions are being raised about risks of emerging contaminant emissions through different waste treatments.

The main goal of WASTEFFECT is to develop robust waste emission and exposure models for waste regulators and companies to anticipate and reduce risks from emerging contaminants. Therefore, one of the main parts of this project is to determine how emerging contaminants behave in different waste streams. As case studies, we are establishing a Norwegian waste emission inventory of legacy and new brominated flame retardants (BFRs), bisphenol-A and antimony, in ee-waste, car waste, plastics, glass and combustable waste. For establishing this waste inventory, we are sampling and analysing air, leachate and solid samples from various waste treatment methods, including incineration, recycling and landfilling, along the entire waste-life cycle. Results for bisphenol A show a considerable subfraction in waste is mainly recycled (36%) and thus not eliminated from the system. The incineration process removes a large subfraction from the environment through thermal decomposition (60%) while landfilling "stores" a small subfraction (4%), though up to 20% of this deposited fraction can be introduced to the environment as water emissions or as sewage sludge used in agriculture.

These data (along the ones for BFRs and antimony) will then be used to make estimates of the contribution of the waste sector to the net burden or exposure on the environment and humans. The main output of this research is to help guide the Waste Management Sector on which of the treatment methods provide the lowest risk in regards to emerging chemicals, and which processes could be optimized.

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INVOLVEMENT OF THE RADICAL CHEMISTRY IN THE NEW ADVANCED OXIDATION PROCESSES DEVELOPMENT

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Many advanced oxidation processes (AOPs) are based on the homogeneous activation of an oxidizer (i.e. precursor) such as hydrogen peroxide (H_2O_2) or persulfate ($S_2O_8^{2-}$) in order to generate radicals such as $HO^\bullet$ or $SO_4^{\bullet-}$ with a high oxidation potential (2.8 and 2.6 V respectively). These radicals can oxidize organic compounds with a second order rate constant between 10^7 and 10^{10} M^{-1} s^{-1}.

Experimental works integrate the use of ferric or ferrous ions in order to enhance the radical generation coupling the process with UV irradiation and/or thermal activation.

In this work we investigate the persulfate activation with an iron (III)-organic complex for application in AOPs. A particular attention was given to the radical formation, their reactivity and their role in the whole process. Iron was previously complexed with a polycarboxylate and stability was checked over a large pH range value. Reaction constants obtained by combined steady-state irradiation and laser flash photolysis experiments were implemented in a kinetic model.

The kinetic modelling coupled with the laboratory experience (continuous and transient irradiation) can represent a first step leading to the physico-chemical parameters optimization for AOPs application in more complex systems such as natural waters or wastewaters.

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SEASONAL MONITORING OF HEAVY METAL AND ARSENIC POLLUTION IN THE MINING AREA OF ATACAMA (CHILE) AND DEVELOPMENT OF A LOW COST WATER TREATMENT PROTOTYPE

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In the Atacama region (Chile), water is one of the most limiting resources in productive activities. Its high pollutant load is mainly due to its high salinity, heavy metal and arsenic content that makes it useless for the development of local communities. This environmental problem was tackled by a join research team formed by the Norwegian Institute for Water Research in Oslo (Norway) and Puerto Varas (Chile) and the University Austral of Chile in Puerto Montt (Chile).

This project has two main goals: mapping the water pollution scenario in Rio Salado (Atacama) and develop a cheaper, more sustainable and environmentally friendly technological process to carry out the detoxification of the polluted effluents.

To get a complete description of the pollution and time variation, seasonal sampling campaigns were planned. Three sampling campaigns in Atacama have been carried out so far and the research consortium has pointed out the presence of huge concentrations of arsenic in some hot-spots in the mining area. In parallel to the monitoring, the research has demonstrated that a treatment based on coagulation and flocculation is able to efficiently remove most of the toxic heavy metals and also arsenic in a primary treatment. A secondary treatment based on biosorption by using marine algae (*Lessonia nigrescens* and *Lessonia trabeculata*) in a continuous bed up-flow reactor is being evaluated after the primary treatment for the final detoxification of the effluent.

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OXIDATIVE REMOVAL OF NALIDIXIC ACID VIA FE-OXIDE/O$_2$-MEDIATED REACTIONS

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Organic pollution has become a critical issue worldwide due to the increasing input and persistence of some organic compounds in the environment. Various minerals, which are ubiquitous in natural waters, sediments and soils, are potentially able to adsorb organic pollutants on their surfaces and to degrade them via oxidative or reductive transformation processes [1]. Recently, increasing attention has been paid to heterogeneous Fenton-like reactions using iron-bearing minerals as catalyst [2]. Iron oxides have attracted attention because of their nanometric-size particles, large surface area, high sorption ability and stability. The modified Fenton process can efficiently oxidize pollutants at different pH values mainly by the generation of reactive oxygen species and allows avoiding some disadvantages of the classic Fenton reaction such as the preliminary acidification and the formation of sludge. However, most of previous studies were focused on the use of strong oxidants [3] and only few of them considered the role of oxygen in the oxidative degradation [4].

In the present study, we explored the oxidative capacity of iron oxides nanoparticles, as catalyst for heterogeneous Fenton-like reactions mediated by oxygen, in the removal of a recalcitrant quinolone antibacterial agent. Results showed an efficient sorption under anoxic conditions, followed by a rapid removal of the model contaminant when exposed to air, while negligible degradation is observed in the absence of oxygen or of iron oxides. Five by-products issuing from the oxidative degradation of Nalidixic acid were observed by liquid chromatography-mass spectrometry. Mass balance analyses however indicate that most of the initial contaminant may have been fully degraded. X-ray powder diffraction and Fe K-edge X-ray absorption spectroscopy were used to investigate mineralogical and iron redox changes upon oxidative degradation of the contaminant. Results indicate a significant and systematic oxidation of the solid phase in the oxic experiments, which suggests that the iron oxide enhances the degradation of the contaminant.

This study points out the promising potentialities of iron oxides for the treatment of soils and wastewater contaminated by organic pollutants.

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DIFFERENT ACTIVATION METHODS OF H_2O_2/FE(III) FOR DEGRADATION OF DIURON

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The use of Classical Fenton process in wastewater treatment plants is well known effective technology aimed to oxidize hazardous compounds presented in water to more harmless by-products, or up to final mineralization of organic matter to CO_2 and water. Ferrous iron plays the major role in activation of Fenton reaction acting as a catalyst and promoting the formation of highly reactive hydroxyl radicals. The main disadvantage of this process is the continuous accumulation of ferric hydroxide sludge formed in clarifiers during the precipitation in the final stage of wastewater treatment. Several studies refer that Fe^{3+} is also capable of promoting oxidation mechanism of organic substrate, but obviously, it is less reactive than the Fenton's reaction. Thus, the main goal of this study was to figure out the alternative technology for purification of wastewaters on the base of Fenton reaction with the use of Fe^{3+} as an activator. The degradation of herbicide Diuron (DCMU) using different combinations of chemicals [(H_2O_2/Fe^{2+}), (H_2O_2/Fe^{3+}), ($H_2O_2/Fe^{3+}/Fe^{2+}$) and (H_2O_2/Fe^{3+}/Ascorbic acid)] was studied. Ascorbic acid possesses the ability to reduce ferric iron to ferrous iron and improves thereby the oxidation of organic matter in reaction mixture. The use of Classical Fenton with the molar ratio of DCMU/H_2O_2/Fe^{2+} = 1/10/1 resulted in 99% of DCMU degradation in first 15 min. (Fe^{3+}/H_2O_2) at the same molar ratio showed weak oxidation potential. Only 26% of target compound was removed after 2h of treatment. The same combination of chemicals in the presence of ascorbic acid with the molar ratio of Fe^{3+}/Ascorbic acid = 1/1 showed significant degradation potential close to that obtained by the Classical Fenton reaction. Nevertheless, the small substitution of Fe^{3+} with Fe^{2+} (molar ratio of DCMU/$H_2O_2/Fe^{3+}/Fe^{2+}$ = 1/10/0.8/0.2) improved the degradation of DCMU comparing to the less potent combination (Fe^{3+}/H_2O_2). The highest mineralization rate of DCMU was achieved by Classical Fenton followed by H_2O_2/Fe^{3+}/Ascorbic acid and combined Fe^{3+}/Fe^{2+} activators. Thus, the effective use of ferric sludge as an activator of Fenton-like process can be possible in the presence of reducing agents in wastewater, or with small addition of ferrous salts into the wastewater treatment reactors.

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OPTIMAL AQUEOUS CONDITIONS FOR RETENTION OF ARSENIC AND CHROMIUM ON GAULT CLAY FORMATION: BATCH EXPERIMENTS

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In France, shallow depth storage in clay-rich rock is favoured for low activity, long lived nuclear waste. The Gault clay formation (Albian, Cretaceous) is an appropriate geological disposal for these wastes. Besides radioactive elements, the geological disposal retention capacities also have to be studied for the hazardous chemical elements of the waste (arsenic, chromium, lead, boron) in order to find aqueous conditions, based on clay rock chemical characteristics, which limit the solubility of their toxic elements.

Laboratory sorption batch experiments on dried clay rock samples were carried out to evaluate arsenic and chromium retention capacity, i) in aerobic and anaerobic conditions, ii) with or without chemical ligands (Organic matter, phosphates, sulfates and nitrates), iii) with or without pH adjustment. The percentage of sorption is calculated by the difference between initial and final solution concentration.

Results show that the arsenic sorption is usually high; 77% in aerobic conditions and 83% in anaerobic conditions. Ion coexistence did not significantly affect arsenic removal except with phosphates. Specifically, phosphates concentration in solution of 100 mg L^{-1} halves the arsenic sorption and beyond 2000 mg L^{-1} of phosphates, arsenic removal is totally inhibited.

However, clay rock holds a low part of chromium in aerobic conditions (9%) but the percentage rises to 47% with an anaerobic environment. Chromium is also very sensitive to the pH value of the solution. Thus the sorption is the highest (90 %) with acid conditions (pH 4).

Arsenic and chromium behaviours are contrasted and they are not sensitive to the same factors. What we are looking for in this study are the best aqueous conditions to maximize both arsenic and chromium immobilization. Toxics elements mobility is controlled first by chemical balance and then by transport. This second way will be studied with columns experiments.

Fe^{2+}-ACTIVATED PERSULFATE PROCESS FOR LANDFILL LEACHATE TREATMENT: REMOVAL OF ORGANIC LOAD, PHENOLIC MICROPOLLUTANTS AND NITROGEN

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The innovative $S_2O_8^{2-}/Fe^{2+}$ treatment technology based on combined sulfate and hydroxyl radicals induced oxidation was applied for the treatment of a mature landfill leachate. The potential of simultaneous removal of organic load (measured as COD, DOC, and BOD_7 values), phenolic micropollutants and nitrogen was evaluated.

The leachate was collected from a municipal landfill, which has operated for more than 10 years. The leachate initial parameters were as follows: pH of 7.85±0.2, COD of 9700±381 mg/L, BOD_7 of 2480±122 mg/L, DOC of 2740±11 mg/L, total nitrogen concentration (TN) of 1760±18 mg/L, and total phenols concentration (TPh) of 24±1 mg/L. The effect of oxidant dose ($S_2O_8^{2-}$/[O]COD m/m of 0.1-1), activator dose ($S_2O_8^{2-}/Fe^{2+}$ m/m of 1-50), and reducing agent addition/dose ($S_2O_3^{2-}/Fe^{2+}$ m/m 0.1-1) on the removal of COD, DOC, BOD_7, TPh, and TN was studied. Additionally, the treatment efficacy of ferrous ion activated persulfate process was compared with the Fenton treatment (H_2O_2/[O]COD m/m of 0.1-1) of the same leachate sample.

Irrespective of used oxidant and activator dose, the removal of organic load and TN was similar and considerably lower than TPh reduction. Thus, the leachate treatment at a $S_2O_8^{2-}$/[O]COD and $S_2O_8^{2-}/Fe^{2+}$ m/m of 0.5:1 and 10:1, respectively, resulted in COD removal of 30%, DOC removal of 29%, TN removal of 27%, and ≥90% removal of TPh. Compared with the Fenton treatment at an identical oxidant and activator dose, the $S_2O_8^{2-}/Fe^{2+}$ process demonstrated almost twice lower efficacy in organic load removal, similar TPh reduction and ≥85% higher TN elimination. The addition of reducing agent to the $S_2O_8^{2-}/Fe^{2+}$ system proved favorable for leachate treatment efficacy improvement and resulted in additional 10-15% COD removal. According to the results of this study, the properly optimized Fe^{2+}-activated persulfate process proved a promising landfill leachate treatment technique for simultaneous organic load, phenolic substances and nitrogen removal.

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NOM-AFFECTED TRANSFORMATION OF THE MICROPOLLUTANTS NICLOSAMIDE AND SULFAMETHOXYPYRIDAZINE BY MnO_2

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Whereas the transformation of xenobiotics by MnO_2 has been well documented in the literature, the role of natural organic matter, a ubiquitous component of soils and sediments, is not well described. The objective of the study was to investigate the effect of NOM when two xenobiotics, niclosamide (2,5-dichloro-4-nitrosalicylanilide) (NIS) or sulfamethoxypyridazine (4-amino-N-(6-methoxypyridazin-3-yl)benzenesulfonamide) (SMP), are transformed by MnO_2. Experiments conducted in absence of NOM showed that micropollutants were sorbed and further transformed by MnO2. The transformation rate of both micropollutants obeyed to a first-order kinetic law between pH 4 and 6. The rate constants of NIS degradation increased from 0.04 h^{-1} to 0.19 h^{-1} at pH 5 for MnO_2 concentrations ranging from 50 to 175 µM. At pH 4, the rate constants of SMP varied from 0.002 min^{-1} to 0.0048 min^{-1} at pH 4 and for MnO_2 concentrations varying from 125 to 510 µM. Hydrophobic isolates of NOM extracted from river water strongly inhibited the degradation of NIS and SMP. Transformation rate of NIS decreased from 0.23 h^{-1} to 0.01 h^{-1} in presence of 1.6 mg C L^{-1}. Similarly, rate constants of SMP decreased from 0.0019 min^{-1} to 0.0004 min^{-1} in presence of 1 mg C L^{-1}. Reduction in reaction rate constants can be explained by competition for active surface sites between micropollutants and NOM. However, the interactions of micropollutants with NOM would also affect their transformation. For example, the presence of NOM enhanced the sorption of NIS on MnO2 but the transformation was strongly inhibited. The sorption of SMP by NOM was also shown in solution by fluorescence extinction measurement. Affinity constants of 0.0365 and 0.0545 L μmol^{-1} were determined for two NOM isolates. This work highlights that the effect of NOM on transformation of xenobiotics by MnO_2 should be considered when studying the behavior of such compounds in soils and sediment.

THE ROLE OF METABOLOMICS IN ASSESSMENT OF HUMANS´EXPOSURE TO BIOLOGICALLY ACTIVE CHEMICALS

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Recently, the potential of diet to modulate toxic effects of environmental pollutants in living organisms has been highlighted by scientists. Metabolomics, an emerging field of "omics" enabling a comprehensive characterization of small molecule metabolites occurring in biological matrices, represents one of the challenging research tools. The techniques most frequently employed for metabolomic fingerprinting and/or profiling of biological samples are nuclear magnetic resonance (NMR) and mass spectrometry (MS) coupled either to separation techniques such as liquid chromatography (LC), gas chromatography, and capillary electrophoresis. Alternatively direct (ambient) ionization methods including direct infusion electrospray ionization mass spectrometry (DI-ESI–MS), desorption electrospray ionization or direct analysis in real time (DART–MS) can be used. Advanced data processing software algorithms and multivariate chemometric tools are typically needed to process complex and multidimensional metabolomics data for the data mining, pre-selection of the signals related to marker metabolites, and for the overall data interpretation.

In the presented study, metabolomics fingerprinting employing an instrumental platform consisting of ultra-high performance liquid chromatography (U-HPLC) / supercritical fluid chromatography (SFC) coupled to tandem high resolution mass spectrometry (HRMS/MS) was used for analysis of human adipose tissue. Special attention was paid to identification of specific markers associated with dietary exposure to various chemicals. Large differences in oxidized lipids and other biologically compounds have been found within the set of examined samples. Challenges in follow-up research will be discussed.

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METAL STABILIZATION IN CONTAMINATED SOILS USING AN AMORPHOUS MN OXIDE (AMO)

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Chemical stabilization of metal(loid)s in soils represents a cheap and environmentally friendly alternative to conventional methods of soil remediation [1]. A newly synthesized amorphous Mn oxide (AMO) was tested as a possible stabilizing amendment for soils contaminated with metals [2]. The AMO was compared with other nano-oxides (maghemite and magnetite) using batch, incubation and column experiments coupled with tests of soil microbial activity. The obtained results showed that the AMO was an effective treatment for the stabilization of metals (Cd, Cu, Pb) in the studied soil samples at the given w/w ratios (0.1, 1, 2%). Its application resulted into significant decreases of exchangeable metal fractions (up to 92, 92 and 93% decreases of Cd, Cu and Pb concentrations, respectively). The adsorption efficiency of the AMO towards Cd, Cu and Pb was 2-3 orders of magnitude higher than those recorded for the other amendments [3]. It was also the most efficient treatment for reducing Cu concentrations in the soil solution. Metal stabilization was a result of combined specific adsorption onto the AMO surface and increase of soil pH promoting the adsorption of metallic cations. Furthermore, the AMO had a positive influence on the activity soil microorganisms, a crucial point in soil remediation [3]. On the other hand, the strongly oxidizing properties of the AMO has to be taken into account as it is able to promote SOM dissolution associated with the (re)mobilization of adsorbed metals. This process was coupled with some dissolution of the AMO, but according to TEM/SEM-EDS analyses, the formation of rhodochrosite ($MnCO_3$) on the particle surfaces stabilized it in the soil [4]. In conclusion, the AMO at lower w/w ratios (especially 0.1%) seems to be an effective and cheap stabilizing amendment. However, its stability and efficiency in rhizosphere environments and field conditions needs to be further evaluated, including experiments with AMO with a surface modified with $MnCO_3$.

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URANIUM (VI) SCAVENGING BY AMORPHOUS IRON PHOSPHATE ENCRUSTING FILAMENTOUS BACTERIA

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During the past decades, the release of uranium from natural sources and anthropogenic activities such as mining, ore processing and waste disposal has increased the need for developing cost effective uranium remediation strategies for contaminated aquatic systems. U(VI) sorption to iron oxyhydroxides, and its precipitation as uranium-containing phosphate minerals, as well as biosorption on bacterial biomass are among the most efficient processes limiting U(VI) mobility under oxidizing conditions. Although phosphate ions significantly influence bacterially mediated as well as iron oxyhydroxide-mediated scavenging of uranium, the sorption or coprecipitation of U(VI) with poorly-crystalline nanosized iron phosphates has been scarcely documented, especially in the presence of microorganisms.

Here we show that dissolved U(VI) can be efficiently bound to amorphous ferric-ferrous phosphate hydroxides during their deposition on *Sphaerotilus natans* filamentous bacteria via Fe(II) oxidation in the presence of phosphate ions. Uranium L_{III}-edge EXAFS analysis reveals the molecular environment of uranium indicating a characteristic U-P distance of 3.6 Å when scavenged by amorphous ferric-ferrous phosphate hydroxide. In addition, when scavenged by *S. natans*, a fraction of the uranyl ions are bound to phosphoryl and carboxyl moeities of the biomass. Furthermore, on the basis of these sorption reactions, we demonstrate the ability of an attached *Sphaerotilus natans* biofilm to remove uranium from solution without any filtration step.

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ISOMER SHIFTS IN HCH COMPOSITIONS OF INDUSTRIAL AFFECTED ENVIRONMENTAL SAMPLES

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Hexachlorocyclohexanes are a group of very wellknown persistent organic pollutions. Despite ceased production and application in the EU in the 90s of the last century, they are still present as prevalent pollutions in the environment today. Influencing quality of water and soil many quantitative studies on HCHs have been performed. Interestingly, in several studies isomeric shifts have been described, e.g. changing the ratio of the isomers from the predominat α-isomer to β-HCH, which is much more persistent and potential carcinogenic.

To understand the reason for these isomeric shifts, isomer specific analyses have been conducted. Samples have been taken from various polluted environmental compartments downstream of a former industrial complex in Germany that produced HCH amongst other chemicals. A huge emission over the last decades from this industrial site is known. In addition to analyses of environmental samples (water, sediments and soils) batch and percolation experiments were performed to investigate isomer specific transport and transfer processes and to simulate corresponding environmental processes like flood events.

Our environmental analyses revealed a broad range of different HCH compositions and, particularly, various isomeric shifts have been detected. Especially in a floodplain soil profile a shift from α-HCH to β-HCH occured with increasing depth. Batch experiments allowed to differentiate the remobilization behaviors of HCH from soil (constant) or sediment (dynamic) pointing to different environmental processes. This implication was based on our approach to link laboratory experiments with natural sample data.

THE ENVIRONMENTAL PHOTOCHEMISTRY OF TRICLOSAN REVISITED: RECONSIDERING THE IMPORTANCE OF INDIRECT PHOTOREACTIONS

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Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) is an antimicrobial agent that is used in liquid soaps, bath foams and other personal care products. It undergoes slow biodegradation in wastewater treatment plants (WWTPs) and in the natural environment and, because of incomplete removal by WWTPs, it is often found in surface waters in both the acidic (HTric) and basic (Tric-) forms (pKa ~ 8) [1]. Triclosan can be photodegraded to produce several intermediates, including a dioxin congener (2,8-dichlorodibenzodioxin, hereafter 28DCDD). The latter is formed from Tric- and causes considerable environmental concern [2].

Based on data of HTric/Tric- photochemical reactivity, the importance of the different photochemical reaction pathways was assessed by means of the software APEX (Aqueous Photochemistry of Environmentally-occurring Xenobiotics) [3], which is based on a photochemical model that has been validated against xenobiotic phototransformation in the field [4]. Differently from current literature reports, we could show that the direct photolysis would not be the only important transformation pathway of triclosan in surface waters. Indirect photochemistry plays a particularly important role for HTric, which could undergo very significant reactions with both ·OH and the triplet states of chromophoric dissolved organic matter (3CDOM*).

Model calculations suggest that reaction with 3CDOM* would be by far the main pathway for HTric phototransformation in deep waters with high dissolved organic carbon (DOC). In contrast, reaction with OH could prevail in low-DOC waters.

In the case of Tric- the direct photolysis is much more important than for HTric, but triplet-sensitised transformation could produce 28DCDD with higher yield compared to the direct photolysis. Therefore, reaction between Tric- and 3CDOM* could play a significant role as dioxin source in deep waters with elevated DOC.

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PHOTOSTABILITY STUDY OF DIFFERENT UV FILTER COMBINATIONS IN SUNSCREENS UNDER DISSINFECTION CONDITIONS

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Sunscreen products are widely used in daily cosmetics. The photostability of UV filters, both organic (such as avobenzone) or inorganic (TiO_2) should be preserved during their application and storing. But, unfortunately, organic molecules are marked by their degradation under UV-light, whereas inorganic filters are triggered by their photocatalytic reactions. Additional challenge in photostability of filters is represented by the media, such as swimming-pool waters with excessive presence of chlorine. For this purpose reference mixtures containing avobenzone, TiO_2 and commercial sunscreenproducts (Hawaiian®, Garnier®, Nivea®) all with protection factor SPF30 were expossed to UVA and UVC radiation in deionised and chlorinated water in order to study the degradation kinetics, by-products and toxicity tests. The kinetics studies revealed different degradation rates, since commercial sunscreen products contain several other components, which could protect the organic molecule from hydroxyl and chlorine radical attacks. Another interesting fact is, that avobenzone in chlorinated water is immediatelly transformed to its chlorinated product, which is insensitive to the photolysis and photocatalysis (since commercial sunscreens contained all TiO_2).

The toxicity of avobenzone in standard mixtures and in commercial products prior and after UVA experiments were assessed employing Vibrio fischeri luminescent bacteria. The assessment revealed higher adverse effects in case of all treated samples (avobenzone and commercial products) in chlorinated waters. In fact, in all cases up to 80% luminescence inhibition was present (chlorinated water expressed only 35%), whereas in non-chlorinated waters ranged from 34% to 87% depending on the commercial product.

PHOTOCATALYTIC PROCESSES ON TiO_2–REDUCED GRAPHENE OXIDE HYBRID MATERIALS: UV-BASED, DYE-SENSITIZED OR VISIBLE-SENSITIZED PHOTOCATALYSIS?

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Graphene oxide (GO) was adsorbed on TiO_2 and chemically reduced at RT. Hybrid materials with different reduced GO (rGO) loadings were produced on anatase and silica and their photocatalytic activity was compared with pristine materials using phenol and methylene blue (MB) under two different irradiation conditions (UV-Vis and Vis only). The aim was to clarify the role of rGO in the photocatalytic mechanism. MB is strongly adsorbed at the surface of the hybrid materials, and the amount of adsorbed dye increases with increasing the rGO loading. Significant MB degradation rates were observed with pristine titania and with hybrid TiO_2-rGO materials, both under UV-Vis and Vis only. The presence of rGO had the largest effects on the degradation kinetics under Vis light. The absence of MB degradations with rGO-silica excludes that MB could inject electrons to rGO. MB is rather degraded by injecting photoexcited LUMO electrons in the TiO_2 conduction band. Therefore, the degradation under Vis-light is due to a dye-sensitized photocatalytic mechanism, while under UV-Vis the semiconductor-based photocatalytic mechanism is working. The role of rGO seems to be limited to that of adsorbent. Conversely, the presence of rGO reduces the rate of photocatalytic transformation for the poorly adsorbed phenol under UV-irradiation, while negligible transformation rates were observed under Vis on both pure titania and TiO_2-rGO. No photocatalytic mechanism is thus operating in the visible. The analysis of UV-Vis absorption spectra at different rGO loadings shows that the decrease of phenol degradation under UV is due to the decrease of the band-gap absorption of TiO_2. From this set of experimental data, it emerges that the beneficial effect of rGO at the TiO_2 surface is related only to the increase of adsorption. Therefore, inferences drawn by single-substrate experiments, particularly with dyes (e.g. MB), or with a single irradiation type can be misleading.

BIOTRANSFORMATION OF VARIOUS SACCHARIDES AND PRODUCTION OF EXOPOLYMERIC SUBSTANCES BY CLOUD-BORNE *BACILLUS SP.* 3B6

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France,

The ability of *Bacillus sp.* 3B6, a bacterial strain isolated from cloud waters, to biotransform saccharides present in the atmosphere was evaluated using in situ 1D and 2D NMR spectroscopy. *Bacillus* is one of a genus most frequently described in the air and atmospheric waters. Sugars present in these environments have a biogenic origin; they include alditols, monosaccharides, disaccharides, oligosaccharides, and polysaccharides.

Bacillus sp. 3B6 was able to efficiently metabolize sugars, which could thus provide sources of energy for this bacterium and allow it to live and to be metabolically active in warm clouds. In addition, a number of these saccharides (L-arabitol, D-fructose, sucrose, D-glucose, cellotetraose, cellulose, and starch) were transformed to EPSs (ExoPolymeric Substances). We have clearly identified the structure of two EPSs as 1,6-α-galactan and partially acetylated polyethylene glycol (AcPEG). 1,6-α-galactan is a newly described polymer. The production of EPSs might protect this bacterium under hostile cloud environment conditions, including low nutrient availability, cold temperature and freeze-thaw processes, UV and radical exposure, and evaporation–condensation processes and thus to desiccation and osmolarity changes. EPSs could also have a potential role in atmospheric processes because they can be considered as secondary organic aerosols and efficient cloud condensation nuclei [1].

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ATMOSPHERIC DEPOSITION OF NUTRIENTS AND FLUX MEASUREMENTS IN FIJI

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Deposition of nutrients (nitrate, sulphate and phosphate) in aerosols and rainwater was investigated for two sites on Viti Levu which is the main island in Fiji. One site was from the windward side (Koronivia) while the other (Lautoka) was from the leeward side. The study period coincided with two dry seasons and one wet season.

The annual nutrient fluxes in aerosol samples were; 1,280.83 mg/m^2 (NO_3^-), 11,577.49 mg/m^2 (SO_4^{2-}) and 122.30 mg/m^2 (PO_4^{3-}) at Koronivia and 3,655,31 mg/m^2 (NO_3^-), 10,679.47 mg/m^2 (SO_4^{2-}) and 310.73 mg/m^2 (PO_4^{3-}) at Lautoka. On the other hand, the nutrient fluxes in rainwater samples were; 397.98 μeq/L (NO_3^-), 8,824.40 μeq/L (SO_4^{2-}), and 35.77 μeq/L (PO_4^{3-}) at Koronivia and 7,218.24 μeq/L (NO_3^-), 18,729.62 μeq/L (SO_4^{2-}) and 6,991.87 μeq/L (PO_4^{3-}) at Lautoka.

Seasonality was observed to influence the nutrient flux at both the sites. The data show that the dry deposition is the predominant pathway for the nutrient flux at Koronivia while the wet deposition predominates at Lautoka.

DISPERSION MODELING OF PAHS IN URBAN AIR: A NEW APPROACH COMBINING DISPERSION MODEL WITH GIS AND PASSIVE AIR SAMPLING

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This study introduces a new approach for evaluating concentrations of atmospheric pollutants, combining air dispersion modelling and a geographic information system (GIS). This approach can be useful in medium and long term air quality assessment.

A dispersion model was applied to four high molecular weight polycyclic aromatic hydrocarbons (PAHs) – benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[123-cd]pyrene in the urban area of Liberec, Czech Republic. This area has significant industrial, traffic and domestic heating sources. The air dispersion modelling was performed using the Czech Gaussian model SYMOS´97. GIS was used both for processing of input data as well as visualization of the modelling results. The outcomes of the dispersion model were compared to the results of passive air sampling (PAS), which was carried out at three urban, two rural and two mountain sites within the study area over a concurrent one year period.

While the model and PAS data capture the same general seasonal trends, the PAS measurements are higher, and include also some unexpectedly elevated concentrations, indicative of sources not captured in the model inputs. Despite discrepancies between measured and modelled concentrations, an approach combining the two techniques is promising for future air quality assessment. Differences between measured and modelled concentrations, in particular when measured values exceed the modelled concentrations, are indicative of undocumented, sporadic pollutant sources such as biomass burning or forest fires. Thus, these differences can also be useful for assessing and refining emission inventories.

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NEEDLE NET – PINE NEEDLES IN A POSITION OF PASSIVE SAMPLER IN HIGH MOUNTAINS SITES

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Needle net project as the cross-border cooperation of the Czech Republic and Slovakia was created due to the implementation of the pilot study. The main objective is to research and verify the new method determining the burden of chemical substances in ambient air using biomonitoring matrices. Needles (two and three years old) of Swiss mountain pine (*Pinus mugo)* were used in a new approach in biomonitoring design and needles of Scots pine (*Pinus sylvestris*) were used as a second suitable type of passive sampler. Both are financially available, easily sampled and there are an appropriate instrument for determining concentration of persistent organic pollutants for selected localities of Little Fatra, Great Fatra and Tatra mountains in Slovakia. Selection of sites for biomonitoring was chosen with geology and weather conditions taking into account. These factors influence the fate sorption of pollutants and their subsequent bioaccumulation in living organisms. Samples of needles were taken at different altitudes because of the demonstration of the potential long-range transport of controlled substances. At higher altitudes (1000 m asl) are no longer present local pollution sources. Long-range transport can be transmitted on the area of air pollutants from southern Poland or the Moravian-Silesian Region (cross-border transport), where is developed heavy industry in many sites. The scope of this study is extensive regarding the analysed compounds. Polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), perfluorinated compounds (PFCs) were analysed. In second important part of research, the samples were used for determination of concentration of heavy metals, genotoxic effects (e.g. abortivity of pollen grains). The project serves to significantly improve cooperation on regional and European level. Evaluation of the results and their access to the professional community, local elected representatives, state legislators and the public can be used as a basis for correcting the situation and taking measures to the reduce the burden on the environment by POPs and heavy metals.

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TOWARD A BETTER UNDERSTANDING OF CLOUD AQUEOUS PHASE OXIDANT CAPACITY: RELATION BETWEEN HYDROXYL RADICAL AND CARBOXYLIC ACIDS FATE

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The physico-chemical composition of cloud aqueous phase collected at the Puy de Dome (pdD) station (1465 m a.s.l.) in France was studied during two campaigns in October /November 2013 and a March/April 2014. During this period only oceanic air masses were collected. Total Organic Carbon (TOC), four carboxylic acids, hydrogen peroxide as well as major inorganic anions and cations concentrations were determined. This work was focused on the quantification of oxidative capacity trough production rate of hydroxyl radical (HO·) using terephtalic acid (TA) probe technique [1]. The main aim is to correlate the contributions of nitrate, nitrite and hydrogen peroxide to the formation rate of hydroxyl radical as function of their concentration. Moreover irradiations in the presence of TA have been performed on synthetic cloud aqueous solutions, in which chemical composition is closed to the real samples. The contribution to the HO· formation rate due to nitrites and nitrates is lower than 10% for oceanic water while the hydrogen peroxide contribution grows up to 80%. This work shows that hydroxyl radical formation rate in oceanic cloud water is mainly due to the hydrogen peroxide photolysis while contribution of nitrate, nitrite, complexed iron (via Fenton and PhotoFenton processes) and dissolved organic matter is negligible. This work reports, for the first time, a correlation between physico-chemical parameters and oxidative capacity of atmospheric aqueous phase. In a second step experimental data will be compared to those obtained using a dynamic air parcel model that was developed to simulate tropospheric cloud events (M2C2) [2] as a function of different air masses origins.

Hydroxyl radical in cloud water reacts with inorganic and organic compounds: when oxidation of organics occurs, the concentration of short chain carboxylic acids increase. This process has been investigated at the end of our work.

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SOFT WALL CAPPING: A BETTER WAY OF CONSERVING RUINS? INVESTIGATING THE USE OF SOIL AND OTHER PLANTS TO PROTECT RUINED WALL HEADS

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This work addresses the role of soft capping method (grass and other plants used to cover wall heads) as a tool for conserving ruins [1]. The aims of the study were to test whether soft capping works effectively and determine the best practice for its implementation. In particular, this investigation evaluates whether soft capping enhances or reduces chemical weathering of vulnerable stone materials in comparison with that occurring on bare ruined surfaces.

For that purpose, some samples of different materials (calcite, limestone and gypsum) were exposed to open air and others covered with diverse kind of caps. The effects were analysed using a multianalytical non-destructive methodology based on the examination of the physical features (colour, hardness, material loss, etc.), followed by a study with Raman spectroscopy and Scanning Electron Microscope. These results were corroborated by chromatographic analysis aided by chemometrics and chemical modeling.

Results showed that the soft capped samples had lower rates of deterioration than the uncovered samples. Limestone and gypsum were more protected using a cap of sedum, whereas calcite showed less degradation with grass capping with sedum plugs. To comprehend the adverse effects, the degradation was studied focusing on the source. The comparison between original and decaying compounds allowed us to identify the reactions that provoked the degradation and to establish that they were initiated by the organic matter and sulphates of the soil.

Therefore, the study concludes that soft wall capping plays a useful role in the conservation of ruined monuments, a method encouraged by its relatively inexpensive and easy installation and maintenance. Additionally, thanks to the combination of the green analytical tools used, the optimum cap and soil characteristics can be selected to improve the conservation of the ruins.

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A PRACTICAL APPROACH TO "GREENING" THE MULTIELEMENTAL ANALYSIS

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The idea of Green Chemistry known form the beginning of the 1990s is a contribution of chemists to the concept of sustainable development; it is a result of the greater consciousness within the chemical community on the impact of chemicals on human health and the environment. Adopted to analytical processes, this approach is known as an area of Green Analytical Chemistry (GAC). Besides typical analytical characteristics (limits of detection, repeatability, sensitivity, etc.), other features such as the reagents/sample amount, waste balance, energy-effective procedures, operation time and safety, etc., should be taken into account in order to meet the GAC principles. The ideal green analysis can be characterized by elimination or minimal use or reagent, minimal use of energy and no waste production. From this point of view, there are still many way in which "greening" applicable to every step of the analytical process from a procedure optimizing, sampling to data processing1-3. In the field of multielemental analysis, widespread atomic spectrometry methods usually involve well-established but environmentally demanding "wet" sample pre-treatment methods.

In this work, main goal was sample downsizing, limiting of the pretreatment steps before ICP-OES/MS analysis and using a low-consumption sample introduction system, which resulted in considerations of: (i) salinity of digests, (ii) matrix effects (ME), and (iii) the environmental footprint of both methods. Possible downsizing of sample mass or final volume of digest is closely connected with the analytical performance of the ICP-OES/MS methods (limits of detection) and, on the other hand, with the degree of salinity of samples. Higher amount of total diluted salts allowed to be introduced to the ICP-OES (up to 30 % w/v, in the ICP-MS only 0.1% w/v) increases the ME risk. The ME was discussed as an effect of individual components or mixtures (Li, Na, K, Ca, Mg, Rb, Ba, La, and acids up to 20 g L^{-1}) in connection with sample introduction system used. Using of the ICP-OES with the low-consumption introduction system resulted to a "nearly matrix-independent" method more environmentally friendly than the ICP-MS method analyzing the same downsized sample.

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IONIC LIQUIDS AS MODIFIERS OF ELECTROPHORETIC SYSTEMS IN DETERMINATION OF AMINO ACIDS, CATECHOLAMINES AND STEROIDS

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In recent years the interest in ionic liquids (ILs) has been increased due to their unique properties. They consist of the bulk organic cations and inorganic anions. ILs are characterized by high viscosity, non-volatility, the ability to dissolve polar and nonpolar analytes, high ionic conductivity. Introduction of ionic liquid into chromatographic and electrophoretic systems and their use in sample preparation could facilitate selective extraction of analytes, reduce analysis time, increase efficiency.

In this work the influence of imidazolium-based ionic liquids with alkyl radicals C12 and C16 (C12MImCl, C16MImCl) on electrophoretic parameters of hydrophilic (amino acids, antioxidants polyphenol type, catecholamines) and hydrophobic (steroids) analytes in CZE and MEKC was studied.

The influence of pH value, background electrolyte concentration and the length of the alkyl radical of IL (C12, C16) on efficiency and migration parameters of analytes in CZE and MEKC were investigated. It was observed, that the addition of IL in background electrolyte (phosphate buffer, pH = 2.0) results in increase efficiency for certain amino acids and catecholamines in CZE and increase separation selectivity in MEKC at 2-3 times.

It was showed the possibility of determination of analytes without absorption in the UV region such as glycine by indirect detection at 220 nm using IL C12MImCl as an additive in electrophoretic system.

The possibilities of on-line preconcentration of bioactive substances using ILs to increase sensitivity of UV detection of analytes were investigated. Using field-amplified sample stacking with C16MImCl as a component of buffer electrolyte allowed to concentrate tryptophan, tyrosine, 3,4-dihydroxyphenylalanine, epinephrine, norepinephrine, dopamine, normetanephrine at 10-14 times. The detection limits of amino acids were 30-55 ng/ml.

It was revealed the possibility of using ILs as a micelle-forming agent. Obtained results were compared with traditionally used cationic surfactant – cetyltrimethylammonium bromide. It was found that addition to the running buffer the ionic liquid C16MImCl at a concentration above the CMC, when it acts as a pseudostationary phase, provides the separation of hydrophobic steroids.

The potential of using hydrophobic imidazolium-based IL with C6 and C8 radicals and tetrafluoroborate and bis (trifluoromethylsulfonyl)imide (NTf2) anions as extracting solvents for amino acids and steroids from aqueous solutions was studied. It was developed a sample preparation of urine for electrophoretic analysis of amino acids with the use of C6MImNTf2 as extracting solvent. The percent extraction of analytes was 92-100%.

The regularities established on model systems were validated on real objects, namely determination amino acids and corticosteroids in urine samples. For determination of amino acids ILs were used both in the extraction step and in electrophoretic separation of analytes, for steroids – only at the last step.

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CAPILLARY LIQUID CHROMATOGRAPHY: GREEN ANALYTICAL TECHNIQUE AND SOME SIMPLE WAYS OF ITS REALIZATION

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Reduction of organic solvents consumption as well as replacement of some solvents with less harmful alternatives is required by the green chemistry philosophy. High performance liquid chromatography (HPLC) is a widely used tool in analytical chemistry. Hence, in the green analytical chemistry, a solvent consumption of new liquid chromatography methods should be reduced substantially. Realization of the HPLC with capillary columns thus represents a straightforward option of the significant solvent consumption decrease. Namely, N-fold reduction of the internal column diameter leads to N^2-fold reduction of the column cross section and the corresponding flow rate as well.

In this presentation, some equations related to the column diameter reduction will be highlighted and resulting demands on the sample injection volume and the photometric detection will be discussed.

Acetonitrile is a common organic modifier in HPLC mobile phases due to UV transparency, low viscosity and low reactivity. However, the green chemistry prefers usage of methanol or even ethanol or acetone as environmentally more friendly solvents. Some properties of these solvents will be discussed as well. Finally, some simple options of the realization of isocratic and gradient capillary liquid chromatography will be presented.

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SULPHATE EXPOSED BEACHROCK CEMENT QUANTIFICATION: THE CASE OF HIGH MAGNESIUM CALCITE

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Beachrocks are coastal formations constituted through the precipitation of carbonates in the intertidal zone. The studied beachrock is uncommonly placed in temperate latitude, in contrast to the most documented tropical and subtropical locations. Surprisingly, it contains abounding slag (composed of iron oxides, tephroite or cristobalite, among others) trapped due to the pollution derived from the strong industrialization of the area (Nerbioi-Ibaizabal estuary).

The main cements between those grains are aragonite and high magnesian calcite. For the latter, known as HMC, a semiquantitative model was developed through Raman spectroscopy basing on the full width at half height (FWHH), where the $MgCO_3$ content resulted to be proportional to the FWHH. Applying this lineal function to real samples spectra, for example a 8-10% of $MgCO_3$ was estimated in the HMC cement.

Additionally, Raman spectroscopy revealed gypsum ($CaSO_4.2H_2O$) together with carbonates in cements of some outcrops. Gypsum crystals were present also in the intraporous space of trapped grains, mixed with augite ($Ca,Mg,Fe,Ti,Al_2(Si,Al_2O_6)$. The presence of these two compounds and carbonates, added to low temperatures and high humidity, might have promoted the formation of thaumasite ($CaCO_3.CaSO_4.CaSiO_3.15H_2O$), identified by Raman and DRIFT. It is a degradation product usually associated to sulphate attack and its chemical formation pathway will be discussed.

The analytical proceeding yielded a semiquantitative model to characterize the carbonate cements and provided information about the kind of reactions that can take place within beachrocks, giving an insight of the complexity of the phenomenon occurring in this marine realm. Thus, environmental concern about this reservoir of contaminants should be increased regarding the possible effects that their disintegration might cause on the ecosystem and human health.

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STABLE CARBON ISOTOPE COMPOSITIONS OF DITERPENOID HYDROCARBONS IN COALS FROM SMEDEREVSKO POMORAVLJE FIELD, KOSTOLAC BASIN, SERBIA

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This study was conducted on Upper Miocene lignite samples from the Kostolac Basin, Smederevsko Pomoravlje field (Serbia), aimed to determine genesis of coal and potential for economic exploitation.

Carbon-isotope composition of the diterpenoid hydrocarbons was determined for ten coal samples that originate from three coal seams: I at depth interval 23.30 m to 67.25 m; II at 56.30 m to 85.20 and seem III at depth interval 83.65 m to 123.00 m [1].

Compound specific stable carbon isotope analyses were carried out by gas chromatography–isotope ratio monitoring-mass spectrometry (GC–irmMS).

Content of total organic carbon falls within the limits typical for lignite and varies between 20.37 % and 52.13 % with average value, 37.85 %. Biomarker analysis of lignite extracts indicate that main precursors of organic matter are gymnosperms and in significantly lower amount microbial biomass, ferns and angiosperms.

The δ13C values of most abundant individual diterpenoids range from -29.9‰ to -25.6‰ for pimarane (average value -27.5‰) and from -28.5‰ to -26.1‰ for 16α(H)-phyllocladane (average value -27.0‰) (vs. PDB), respectively.

Although it was proven that several gymnosperm families produce precursors of both biomarkers (*Cupressaceae, Podocarpaceae, Araucariaceae*) [2], slight difference between δ13C values of 16α(H)-phyllocladane and pimarane, indicate that these biomarkers in addition to their mutual precursors have additional sources. 16α(H)-Phyllocladane can be related to Phyllocladaceae (which do not produce pimarane structural class), whereas different δ13C values of pimarane can be attributed to contribution of Pinaceae. Such gymnosperm assemblage in investigated lignite indicate moderately continental climate with seasonality between winter and summer and moderate precipitation during Upper Miocene in Serbia.

These results indicate that carbon isotope data could be useful for analyses of the organic matter which will allow reconstruction of paleoenvironmental and climatic conditions, as well as to attend changes in modern environment.

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THE INFLUENCE OF IRON IONS ON THE PHOTO-DEGRADATION OF POLYETHYLENE

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Polyethylene (PE) is one of the most widely used materials in the world and accumulated in the environment due to their very low biodegradability. However, to increase the bio-degradation rate, metal salts used to promote the oxidation resulting in micro-fragments of PE, which is an important stage for potential bio-degradation, and metals which will remain in the environment carry no risks of pollution.

This study investigates the influence of ferrous and ferric ions on the photo-oxidative degradation process of low density polyethylene (LDPE) under accelerated test conditions. LDPE was blended with iron (1% in weight) by using HAAKE MiniLab twin-screw micro compounder. Samples were initially exposed to various times of UV radiation and periodically analyzed by means of spectroscopic and rheological tolls. The chemical evolution of the irradiated samples was examined by monitoring the photo-oxidation products using FT-IR spectroscopy. Moreover, the UV-vis spectra suggest a reduction of Fe(III) into Fe(II) during sample irradiation. Changes in the molecular structure of samples were followed by an original methodology based on melt rheology. It is well known that the evolution of the rheological material properties directly reflects changes in molecular parameters. The linear viscoelastic properties in dynamic experiments are sensitive both to the chain scission and to the three-dimensional network formation. Thus, melt rheology allows the prediction of the particular behavior due to the competition of chain scissions and recombination reactions occurring through aging.

The results demonstrate that neat LDPE samples did not exhibit significant changes during the evaluated irradiation period. Nevertheless, addition of iron ions (Fe(II) and Fe(III)) play an important role in the decomposition of hydroperoxide and, as consequence, accelerates the photo-degradation of LDPE. The UV-vis spectra suggest a reduction of Fe(III) into Fe(II) during sample irradiation and consequent oxidation of polymer. The occurrence of a heterogeneous oxidation in blends films through photo-aging was observed, scissions/recombinations counterbalance and the photo-aging could involve successive steps. At last, chain scissions are predominant. The efficiency of Fe(III) addition was more important than Fe(II) to accelerate the photo-degradation of LDPE. Finally, the obtained results were compared to samples analyzed with a UV coupled melt rheology (UV in situ irradiation) which is even less common way to assess photo-oxidation of polymers. The results are in agreement with trends observed with the precedent analysis methods and show that iron ions are a powerful way to obtain controllable-degradation PE.

FLAME RETARDANTS AND THEIR OCCURRENCE IN THE TERRESTRIAL ECOSYSTEM

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This study was focused on the analysis of four compounds from a brominated flame retardants group, namely pentabromoethylbenzene, hexabromocyclododecane, hexabromobenzene and tetrabromobisphenol A. Matrices were represented by four soil samples and four seats of fire samples. In addition, bisphenol A was also examined. As a first step, the process of extraction of the analytes from matrices was optimized. Three different extraction techniques were tested (pressurized solvent extraction, microwave-assisted extraction and ultrasound-assisted extraction). The next step was to verify the stability of target compounds in strongly acidic conditions and to optimize the clean-up of an extract by a column chromatography using different types of sorbents and eluting solvents. On the basis of several experiments, the gas chromatography with electron capture detection (GC-ECD) was chosen as an appropriate analytical method for the determination of brominated flame retardants. Bisphenol A was investigated by the gas chromatography with mass spectrometric detection (GC-MS). Phenolic analytes were derivatized before their final analytical determination. The most abundant analyte was the hexabromocyclododecane which was quantified in all matrices in the range of 7.018-81.88 ng/g dry weight. On the contrary, tetrabromobisphenol A was not proven in any of analyzed samples. The ash from the Brandýs nad Labem restaurant fire contained the highest amount of all target compounds (total 118.2 ng/g dw). The least contaminated place was the forest burnt-out area near Velmovice (hexabromocyclododecane only, 7.843 ng/g dw). As for soil samples, greater concentrations were found in the area near the industrial site in Chropyně, where a store of plastic materials burnt down in 2011. The analysis of the seat of fire samples showed that compounds of interest are more abundant in ash than in a soil part (some of them were mixtures of ash and soil). All measured concentrations fall within a range in which these analytes are present at many other places in the world (tenths to tens ng/g dw).

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DEGRADATION OF GLYCOL BASED HEAT TRANSFER FLUIDS

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Glycol based heat transfer fluids represent the largest part of antifreeze liquid heat transfer media in the automotive, buildings, solar thermal systems and aviation as deicers. World annual consumption ranges in units of millions of tons and is continuously growing. This amount naturally is putting certain demands on the environment. There are two main reasons for this. The first one is given by production, as the primary raw materials for the production of glycols are oil and coal and the second is due to a very benevolent handling of the spent media.

Glycols are well degradable in environment and their half-life is in the order of days or tens of days. The problem arises only when a large amount of glycols gets into the aquatic ecosystem at a time, because for their biological degradation is needed a large amount of oxygen. Unfortunately glycols, which have been used as anti-freeze component, are contaminated by their own products of degradation and by the corrosion products. Furthermore there is no comprehensive study that would address the toxicity of the spent glycol based mediums, because with the variability of the thermal systems and the different phase of the degradation is virtually impossible to obtain relevant data.

Our long-term research in this area is focused on the analytical determination of the general degradation products formed during common use of these fluids in the thermal systems. The aim is to identify the major products, their toxicity and what influences their formation. The current results clearly demonstrate the dependence between temperature stress and the formation of some degradation products, which are dangerous for the environment. In particular, the formation of organic acids formed by oxidation of present alcohols even without oxygen was observed. Namely we have identified formation of formic, acetic, lactic, glycolic and oxalic acids.

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POSTER PRESENTATIONS

Session A:

Soil chemistry, Soil contamination, Remediation technologies

Posters A-01 – A-07

Poster A-01

THE CRITICAL MICELLE CONCENTRATION OF HUMIC ACIDS OF DIFFERENT ORIGIN

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The formation of humic acids is one of the least understood aspects of humus chemistry and one of the most intriguing. Humic acids are found in high concentrations in different types solid caustobiolites (peat, coal and sapropel), soil and water bodies. They play an important role in protecting the environment through a variety of physical and chemical properties [1-2].

For the implementation of specific environmental features not responsible humic acid as a whole, but the individual components. Knowing the concentrations at which the humic acids are in the form of micelles may be obtained from their homogeneous group of compounds with known properties [3-5].

As objects of study were two different types of peat genesis: eutrophic alder peat, mesotrophic sphagnum peat and sapropel of the Upa River in Tula region.

Humic acids isolated by the procedure recommended by the International Society for the study of humic substances. The standard method using stalagmometry, got dependence of surface tension on the concentration of humic acids. The isotherm of each sample of humic acids $\sigma = f(C)$ have a characteristic appearance for surfactants.

At concentrations lower the critical micelle of concentration of humic acids are in the form of separate molecules of surfactants and at concentrations above the critical micelle of concentration of humic acids gather in the micelle. For humic acids eutrophic alder peat critical micelle concentration is 0.25 g/100ml, for mesotrophic sphagnum peat - 1.0 g/100ml, for sapropel - 1.5 g/100ml.

Humic acid older sediments in the aqueous solution are in the form of micelles, but young humic acids represent individual polymer molecules.

Humic acid tend to form micelles, which are characteristic for sorption properties. Humic acids with high values of the critical micelle concentration should have large sorption capacity with respect to heavy metals and organic compounds.

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POPs AND HEAVY METALS IN MID-SIZE URBAN, AGRICULTURAL AND FOREST SOIL TYPES OF BRNO: BUILDING GIS DATABASE OF POLUTANTS FOR FATE ANALYSIS AND PREDICTIVE MODELS

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Geological mapping 1:25 000 of the broader region of Brno provides a multilayer geographic information system. Each of the 8 map sheets is represented by 60 soil sampling sites and 20 additional subsoil specimens. A series of the GIS layers show the spatial distribution of persistent organic compounds (POPs) and selected heavy metals in soil. The POPs include the 16 priority PAHs, PCBs, DDT and their metabolites. The absolute amounts of POPs show different relationships to total organic carbon (TOC) in the soils which acts as the principal pollutant sorbent. Samples with natural background values show a basal trend of POPs with TOC while those anomalously contaminated form their separate trend. Pollutant types are characterized by selected ratios of compounds, e.g. PAHs originating from petrogenic and pyrogenic processes. Multivariate statistics, such as cluster analysis and PCA, is applied to evaluate similarity of the chromatographic fingerprints and 8 groups are identified suggesting contamination of certain source and fate. The heavy metal distribution patterns show areas with increased amounts of selected more toxic elements. From the analysis of spatial relationship of sampling locations and the geological substrates the possible contribution and mixing of the heavy metals of geological and anthropogenic origin are evaluated. The GIS database is built together with other factors affecting the contaminant amount and geographical distribution, such as soil type, vegetation, land use, agricultural history, industrial sources, landscape topography, and climatic data. As many of the pollutants are transported primarily on nanoparticles in the air, the dynamics of the atmospheric processes is also included in the database following the approach used e.g. by [1]. The first graphic solutions show the promising future possibilities of testing alternative models of POPs and heavy metal distributions, origin and fate using 640 sample dataset in mid-size urban systems of about 1040 km^2 with forest and agricultural surroundings.

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Poster A-03

COUPLED CONCENTRATION AND ISOTOPE ANALYSES AS A TOOL FOR IDENTIFYING Pb MIGRATION IN SMELTER-IMPACTED DECIDUOUS AND CONIFEROUS ORGANIC SOIL HORIZONS

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The retention of Pb in smelter-impacted coniferous forest soil horizons L, F+H, A and C, were studied using a column experiment. Based on the addition of Pb with a specific Pb isotopes composition (*American galena*) it was found that with the exception of the L horizon, all of the added Pb was completely retained in soil horizons. The isotope composition of Pb in eluate from the L horizon was represented by linear mixing between the original and added Pb sources. Based on the calculation, under natural conditions, the majority of Pb would be completely eluted from the L horizon after less than 5 years.

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PESTICIDE PERSISTENCE IN AN AGRICULTURAL MEDITERRANEAN SOIL. ROLE OF ALTERNATIVE INFLUENT SOLUTIONS

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Degradation is the most important process affecting disappearance of pesticides from soils. The effects of irrigation with control water (MQ), wastewater (WW) and dissolved organic carbon solutions from sewage sludge at two concentrations (30 and 300 mg L^{-1}, DOC-30 and DOC-300) on the degradation in an agricultural soil of thiacloprid (THC), pendimethalin (PDM) and fenarimol (FEN) were assessed. Soil was sterilized to evaluate the biotic contribution and dehydrogenase activity (DHA) was determined as an index of microbial oxidative activity. Degradation rate was ranged in the order THC >> PDM > FEN and did not correlate with pesticide hydrophobicity. FEN degradation was not influenced by the use of the different solutions. WW slightly increased PDM persistence, in accordance with the lower DHA along the experiment, but it did not influence the rapidly degraded THC. DOC solutions produced different effects on THC and PDM. While DOC-300 did not alter the persistence of THC, the use of DOC-30 slightly reduced it. This fact agrees with a higher soil DHA in the first month of the experiment with the DOC-30 solution. At the same time DOC-30 enhanced the persistence of PDM (moderately persistent), while DOC-300 led to the lowest persistence. Soil DHA with DOC-300 tends to increase in the second half of the experiment. It is possible that two opposite processes occur at the same time, the capacity of DOC to enhance pesticide bioavailability and the increase in microbial population. The effect of organic amendments on pesticide degradation and soil microbial activity has been reported to be dependent on OC source, application rate and chemical nature of pesticides [1]. Although microbial degradation was predominant for the three pesticides, with biological contributions ranging from 0.57-0.75 for PDM, 0.65-0.78 for FEN, and 0.91-0.96 for THC, chemical processes cannot be totally excluded.

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Poster A-05

SOIL RESPIRATION AS A QUALITY INDICATOR OF A MINING SOIL AMENDED WITH THREE TYPES OF SEWAGE SLUDGE

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Soil biological indicators include measurements of micro- and macro-organisms, their activities or functions. Soil microbial biomass compared with that of macro-organisms is a more sensitive indicator and is influenced by different ecological factors, like soil organic matter content. As microorganisms play an essential role in maintaining biogeochemical cycles in the soil, microbial respiration is a frequently measured parameter in soils, reflecting the basic turnover rates and responding rapidly to perturbations or soil management changes. However, it is important to know that these biological indicators have advantages and disadvantages and their selection should be based on easiness of measurement, reproducibility and sensitivity to variables that control quality and soil health. Therefore, our aim was to analyse whether and to what extent microbial abundance and activity were affected by the amendment of exogenous organic matter to a mine soil.

Incubation experiments were carried out with a limed acid mine soil (Riotinto, Spain) plus stabilized (SSL), composted (CSL) and co-composted (CLV) sewage sludge at several doses. Substrate induced respiration (SIR) and soil chemical properties (pH, EC, OC) were determined at different times during 45 d of incubation. Several indicators as C mineralization quotient (qM), microbial community activity (metabolic quotient, qCO_2) and soil basal respiration (SBR) were calculated. An increase of soil microbial respiration upon application of sludge was found, CLV>CSL>SSL, and soil microbial respiration was dependent on application rates. This effect was, on the one hand, attributed to the input of microbial biomass from the three amendments (no differences among types) and, on the other hand, it was assumed that additional C contained in these organic substrates activated the indigenous soil microbiota. Addition of co-compost induces a decline in the substrate utilization efficiency of the soil microbial community.

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Poster A-06

SOIL ORGANIC CARBON STABILIZATION BY TECHNOSOLS MADE UP OF COMPOST AND FE-RICH MUD

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The application of organic substrates to soil aims to increase stocks of organic carbon (OC) to preserve and enhance soil fertility and productivity. However, these amendments generally provide sources of labile carbon (C) that are rapidly mineralized in soil. Therefore, more efficient strategies for C storage in soil are currently needed. The preparation of technosols derived from unconsolidated wastes is increasingly considered a cost-effective strategy for land restoration that contributes to increase C stocks in soil while re-using waste products. Technosols were prepared from compost (municipal sewage sludge) and Fe-mud (by-product from an iron mine with a 45% Fe oxide) at 90:10 and 70:30 ratios (w:w). The technosols were acidified and water saturated to promote the formation of organomineral interactions, this being a mechanism that can contribute to increase C resilience in soil. The mixtures were incubated at 28°C for 9 d. Saturated and incubated compost was used as control. The characteristics of dissolved organic carbon (DOC) and mineralization rates were used as indicators of OC chemical stability in a degraded soil amended with these technosols. The DOC was isolated from the technosols and analysed by spectrofluorometry. The technosol derived from Fe-mud previously acidified (pH = 5) showed the most effective protection against OC mineralization reducing twice the soil respiration rate, which was likely related to the decrease of DOC concentration (up to 3 times). Application of composite amendments to degraded soils might constitute a highly effective approach for increasing soil C stocks and a suitable alternative to conventional strategies based on single organic amendments.

Poster A-07

ASSESSMENT OF QUALITY INDICATORS FOR ORGANIC WASTES AS SOURCES OF ESSENTIAL NUTRIENTS

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The addition of organic wastes to degraded soils can increase soil organic carbon (OC) stocks while providing a source of essential nutrients for plant growth. The development of sustainable strategies for the increase of crop productivity requires nutrients release (N and P) from wastes to meet vegetation requirements with minimum CO_2 emissions and N and P losses by runoff or lixiviation. Accordingly, organic matter turnover and nutrient release were assessed by measuring biological indices following the application of two types of municipal sewage sludge (stabilized or co-composted) and a biodiesel by-product to a degraded soil. The sewage sludges were applied at several doses and the biodiesel by-product was used as single amendment or combined with the sewage sludges. The amended soil was incubated at 25°C and 40% of water holding capacity during 45 days. At the end of the incubation, pH, conductivity, OC content, available N and P, microbial biomass, enzymatic activity, and OC, N and P mineralization were determined. The application of the different amendments increased N and P availability and microbiological activity but caused changes in metabolic pathways and the release of metabolites such as CO_2, ammonium, nitrate and phosphate.

The labile OC in biodiesel by-products and stabilized sludge undergo rapid mineralization, causing a sharply increase of microbial biomass and activity and, consequently, high CO_2 emissions. Both amendments cause P immobilization while the stabilized sludge promotes N mineralization and biodiesel by-products does not affect N concentration. Conversely, co-compost provides a source of humified OC, similar to the native soil, which maintains the balance of the microbial population and promotes build-up of OC stocks in the soil, N immobilization and slow P mineralization. Therefore, from an agronomic and environmental perspective the co-compost is the most suitable amendment.

Session B:

Water chemistry, Water treatment, Reuse

Posters B-01 – B-22

Poster B-01

DEGRADATION OF LEVOFLOXACIN IN AQUEOUS SOLUTION BY FERROUS ION-ACTIVATED HYDROGEN PEROXIDE, PERSULFATE AND COMBINED HYDROGEN PEROXIDE/PERSULFATE SYSTEM

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Levofloxacin (LFX) is a synthetic broad spectrum antibiotic of the fluoroquinolone drug class, which is used to treat severe or life-threatening bacterial infections. It is known to be extremely resistant to conventional biological oxidation and usually escapes intact from wastewater treatment plants (WWTPs). As a result, permanent LFX occurrence in WWTPs effluents may cause long-term concerns such as bioaccumulation and toxicity in the environment. To prevent LXF escape into receiving water bodies, radical-based advanced oxidation technologies could be applied as the main or supplementary (polishing step) water/wastewater treatment techniques.

In the present study the efficacy of Fenton (H_2O_2/Fe^{2+}), $S_2O_8^{2-}/Fe^{2+}$ and combined Fenton/persulfate ($H_2O_2/S_2O_8^{2-}/Fe^{2+}$) systems to degrade LFX in aqueous solution was investigated and compared. The LFX degradation by classical Fenton oxidation followed a pseudo-first-order kinetic law during an entire reaction. In the case of $S_2O_8^{2-}/Fe^{2+}$ system, a fast degradation of LFX was observed within the first minute, and then the target compound was gradually degraded within the left reaction time. A similar tendency in the LFX degradation was observed in the combined Fenton/persulfate system. Accordingly, without consideration of the first minute, the rest LFX degradation in $S_2O_8^{2-}/Fe^{2+}$ and combined Fenton/persulfate systems also followed the pseudo-first-order kinetic model. The LFX oxidation in H_2O_2/Fe^{2+} and $S_2O_8^{2-}/Fe^{2+}$ systems at a LFX/oxidant/Fe^{2+} m/m/m of 1/10/1 resulted in more than 99% (in 30 min) and 88% (in 3 h) target compound removal, respectively. The application of combined Fenton/persulfate oxidation was promising and demonstrated up to 99% LFX removal in 2 h and 45 min at LFX/$H_2O_2/S_2O_8^{2-}/Fe^{2+}$ molar ratios of 1/5/10/1 and 1/10/5/1, respectively. The highest mineralization was observed in the classical Fenton system followed by combine Fenton/persulfate process. Nevertheless, it is suggested in this study that all studied radical-based advanced oxidation technologies if properly optimized are capable of removing levofloxacin from water efficiently.

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CYANOBACTERIA AND MICROALGE: A PROMISING BIOTECHNOLOGICAL STRATEGY FOR THE REMOVAL OF HEAVY METALS AND ARSENIC FROM AQUEOUS EFFLUENTS

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Recent research on the field of microalgae and cyanobacteria has revealed relevant properties as potential sorbents for heavy metals. A variety of cyanobacteria is known to produce large amounts of polysaccharides which have, among other characteristics, biosorption function. These polysaccharides can be released into the medium or, as capsule or mucilage, be attached to the cell wall. Additionally the presence of proteins, pyruvate, acetate and sulphate groups that might be present in the mucilage provide extra sorption potential to these microorganisms.

Over a span of 50 years, the Norwegian Institute for Water Research (NIVA) has built up a significant collection of algae cultures that nowadays contains more than 930 strains (website: https://niva-cca.no). A screening among them has been carried out and 10 promising strains were cultured and evaluated in sorption experiments. These strains were exposed to a multimetal and arsenic cocktail and the removal was evaluated by a mass balance on the supernatant before and after exposure. The assays with the selected microorganisms have demonstrated an excellent sorption performance in the removal of the heavy metals: Mn(II), Zn(II), Ni(II) and Cu(II). Two of the strains of microorganisms demonstrated also a special high performance in the removal of As(III).

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Poster B-03

EXHAUSTED COFFEE: A NOVEL SORBENT FOR ELECTROPLATING WASTEWATER TREATMENT

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A novel sorbent based on exhausted coffee waste has been investigated for its potential to remove metals from electroplating wastewater. The sorbent proved to be efficient for the removal of chromium (VI) and divalent metals like copper (II) and nickel (II) from synthetic solutions in single solutions and binary mixtures.

In this work, exhausted coffee waste from soluble coffee production has been used for the removal of metals from two electroplating wastewater effluents: rinsing bath after chromium plating and exhausted nickel solutions of nickel plating, from a metal finishing industry from Barcelona (Spain).

Wastewaters were first characterized to know metal content. Batch sorption experiments were carried out at room temperature by using exhausted coffee wastes with 0.25-0.50 mm particle size. Kinetics studies were performed to determine the process operation time to achieve equilibrium and to evaluate the efficiency of the sorbent in removing metal ions. The pH of the wastewaters was adjusted at pH 3 and pH 5.5 for Cr(VI)and Ni(II) bath effluents, respectively. The weight of sorbent/volume ratio was 6.67 g/L for chromium effluents and 66.7 g/L for nickel effluents.

The concentrations of the different metal ions in the wastewater from the chromium plating rinsing effluent were in the range: Cr(VI): 108.50-147.18, Cu(II): 5.04-8.20, Ni(II):0.93-1.23, Fe(III) 4.24-8.54 and Al(III): 0.66-0.99 mg/L. The concentration of nickel in the exhausted nickel solution was 540 g/L. These solutions were conveniently diluted with wastewaters free of metal ions coming from the different processes performed in the industrial plant.

The results proved high efficiency of the proposed technology based on exhausted coffee for the treatment of industrial wastewater containing hexavalent chromium in the presence of divalent metals. In the case of the plating rinsing the sorbent was able to eliminate 70% initial chromium concentration. It is important to remark that the remaining chromium in solution (30%) was in its trivalent form. The sorbent was not efficient to totally eliminate divalent metals. A second step based on precipitation by using $FeCl_3$ (s) as flocculation agent was necessary to eliminate the remaining Cr(III) and the rest of divalent metals. After precipitation metal ions concentration in solution are below the regulated discharge limits.

When the technology was applied to eliminate nickel from exhausted nickel solutions the maximum percentage of nickel elimination was 84% when Ni(II) initial concentration in the effluent was equal or lower than 20 mg/L, and lower metal elimination percentages were achieved when increasing nickel concentration in the effluent. Further work will be necessary to optimize the operational conditions to enhance nickel removal yields.

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Poster B-04

DUMPING OF POLLUTED DREDGED SEDIMENTS IN SARONIKOS GULF. EFFECTS ON HYDROCARBON GEOCHEMISTRY.

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The hydrocarbon levels, composition and geochemistry were studied in the water column and sediments of a coastal site in Saronikos gulf, Greece, where the dredged urban river (Kifissosriver) sediments were dumped for a period of 20 months (May 2010 - December 2011). Kifissosriver is the metropolitan river of Athens and is contaminated by both aliphatic and polycyclic aromatic hydrocarbons (PAH). Surface sediments were collected from 5 stations prior of dumping, during dumping operations (October 2010, April 2011, October 2011) and four months after the end of dumping. Seawater samples were collected from the surface and bottom layer, every month from April 2010 to July 2012. Hydrocarbons were determined by gas chromatography - mass spectrometry applying the appropriate procedures.

Total aliphatic hydrocarbon concentrations in sediments were increased from 98 μg/g to 1800 μg/g during dumping and remained high (1003 μg/g) four months after dumping. The examination of various ratios and indices (CPI, U/R ratio, composition of hopanes) showed significant quantities of petroleum residues during and after dumping. Total PAH were also increased in surface sediments from 451 ng/g to 6175 ng/g during dumping and decreased to 3351 ng/g after dumping. The composition of PAH mixtures and the examination of specific isomeric PAH ratios revealed a clear predominance of pyrolytic compounds before dumping. During dumping high abundances of methylated PAH were recorded, showing petrogenic origin, while after dumping a part of methylated derivatives were lost, resulting in equal amounts of pyrolytic and petrogenic PAH. In seawater, an 5-fold increase of PAH concentrations was observed 9 months after the beginning of dumping, while six months after the end of dumping PAH values in the whole water column were still higher than those prior to dumping. PAH with 2-3 aromatic rings, along with the methyl substituted ones were dominant in all cases.

Poster B-05

GROUNDWATER REMEDIATION BY "IN SITU CHEMICAL OXIDATION" - ADVANTAGES AND PITFALLS

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In situ chemical oxidation is referred to as advanced technology for economically feasible compliance of remediation limits. Absence of groundwater pumping and ongoing treatment is mentioned as main advantage of this technology. Similarly, no restrictions in target pollutants are often announced. Field experience, however, brings some knowledge on limitations of this technology as well. In this contribution, we show both examples of successful applications of in situ chemical oxidation and some unrealistic expectations connected to this technology.

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Poster B-06

PHOTOCHEMICAL DEGRADATIONOF SULFONYLUREAS PESTICIDESBY THE COMBINATION OF IRON (II) AND IRON(III) SPECIES UPON SOLAR LIGHT EXCITATION: KINETIC AND ANALYTICAL STUDIES

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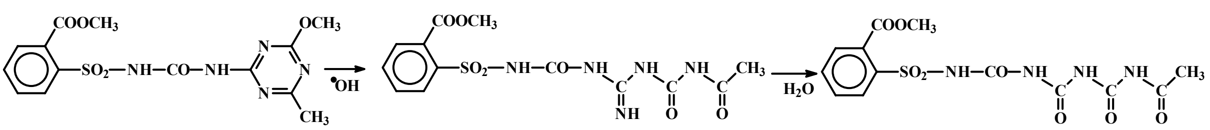
Environmental pollution by organic molecules creates an ecological problem, which is complicated by the fact that some related compounds undergo slow biodegradation process or with an inefficient manner. Information about possible degradation mechanism in the environment is of interest in order to elucidate the factors that influence their behavior. Among the different transformation processes (biotic and abiotic) the photodegradation appears to be among the important factors that influence the fate of the pollutants. For these reasons, for environmental considerations and also for its cost, the solar induced photodegradation of pollutants in aqueous solutions is of particular interest. Extensive research has been focused on the formation of hydroxyl radicals which react with the majority of organic pollutants in a non selective manner and lead to their total degradation and mineralization.

The present work deals with the degradation of selected sulfonylurea pesticides by homogeneous photocatalysis. This was undertaken in aqueous solution by using very low concentration of iron (III) aquacomplexes(< 10 µmol L^{-1}).This processes proceeds through the generation of hydroxyl radical as a main reactive species.The work was devoted to the optimization of experimental parameters by using very low amount of iron (III) and special efforts have concerned the elucidation of the mechanism for the regeneration of iron (III) from iron(II) species.The obtained results show that a charge transfer between an excited iron (III) and iron(II) allows the increase of the iron (III) concentration in the solution during solar light excitation. In a second part, we studied the kinetics and analytics parameters of the complete degradation of those pesticides.The photoproducts chemical structures were obtained by careful analysis and detailed studies of theirLC/MS^2 spectra. Beside the general hydroxylation and bridge scission products, the opening of the recalcitrant triazinic cycle was also obtained. The kinetic as well as the analytical studies gave a better insight into the degradation mechanism of sulfonylureas under homogeneous photocatalysis through iron(III) excitation.

$$Fe^{3+} \xrightarrow{h\nu} Fe^{3+*}$$

$$Fe^{3+*} + Fe^{2+} \longrightarrow Fe^{3+*}{/\!/\!/\!/\!/\!/\!/}Fe^{2+} \longrightarrow Fe^{3+} + Fe^{2+*}$$

$$Fe^{2+*} + O_2 \longrightarrow O_2^{\bullet -} + Fe^{3+}$$



Poster B-07

CONTAMINATION OF WATER AND SEDIMENT FROM OSLAVA AND JIHLAVA RIVERS, AND NOVÉ MLÝNY WATER RESERVOIR (CZECH REPUBLIC) BY SELECTED ANTIBIOTICS

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The work was focused on the assessment of contamination level of aquatic ecosystem of the Oslava and Jihlava rivers and of the Nové Mlýny water reservoir, situated in South Moravian region of the Czech Republic, by residues of selected veterinary pharmaceuticals. The study dealt with the isolation and determination of 10 antibiotics from the group of sulfonamides in samples of surface water and bottom sediments.

Antibiotics, including sulfonamides, are a large group of pharmaceuticals whose consumption in both human and veterinary medicine is still growing. In both human and animal body they are metabolized and excreted in the urine or faeces, while up to 30 - 90 % of them can be excreted in active form. In this way, directly or via use of livestock manure as a fertilizer or via wastewater treatment plant, antibiotics in their original or metabolized form can enter the environment. There they can accumulate, persist and thus negatively affect ecosystems, including water ecosystem, where there are toxic especially to aquatic organisms. The occurrence of residual antibiotics in the environment then results in an increased incidence of resistant bacteria, which may in future become a potential threat to human health.

The target analytes included ten sulfonamides (sulfaguanidine, sulfadiazine, sulfathiazole, sulfapyridine, sulfamerazine, sulfadimidine, sulfamethoxazole, sulfadoxine, sulfaclozine and sulfadimethoxine) that were isolated from samples using optimized methods. Concerning the water samples, solid phase extraction (SPE) was used for pre-concentration and purification of the sample as well as for extraction of monitored sulfonamides. For the extraction of sulfonamides from sediment samples, the method of pressurized solvent extraction (PSE) was used; SPE was then used for purification and pre-concentration of sediment extracts. Final identification and quantification were carried out by high-performance liquid chromatography coupled with diode array detector (HPLC/DAD). According to the obtained results the concentrations of residues of selected antibiotics were determined and therefore the water ecosystem burden in selected rivers of South Moravian region was identified.

Acknowledgement:
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Poster B-08

ORIGIN OF HEAVY METALS, PAH AND PESTICIDES IN SEDIMENTS FROM TISZA RIVER (SERBIA)

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An important issue in the European Union is water quality. There is a growing concern related to the presence of emerging and priority substances in surface water and sediment. To precisely evaluate whether contamination of sediments occurred at a given location it is essential to compare obtained values with reference samples. Most adequate reference samples are sediments that have same geological origin but were never under anthropogenic influence. However, it is not always easy to find such sediments in nature, so in order to evaluate sediment contamination, traditionally, the obtained concentration were compare with average composition of upper continental crust or concentration of elements in average shale. Nowadays, sediment quality assessment methods used in Europe and worldwide, mainly rely on a chemical approach, i.e. total environmental concentrations are measured and then compared to available reference, target, recommended or quality values. In order to improve the protection of waters quality in Republic of Serbia the Ministry responsible for Environmental Protection – Division of Water Protection, in accordance with the Water Framework Directive prepared set of regulations, and the Government of the Republic of Serbia adopted the following provisions. In this paper, special attention was given to Regulation on limit values for pollutants in sediments and deadlines for their achievement, with the main objective to use the case study of Tisza River to test the advantages and limitations of this Regulation in order to improve the water quality in the territory of the Republic of Serbia. This provision defines limit values (LV) and maximum legal concentration (MLC) for (i) heavy metals (ii) PAH and (iii) pesticides. The survey results show that the sediment samples for all Tisza River sites contained elevated concentrations of Cd, Cr, Cu, Ni and Zn. With regard to Serbian Regulation ("RS Official Gazette" No. 50/12) concentrations of Cd, Cr, Cu and Zn are below MLC, except Ni and Zn in some samples which concentrations are above MLC. Concentrations for Naphthalene, Fluoranthene, Phenanthrene, Benz(a)anthracene and Benzo(b)fluoranthene in sediments of Tisza River were below the LV, but above the MLC, except for Anthracene only a few samples where the values are below the MLC. Concentrations of Chrysene, Benzo(a)pyrene, Indeno(1,2,3-cd)pyrene and Benzo(g,h,i)perylene were equal to LV. The sum of all PAHs in sediments of Tisza River was below the LV, but above the MLC. Concentrations of pesticides in all samples were above the limits proposed by Serbian Regulation, except for DDT in some samples where the values are below the LV. Alpha, beta and gamma HCH have concentrations above the LV. Values of heptachlor, heptachlor-exo-epoxide, aldrin, endrin and endosulfan (I) are also above the LV. Based on the limit values, Serbian regulation does not show clearly origin and anthropogenic contribution of heavy metals and PAHs in sediment, which is certainly limitations. In determining the limit values for pesticides no limitations were found.

Poster B-09

ASSESSMENT OF THE CONTAMINATION LEVEL OF METHYLMERCURY AND TOTAL MERCURY IN THE WASTE WATER

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The aim of this study was to determinate the methylmercury and total mercury in waste water from waste water treatment plant situated at the University of Veterinary and Pharmaceutical Sciences Brno. Mercury is an environmental contaminant that appears in different chemical forms [1]. Methylmercury is considered to be most toxic form of mercury that is produced by biomethylation or abiotic methylation of inorganic forms of mercury by bacteria living in sediments [2]. Methylmercury enter aquatic organisms via water and accumulate in the food chain, and it presents the great environmental risks to human health [3].

The samples were taken from local waste water treatment plant during two weeks period. Methylmercury was extracted from the water using the analytical method “head space” solid phase microextraction (HS-SPME). The analytical procedure involves derivatization of ionic mercury with sodium tetraethylborate in a sample vial and following extraction with a silica fibre coated with 100 µm polydimethylsiloxane under the certain conditions (time, temperature, pH) [4]. Then the fibre is placed into the injection space of gas chromatograph, where the temperature is very high and the substance adsorbed on the fibre desorbs immediately [5]. Methylmercury was determined by the method of gas chromatography (Agilent Technologies 6890 Series) with electron capture detector (^{63}Ni). The capillary column DB 17 (30 m, 250 µm I.D., 0.25 µm film) was used. Total mercury content was determined using the system AMA 254 (Altec Ltd., Czech Republic).

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OZONATION OF RHODAMINE 6G WITH pH-SPECIATION PHENOMENA

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The objective of this study is to evaluate the ozone as oxidant to achieve the decolorization and degradation of a xanthene dye. The effect of pH, fundamental reaction parameter in ozonation processes, was studied. Rhodamine 6G was used as a model of dye wastewaters trying to get the basis for the design of efficient ozonation process. The initial pH of solution plays an important role both in the primary degradation of Rhodamine 6G and in the dyed intermediates responsible of color removing. Primary degradation and decolorization processes were characterized by pseudo-first order kinetic constants. Decolorization constants are slightly lower than those of Rhodamine 6G but, at medium pHs in the presence of substances capturing radicals like tert-Butanol, the difference is more significant and can be up to a 40 %. In this work, an ozonator consisting on a generator of 30 g/h maximum production of activated oxygen (O_3) concentration was used. Ozone was bubbled in a batch 2 L contactor where a water solution of 50 ppm dye compound was previously introduced.

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Poster B-11

COMPARATIVE INVESTIGATION OF THE ADSORPTION OF MANGANESE AND COBALT FROM INDUSTRIAL EFFLUENTS USING ETHANOL AND PENTANOL MODIFIED RICE HUSKS

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A research on the adsorption of manganese and cobalt using ethanol and pentanol modified rice husks from two different rice fields (Otukpo and Idah in central Nigeria) was carried out using Flame Atomic Absorption Spectrometry and Fourier Transform Infrared Spectrometric Techniques. This method was developed as a means of recovery of manganese and cobalt from industrial effluents using available and locally sourced agricultural adsorbents. Results of this study indicates that pentanol treated rice husk (PTRH) at 40 µm particle size (PS) had more percentage recovery for cobalt (99.917 %), while ethanol treated rice husk (ETRH) of particle size 20 µm had more percentage recovery for manganese (99.987 %). It was equally observed that the surface area of the OH binding sites and the intensity of the OH contributed immensely to the adsorption of the manganese and cobalt species. The FTIR studies indicates the predominant presence of the OH functional group at 3418.94 cm^{-1} (Otukpo ETRH at 40 µm PS), 3424.73 cm^{-1} (Otukpo PTRH at 40 µm PS), 3429.55 cm^{-1} (Otukpo ETRH at 20 µm PS), 3429.55 cm^{-1} (Otukpo PTRH at 20 µm PS), 3410.26 cm^{-1} (Idah ETRH at 40 µm PS), 3411.22 cm^{-1} (Idah PTRH at 40 µm PS), 3471.02 cm^{-1} (Idah ETRH at 20 µm PS) and 3412.19 cm^{-1} (Idah PTRH at 20 µm PS). Thus the higher the intensity and surface area of the OH binding sites, the higher the adsorption of manganese and cobalt species.

Acknowledgement:
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Poster B-12

PHOTOCATALYTIC OXIDATION OF ESTRIOL

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In recent years, there has been an increasing interest in occurrence of hormonal substances in aquatic ecosystems. Attention is paid especially to estrogens (female sex hormones). These steroids play an important role in medicine, they are part of oral contraceptives and are used for hormone substitution therapy [1]. They can be difficult to remove completely by wastewater and drinking water treatment technologies therefore they are found in natural aquatic ecosystems and in potable water [2, 3]. This fact is associated with a potential serious risk to the environment and human health [1]. Photocatalysis is one of promising methods for elimination of estrogens from water [4] therefore in this study we focused on assessment of TiO_2 photocatalysis to remove natural estrogen estriol. Photocatalytic experiments were conducted in a glass circulated reactor with a rotary holder of immobilised TiO_2 and UV-A LED light source (365 nm emission wavelength). Printing ink was prepared from water dispersion Tiodispers NA-AS (Centre for Organic Chemistry, Czech Republic) and deposited by inject printing onto soda-lime glass substrate [5]. Initial concentration of estriol in ultrapure water samples was 5 mg/L. Estriol levels were measured by HLPC-MS method. Four hours photocatalytic process led to decrease in estriol concentration about 54 %. The same time of photolysis (without TiO_2) or adsorption (without light) had no effect to estriol concentrations.

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Poster B-13

PROCESS DEVELOPMENT FOR THE REMOVAL OF HEAVY METAL ION SPECIES FROM LANDFILL LEACHATE USING PLUM KERNELS AS A NEW ADSORBENT

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Intense industrial and commercial growth in many countries around the world has been accompanied by rapid increases the municipal waste generation rates. In most developing countries, as well as in Serbia, uncontrolled landfilling and sanitary landfills is nowadays the most common way to eliminate municipal solid wastes (MSW). One of disadvantages of landfills is generation of leachate that could have negative impact on environment. In general, landfill leachate is defined as any contaminated liquid effluent percolating through deposited waste and emitting within a landfill or dump site through external sources.

Landfill leachate treatments methods can be classified into three major groups: (1) leachate transfer, (2) biodegradation, (3) chemical and physical methods like adsorption.

Activated carbon, an adsorbent with large porous surface area, controllable pore structure and thermo-stability is recognized as the most efficient and promising fundamental approach in the wastewater treatment processes (removing of dyes, heavy metals and polyaromatic hydrocarbons). Ligninocellulosic materials, such as fruit stones and nutshells, are very good precursors for the production of activated carbons. In the sense of environmental protection, the utilization of this low-cost biomass residue has awakened the interest for development of processes for production of carbon adsorbents based on agricultural wastes.

The objective of this study was to synthesize a low-cost activated carbon from the plum (*Prunus domestica* L.) kernels, derived from fruit-processing waste by chemical activation using H_2SO_4 (sulfuric acid) and to investigate the efficiency of removal certain pollutants such us Pb^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+} and reducing the concentration of COD. In addition, correlation of efficiency between plum kernel adsorbent and commercial activated carbon (CAC) is investigated in batch studies using landfill leachate water from Novi Sad, Serbia.

The results indicate that the prepared activated carbon is economically promising for the treatment of wastewaters/leachates and has a high efficiency.

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Poster B-14

EUTROPHICATION PROBLEMS RELATED TO SEWAGE DISCHARGE IN A SEMI-ENCLOSED AREA OF THE AEGEAN SEA (EAST MEDITERRANEAN)

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World-wide, eutrophication is a major threat to the integrity of marine ecosystems. Direct wastewater discharge is one of the main causes of increased eutrophication in many near-shore waters. Wastewater discharged into the marine environment through long underwater outfalls results in sewage decomposition and mineralization. The study is focus on changes in nutrient concentrations related to the sewage discharge into the eastern part of Elefsis bay and assesses the eutrophication status of the area before and after the operation of Wastewater Treatment Plant (WTP). Elefsis bay is a shallow (32 m maximum depth), semi-enclosed marine area of the Eastern Mediterranean Sea, affected by the industrial zone of Athens (oil refineries, shipyards, chemical plants, food, metal cement industries etc). The eastern part of the bay, with maximum depth 20 m, receives the effluents from the WTP, discharging at 14 m depth. The WTP has recently begun to treat the domestic and industrial wastes of the western Attica. The average nutrient concentrations were 0.034 ± 0.015 mmol.m^{-3} and 0.042 ± 0.016 mmol.m^{-3} for phosphate; 0.797 ± 0.939 mmol.m^{-3} and 2.141 ± 0.871 mmol.m^{-3} for nitrate; 0.458 ± 0.313 mmol.m^{-3} and 0.698 ± 0.427 mmol.m^{-3} for ammonium; 0.092 ± 0.089 mmol.m^{-3} and 0.246 ± 0.066 mmol.m^{-3} for nitrite; and 1.378 ± 2.058 mg.m^{-3} and 2.058 ± 0.603 mg.m^{-3} for phytoplankton biomass, before and after the WTP operation, respectively. A synthetic Eutrophication Index (E.I.) has been applied under the EU Water Framework Directive and the EU Marine Strategy Framework Directive, in order to assess the water quality status. The E.I. combines the concentrations of nutrients (phosphate, nitrate, nitrite, ammonia) and chlorophyll-α biomass into a single formula. E.I. showed a significant degradation of the marine environment of the eastern Elefsis bay from “Moderate” to “Poor” status after the sewage discharge.

INFLUENCE OF OVERALL MINERALIZATION AT THE OPTIMAL DOSE IN DRINKING WATER TREATMENT

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One of the most common and economically feasible chemical process for drinking water treatment is considered to be coagulation. Coagulation can caused the violation of stabilizing mechanisms; in consequence undesirable matters collide with each other and form larger structures which can be remove various processes, such as Dissolved Air Flotation (DAF), sedimentation or Activated Carbon (AC) Filtration.

Coagulation efficiency depends on chemical quality of coagulants and quality of crude water, i.e. chemical and physical characteristics (e.g. pH, temperature, and overall mineralization).

One of the most important tests of this work was to study the effects of the overall mineralization at the optimal dose of coagulant. The overall mineralization of studied water was increased by saturated solutions $CaCl_2$ and Na_2SO_4 in certain ratios (assessed the influence of individual ions) and was measured by conductivity.

The measured values and figures indicate that the optimal dose of coagulant decreases with increasing of overall mineralization. Using ferric coagulant shows larger range of optimal dose: from 160 µmol/L at conductivity 7 mS/m to 75 – 80 µmol/L. The influence of mineralization to alum coagulant was less, the values were in the range from 100 µmol/L to 75 – 80 µmol/L. In comparison with both coagulants we can notice, that the differences between doses of ferric and alum coagulants were minimal, even at the highest value of mineralization graphs are similar.

The mineralization was studied by several ions (Ca, Na) in model water. The ratio of individual ions to overall mineralization has not the influence to optimal dose of coagulant. The results of absorbance at 254 nm indicate that the optimal dose increased in ratio 1 Ca : 10 Na at 300 mS/m conductivity.

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Poster B-16

A pH-OPTIMIZATION APPROACH FOR AN EFFICIENT OZONATION OF DYESTUFFS

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The oxidation of rhodamine 6G (R6G) in aqueous solution by ozone process was investigated in a pilot scale ozonation reactor as a model dye pollutant. These kind of heterogeneous oxidation systems are usually limited by the mass transfer resistance of gaseous oxidant to diffuse into bulk reaction.

In this study a special emphasis was laid on the valorization of control situations of mass transfer from gas to liquid phase and chemical reactions during R6G oxidation. A mathematical model was proposed to analyze the removal of R6G including ozone mass transfer coefficients from gas to liquid phase, oxidant consumption rate because of reaction with R6G dye, and the shelf-decomposition because of the solution characteristics such as pH and temperature.

The mathematical model study the effect of the controlling step, whether mass transfer or chemical reaction, based on the ozone balance to the reacting system. It was satisfactorily verified in a wide range of pH, showing that initially, dealing basically with primary degradation, the process is controlled by the G-L mass transfer step but, as the R6G ozonation progresses, the process becomes to be controlled by the kinetic reaction between ozone and rhodamine 6G. While the 99% of rhodamine dye is removed during mass transfer control stage regardless of pH values, the percentage of TOC elimination is increased during kinetic reaction control step.

The particular effect of pH, depending on the controlling step (mass transfer or chemical reaction), is decisive to select the most suitable pH under performance criteria of pollutant removal.

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Poster B-17

DETERMINATION OF THE PRESENCE OF PHOSPHODIESTERASE INHIBITORS IN MUNICIPAL WASTEWATER

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This work is focused on the determination of phosphodiesterase 5 selective inhibitors in communal waste waters.

Phosphodiesterase inhibitors are the main active ingredients of medicaments which are used in the treatment of erectile dysfunction. The aim of this work was determination of concentration of three phosphodiesterase inhibitors in communal waste waters; specifically it was sildenafil citrate, vardenafil hydrochloride and tadalafil. These inhibitors are the main active ingredients of medicaments with trade names Viagra, Levitra and Cialis.

In this study phosphodiesterase inhibitors levels in municipal waste waters from sewage treatment plants with different numbers of equivalent inhabitants were analysed. Namely it was sewage treatment plants in Brno – Modřice, Luhačovice and Hodonín. In each of the above mentioned facilities 24 - hour cumulated samples of the influent and effluent waste water were collected. On the Brno - Modřice sewage treatment plant also weekly monitoring of the concentration of phosphodiesterase inhibitors was realized.

At first, the analytical method was optimized and then applied on real waste water samples. Solid phase extraction (SPE) was used for the pre-treatment of waste water samples. For identification and quantification of the studied compounds, high performance liquid chromatography-mass spectrometry (HPLC/MS) was used.

It was assumed that the most widely used of these drugs is Viagra, so sildenafil will be found in the largest quantities. In spite of these assumptions, only vardenafil was detected at concentrations greater than the limit of detection and quantification.

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Poster B-18

INVESTIGATION OF THE EFFICIENCY OF SOLAR PHOTOCATALITIC DEGRADATION IN REMOVAL OF TOLUENE, ETHYLBENZENE AND XYLENES FROM WATER CONTAINING HIGH CONCENTRATION OF PETROLEUM HYDROCARBONS

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Methods based on photolysis and chemical catalysis are proven to be efficient in treatment of wastewaters containing small amounts of refractory organic substances [1]. In treatment of waters containing low amount of petroleum pollutants, the solar light/TiO_2 slurry system was able to remove up to 70 % of benzene, toluene, ethylbenzene and xylenes (BTEX) and total petroleum hydrocarbons TPH during 4 h [2]. However, solar photocatalitic degradation was shown to be of limited usage in treatment of waters containing high amount of petroleum pollutants [3].

In the present research we investigated the efficiency of the solar light/TiO_2 slurry system in removal of toluene, ethylbenzene and xylenes from water containing high concentration of petroleum hydrocarbons.

Mixture of commercial desulfurized diesel fuel, water and TiO_2 was solar irradiated for five hours. Simultaneously, comparative samples of mixture of diesel fuel and TiO_2 were solar irradiated. Diesel fuel was treated under the same conditions in the dark to evaluate the evaporation loss. At the end of the experiment, organic phase was separated from water and/or the catalyst, diluted with n-hexane and analyzed by gas chromatography – mass spectrometry (GC-MS) technique.

After 5 h of aqueous solar irradiation, more than 70 % of toluene, ethylbenzene and xylenes were removed from the reaction mixture.

These results show that solar light/TiO_2 slurry system can easily remove more than 70 % of toluene, ethylbenzene and xylenes from water containing high concentration of petroleum hydrocarbons. However, the remaining of the nondegraded pollutant should be treated with some other, more efficient techniques.

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Poster B-19

THE OCCURRENCE OF SURFACTANTS IN THE AQUATIC ECOSYSTEM

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This study is focused on the determination of five selected surfactants (sodium octylsulphate, sodium dodecylsulphate, sodium dodecylbenzensulphonate, N-Dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate and Triton – X100) in real samples from Thurso river water (Thurso, Scotland) and from 6 rivers in Moravian region, Czech Republic (rivers Syrovinka, Velicka, Morava, Kyjovka, Trkmanka, Litava). Surfactants are widely used in the consumer, industrial, agricultural, and pharmaceutical markets in products as personal cleaning agents, pesticides, detergents and cosmetics. Many different types of these compounds have been synthesized, although they can be classified into three main groups according to their charge: anionics, non-ionics, and cationics. From each group at least one compound was selected. Solid phase extraction (SPE) as preconcentration technique was tested, but with no positive results. Samples were filtrated throw 0.45 µm PTFE filter. For identification and quantification LC/MS method was employed. Triton – X100 wasn't present in any sample both in Moravia and Thurso. N-Dodecyldodecyl-N,N-dimethyl-3-ammonium-1-propanesulfonate and sodium octylsulphate wasn't present in any sample in Moravia region. Other compounds were found in various concentrations.

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Poster B-20

INVESTIGATION OF THE APPLICABILITY OF UV PHOTOCATALYTIC DEGRADATION IN TREATMENT OF WATER CONTAINING HIGH CONCENTRATION OF PETROLEUM HYDROCARBONS

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The photolytic degradation process is considered one of the most efficient remediation techniques in wastewater treatment [1]. In treatment of waters containing low amount of petroleum pollutants, the solar light/TiO_2 slurry system was proven to be able to remove up to 70 % of total petroleum hydrocarbons during 4 h [2]. However, In the case of water containing high concentration of petroleum hydrocarbons, solar photocatalitic degradation was shown to be of limited usage [3].

Considering limitations of solar energy due to the seasonal and daily variations, in the present research we investigated the efficiency of the UV light/TiO_2 slurry system for treatment of water containing high concentration of petroleum hydrocarbons.

Mixture of commercial desulfurized diesel fuel, water and TiO_2 was UV irradiated for five hours. Simultaneously, comparative samples of mixture of diesel fuel and TiO_2 were UV irradiated. Diesel fuel was treated under the same conditions in the dark to evaluate the evaporation loss. At the end of the experiment, organic phase was separated from water and/or the catalyst, diluted with n-hexane and analyzed by gas chromatography – mass spectrometry (GC-MS) technique.

The results obtained were very similar to the results of the experiment with aqueous solar irradiation [3]. After 5 h of aqueous UV irradiation, significant loss of hydrocarbons was noticed only in the fraction of hydrocarbons having less than 15 carbon atoms. Additionally, among n-alkanes, iso-alkanes and isoprenoids, preferential removal of higher homologues was noticed as well. However, at the end of the experiment, the majority of the pollutant remained nondegraded.

These results show that the efficiency of both, solar and UV/TiO_2 slurry system in treatment of waters containing petroleum pollutants is highly dependent on the amount of the contaminant. In the case of water containing high concentration of petroleum hydrocarbons, these systems were shown to be of limited usage and, accordingly, much less efficient comparing to other known remediation techniques.

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Poster B-21

DETERMINATION OF DDT AND METABOLITES IN THE WASTE AND SURFACE WATER IN THE VICINITY OF NOVI SAD, SERBIA

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Screening and target analyses were conducted within NATO Project at the selected sampling points of collectors of four sewage discharges in the vicinity of Novi Sad, as well as of surface water from Danube River 100 meters downstream of the each discharge. Collected water samples were analysed by GC-MS. Results indicated the occurrence of DDT and its metabolites in surface and waste water samples. p,p'-DDE detected upstream of the city of Novi Sad, before all discharge points, indicated the ecotoxicological status of the river Danube prior to any local urban impact. Concentrations of p,p'-DDE were not amplified at the other sampling sites, hence the pollution of Danube river with these chemicals came upstream from other European countries. p,p'-DDD (Rhothane), metabolite of DDT, the most lipofilic with the lowest value of K_{OW} of 4.73 within the metabolites of DDT, was detected in almost all samples with extremely high values at two sampling sites, which confirms historical contamination, but also recent contamination inputted upstream of the city of Novi Sad. According to the concentration ratio of p,p'-DDD and p,p'-DDT at sampling points with the highest concentrations, the values of 1.24 and 1.29 indicated historical contamination with these chemicals. Increasing trend of DDT concentrations was determined in this study. Results indicated not only historical contamination, but also recent contamination of surface water since DDT was detected in relatively high concentrations. This type of research was conducted for the first time within the NATO Project at four sampling sites of waste water and five locations of Danube surface water in the vicinity of Novi Sad, Serbia.

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Session C:

Atmospheric chemistry, Air pollution, Modelling of pollutants transport

Posters C-01 – C-05

Poster C-01

POTENTIAL IMPACT OF MICROBIAL ACTIVITY ON THE OXIDANT CAPACITY AND THE ORGANIC CARBON BUDGET IN CLOUDS

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Within cloud water, microorganisms are metabolically active; so they are suspected to contribute to atmospheric chemistry. This paper is focused on the interactions between microorganisms and Reactive Oxygenated Species present in cloud water since these chemical compounds are driving the oxidant capacity of the cloud system [1]. For this, real cloud waters with contrasting features (marine, continental, urban) were sampled at the Puy de DômeMountain (France). They exhibit high microbial biodiversity and complex chemical composition. These media were incubated in the dark and subjected to UV-light radiation in specifically designed photo-bio-reactors. The concentrations of hydrogen peroxide (H_2O_2), organic compounds and the ATP/ADP ratio were monitored during the incubation period. Microorganisms remained metabolically active in the presence of hydroxyl radicals (•OH) photo-produced from H_2O_2. This oxidant and major carbon compounds (formaldehyde and carboxylic acids) were biodegraded by the endogenous microflora. This work suggests that microorganisms could play a double role in atmospheric chemistry: first, they could directly metabolize organic carbon species; second they could reduce the available source of radicals due to their oxidative metabolism. Consequently, molecules such as H_2O_2 would be no longer available for photochemical or other chemical reactions, decreasing the cloud oxidant capacity.

Acknowledgement:
This project was funded thanks to the CNRS LEFE-CHAT program. M. Vaitilingom PhD fellowship was funded by the French ministery of research.

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LICHENS AS BIOINDICATORS FOR MONITORING OF PLATINUM GROUP ELEMENTS

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The subject of this study was the assessment of actual contamination air by platinum group elements in Brno. There was used active biomonitoring, so called dry „bag“ monitoring technique, with lichen *Hypogymniaphysodes*. Lichens are poikilohydric organisms witch are able resist the adverse conditions and stress factors. The thallus is not covered with cuticle, breathes the entire surface of the body, which allows a large degree of adsorption of risk elements. Samples of lichens were placed to the inside of the crash barrier along roads with heavy traffic. For time gradual variation exposure, there were placed three "bags" in each sampling point. Samples after exposure were collected sequentially after 90, 120 and 150 days.

Palladium together with platinum and rhodium form an active catalytic layer in automotive catalysts eliminating toxic exhaust gases from the combustion process of fuel. The high temperatures of exhaust gases, mechanical abrasion, catalyst poisons and riding style leads to damage and releasing catalytic layer of platinum metals in the form of oxides or nanoparticles. This issue is particularly troubling large urban agglomeration and it is therefore necessary to assess the extentof bioaccumulation and hazards affecting the health of the population.

Sampling was preceded the optimization of SPE preconcentration method using modified silicagel and Quadrasil TA sorbents and optimization of ET–AAS determination.

The obtained results confirmed emissions of palladium, however, failed to determine the dependence of exposure time on the amount of emitted palladium. We believe that lichen crossed in the latency phase influence of excessive of action pollutants from automobile traffic. There were minimized its bioaccumulation, metabolism and photosynthetic functions during exposure. Lichens are quite complex matrix, but because of their appropriate use as biomarkers of environmental pollution, they should continue to be paid more attention.

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Poster C-03

NEEDLE NET - PHYTOINDICATION OF THE GENOTOXIC EFFECTS OF AIR POLLUTANTS IN HIGH MOUNTAIN HABITATS

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The main topic of project Needle net is developing of cooperation between Czech Republic and Slovakia in question of determination of air contamination. Plants are very sensitive organisms and bioindicators of air pollution. They give us information about changes in environmental quality according to specific responses. Cytotoxic, cytogenetic and mutagenic effects can be observed even at very low concentrations. This study aimed to evaluate the rate of genotoxicity caused by transboundary pollutants at sites in the Slovak mountains using pollen grain abortion assay. Pollen grain abortion assay provides picture of the overall (mixed) toxicity of the investigated environment. The abortion pollen grains were determined on the basis of altered and unformed form, more air sacs, higher size and staining deficiency (Mičieta and Murín 1996). Swiss mountain pine (*Pinus mugo*) was used such as suitable bioindicator to monitoring environmental pollution in mountain and alpine habitats of Little Fatra, Great Fatra and Tatra Mts. Control site was chosen in Belianske Tatras. This species was satisfying all criteria for selection (Murín 1987). The correlation between genotoxic load (pollen grain abortivity) and altitude was evaluated. Sampling was conducted on the various slope exposures for flow direction identification of the pollutants. The results showed the highest genotoxicity in Great Fatra on the north slope of Krížna Mt. in altitude 1.574 m asl., where the frequency of abortive pollen grains was 7.9 times higher than at the control site. On the other hand the lowest value of abortivity (0.37 ± 0.08) was registered in Little Fatra on the east slope of Suchý Mt. in altitude 1.414 m asl. The increase of genotoxic load was found with rising altitude. Determination of heavy metals (especially lead and cadmium) in pine needles by chemical analyses (XRF spectrometry and AAS) is a part of the ongoing research of Needle net. Accumulation potential of *Pinus mugo* and differences in the lead and cadmium distribution in various parts of the plant (one-five year old needles) are assessed.

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COMPARISON OF AIR AND SOIL CONTRIBUTIONS TO THE TOXIC METAL POLLUTION LOAD OF BIOMONITORING CONIFERS (COMMON YEW)

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Taxusbaccata (common yew) can be used as biomonitor for the assessment of the toxic metal pollution in urban areas. This species is very resistant and can grow in very polluted areas, which might be uninhabitual to the other conifer species. Toxic metals can be easily extracted from the plant's leaves. It remains unclear what sort of the pollution do we actually follow with this procedure. Toxic metals can be accumulated over time in the leaves, either as the result of atmospheric deposition or by extraction from the soil via plants root system. Plants are able to accumulate toxic metals or block their transfer to the leaves. These processes contribute to the complexity of toxic metals dynamics in the plant and interfere with the biomonitoring of air pollution.

Samples of the soil, one year old leaves and recently emerged shoots were collected in the Belgrade urban area from the locations with various pollution loads. Soil was sampled at different depths ranging from 0.5 m to the top layer. Samples were analyzed with WD-XRF technique combined with Uniqunantstandardless procedure which gave us estimation of total metal content of all metals present in the soil and their trends along the depth gradient. Metals from the soil samples collected at the highest depths were extracted with EDTA dissolved in CH_3COONH_4 / CH_3COOH buffer at pH 4.65. This method is capable to extract metals from several sequential extraction fractions (exchangeable fraction, carbonates and metals bound to organic fraction), which mimics bioavailability of analyzed metals to the plant's root system. WD-XRF was applied again to the soil sample residuals after EDTA extraction. Plant material was digested in microwave oven with concentrated nitric acid and hydrogen-peroxide. Metal concentrations in digestates and EDTA extracts were determined with ICP-OES technique.

Ca had highest ratio between EDTA fraction and total soil sample content, which was expected since it is major constituent of the carbonate fraction in the soil. Al, Ba, Ca, Cr, Cu, Fe, Li, Mn, Na, Pb and Sr had higher concentrations in older leaves than in shoots while K, Ni and Zn did not accumulate in leaves over time, therefore yew might not be suitable for the biomonitoring of these 3 elements. Statistically significant correlation between EDTA extracts and plant material digestates were noticed only for K ($P<0.01$) and Li ($P<0.05$). EDTA extracts have similar correlations with shoot and older leaves digestates. These results imply that atmosperic deposition is majour contributant to the toxic metal load in the yew's leaves.

Poster C-05

STATISTICAL EVALUATION OF THE DATA DETERMINATION OF PLATINUM IN AIR IN THE CITY OF BRNO BY ET-AAS AFTER SPE PRECONCENTRATION

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This study investigated occurrence of platinum in urban dust in the city of Brno. Platinum is relatively new pollutant in the environment. The concentration of platinum is very low in various parts of environment. The preconcentration this element is necessary from this reason. The solid phase extraction was used in our experiment and octadecyl modified silicagel was used for sorption as suitable sorbent. It was essential to determine the suitable conditions for preconcentration and measurement of platinum. We were focused on selection of suitable type of eluent mixture, suitable acidity of final solution and suitable concentration of cationic surfactant Septonex. All these partial experiments were statistically evaluated.

This method was used for preconcentration of platinum from urban airborne dust. The glass microfibre filters GF/C Whatman were used for sampling air dust and furthermore for analysis. The resulting concentration of platinum was measured by atomic absorption spectrometry with electrothermal atomization.

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Session D:

Ecotoxicology, Biomarkers, Bioindicators

Posters D-01 – D-06

Poster D-01

ECOTOXICITY ASSESSMENT OF ARSENIC-CONTAMINATED SUBSTRATES USING SENTINEL ORGANISM *HELIX ASPERSA*

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This work discusses possible using of terrestrial gastropod *Helix aspersa* (or *Cantareus aspersus*) in soil ecotoxicology. The main aim is to evaluate the possible toxic effect of different substrates (composts and vermicomposts) highly contaminated by arsenic using four different life stages of the mentioned organism. These four life stages are: eggs, new hatchlings, juvenile snails and adults. The impact of two (nutritionally different) types of food was also observed. The first one was commercial food, Helixal®, which is commonly used as a food rich in nutrients at snail farms in France. The second one was lettuce (*Lactuca sativa*), which was freeze-dried and ground to obtain powder form. In this case, the nutritional value was very low in comparison with the first type. There were few endpoints monitored during and after the tests: mortality, hatching success, growth inhibition (body mass and shell diameter), and the state of the albumen gland (one of the key parts of the reproductive system). The results demonstrated that different life stages of the terrestrial snail show a variable sensibility to contaminated substrates. The impact of different types of food was also confirmed – the growth inhibition level was much lower at snails exposed to nutritionally rich food than in those exposed to *L. sativa*. The toxicity of substrates differed depending on the type of the substrate, e.g., vermicomposted samples showed a higher degree of toxic effects than the traditionally composted ones. This is a rather curious situation because the results of the previous chemical analysis showed quite the opposite with regard to the amount of extractable arsenic content. This suggests that the analytical approach alone may not be sufficient to fully predict effects of various contaminants on biota of terrestrial ecosystems.

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Poster D-02

OXIDATIVE STRESS AND HISTOPATHOLOGICAL ALTERATIONS ARE EARLY BIOMARKERS OF PB-INDUCED DAMAGE IN EUROPEAN SEABASS, *DICENTRARCHUS LABRAX*

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The aim of the present study was to assess the potential induction of oxidative and histopathological damage after a waterborne Pb-exposure in gills, muscle, liver and brain of *European seabass*, *Dicentrarchus labrax*, the most important commercial fish widely cultured in the Mediterranean. Juvenile fish were grouped in 30 L tanks and exposed under laboratory conditions for 24 or 96 hours to nominal Pb concentrations of 0 (controls), 0.01, 0.1, 1 and 10 ppm by adding $Pb(CH_3COOH)_2$. Actual Pb concentrations were analyzed in water samples by ICP-AES or DPASV and in fish tissues by ICP-MS. A set of biomarkers of oxidative damage including lipid peroxidation (LPO), superoxide dismutase (SOD), catalase (CAT) as well as the presence of histopathological alterations, were evaluated. Pb concentrations (mg/kg d.w.) observed in tissue samples, ranged between 0.33 and 28.16 (gills); 0.014 and 5.24 (brain); 0.011 and 2.83 (liver); and finally 0.026 and 0.339 (muscle). Regarding the time of exposure, Pb concentration increased significantly in gills and slightly in liver and brain; muscle was affected to a lesser extent. After Pb exposure, HP (hydroperoxides) content was increased in all the studied organs, but the higher HP levels were observed in gills. SOD activity was higher in gills and liver, although it was also stimulated in brain tissue. CAT activity were increased by Pb in descending order gills>liver>brain>muscle. Histopathological lesions as steatosis, blood cells accumulation in vascular system and cellular atrophy leading to parenchyma disorganization were detected in liver. Gills showed alterations as oedemas, aneurysms, hypertrophy of lamellar epithelia and epithelial desquamation. These results strongly suggest that Pb exposure caused an accumulation of the metal that correlated with the induction of oxidative stress and organ specific antioxidant response and histopathological damage in the fish tissues, which may serve as early biomarkers of Pb toxicity in fish.

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Poster D-03

ARSENIC BIOACCUMULATION AND HISTOPATHOLOGICAL EFECTS IN SEA BREAM (*SPARUS AURATA*) AFTER SHORT-EXPOSURE

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The increasing pollution by metals and metalloids in the water bodies has raised concern about to know their potential toxicity to aquatic life. The studies are focus on metal such as Cu, Pb, Hg, but biological effects caused by arsenic in fish have been few accomplished. It has been shown that certain organisms accumulate arsenic mainly in liver, followed in the gills, but brain and muscle present low concentrations of this metalloid; the most common damages are aneurysms and hyperplasia of the epithelium in gills and necrosis and vacuolization in liver.

In this work, the bioaccumulation and histopathological effects in Sea bream (*Sparus aurata*) after short-exposure to As were studied to correlate potential toxic levels of metal in water with biological effects in fish tissues. The bioassays were carried out in laboratory and gill, muscle, liver and brain tissues of Sea bream were analyzed. This specie is one of the most important commercial fish widely cultured in the Mediterranean being very interesting to develop aquatic quality criteria to this metalloid.

The results demonstrated that sublethal concentrations of 0.0076; 0.076; 0.757 and 7.575 mg/L of arsenic were mainly more accumulated in liver and gills than muscle and brain and caused moderate histopathological lesions in liver. In addition, correlations among the arsenic content in tissues, the concentration of arsenic in water and histological alterations were found. It is remarkable that the Sea bream showed correlations among arsenic content in brain and the histological alterations, showing necrosis in liver and hypertrophy and hyperplasia in gills by high content of metalloid. Therefore, the control of liver and gill tissues of Sea bream can be a good indicator of pollution by arsenic in aquatic ecosystems.

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OCCURRENCE OF LINEAR MUSK COMPOUNDS IN BIOTIC MATRICES

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Synthetic musks are man-made chemicals produced in large quantities and widely used as fragrances in numerous consumer products, such as cosmetics and hygienic products (e.g. perfumes, body lotions, soaps, shampoos), fabric softeners, laundry detergents, air fresheners, food additives and fish bait. Musk compounds are reported to be ubiquitously present in the environment [1, 2, 3]. These compounds are continuously introduced into the environment mainly via urban wastewater effluents. Wastewater treatment plants (WWTPs) have been identified as a major point source of synthetic fragrances entering the environment since they receive continuous inputs of these compounds. However, the efficiencies in WWTPs are often low and compounds which are not removed are released to the surface waters, groundwater, air and biota [4]. As most of these compounds are very lipophilic, they tend to accumulate in sediments, sludges and biota, such as fish [5]. Musk compounds belong to persistent organic pollutants (POPs) because of their persistence, bioaccumulation potential and toxicity.

The aim of this study was determination of selected synthetic fragrances in fish muscle. Fish (*Squalius cephalus*) were caught from the Svratka river upstream and downstream of the WWTP Brno – Modřice (Czech Republic) and analysed to determine the presence of musk compounds. Four representatives from the group of linear musk compounds (Dihydromyrcenol, Cyclohexylethylacetate, Arofir, Cyclacet/Jasmocyclene) were choosen for the monitoring. Selected musk compounds were extracted from fish muscles using the pressurized solvent extraction method (PSE). After extraction, the samples were purified by column chromatography using florisil as a sorbent. Analytes were identified by gas chromatography coupled with mass spectrometry (GC-MS). Selected musk compounds were quantified using calibration curves measured for individual analytes.

Acknowledgement:
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Poster D-05

DETERMINATION OF METAL CONCENTRATIONS AROUND THERMAL POWER PLANTS AND IN URBAN AREAS USING HONEYBEES (*APIS MELLIFERA* L.) AS BIOINDICATORS

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Coal power plants have a long history of environmental unfriendliness due to their emission of organic and inorganic pollutants. During coal combustion, a significant amount of various metals some of which are toxic (such as Pb, Cd, Hg, etc.), are emitted to the environment through different pathways [1]. It is important to monitor the amounts of those elements in the environment. Since earlier studies show that the bee organism reacts quickly to various external factors, it makes it possible forhoney bees to be used as an accumulative and reactive indicator for biomonitoring related to environmental quality [2, 3].

The aim of this study was to determine and compare the levels of Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn in bodies of honeybees around thermal power plants and in urban areas. The sampling was conducted at five different apiaries. Two sampling stations were located in an urban area (city of Belgrade). Three were located in the vicinity of two coal fueled power plants (Thermal Power Plant (TPP) Kostolac A and B). Samples were mineralized using microwave digestion. Quantitative analysis was done using ICP-OES.

Average values of the two sampling stations in Belgrade were compared to the average values of the three sampling stations around TPP Kostolac. It was found that most of the analyzed elements had higher concentrations around Thermal Power Plant Kostolac. Only Cd, Cu and Pb had higher concentrations in the urban area. The biggest difference between concentrations was found for Al, after that for Li and Cr in favor of the TPP area. The smallest differences were found for Mg, Ca and Ba.

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SEWAGE SLUDGES - THEIR POSSIBLE ECOTOXICITY

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The aim of this work was to evaluate the influence of contaminated matrices introduced into the ecosystem generated by anthropogenic activities in terms of ecotoxicity. For experimental purposes sewage sludge as the bulk waste with the ever-increasing production were chosen. It is expected that in 2020 the EU will produce 13 million tons of sludge. On the one hand there is the effort to reuse sludge by composting as fertilizers or as reclamation material and to recycle organic matter and nutrients. On the other hand, there is a real risk of environmental contamination due to possible present contaminants. Sewage sludge was tested with regard at its most common use – application on the agricultural land. Possible application and application rate is limited by legislative (Decree No. 382/2001 Coll. conditions of use of treated sludge on agricultural land) through the concentration limits of hazardous elements, however it doesn´t require to test the sludge in terms of their potential ecotoxicity. For this reason, the potential ecotoxicity of sludge was evaluated. Ecotoxicological evaluation was performed using the contact bioassays. As the test animal organisms *Eisenia foetida, Folsomia candida*, *Heterocypris incongruens* and plant organism *Lactuca sativa* were selected. Tested sludge derived from wastewater treatment plants Brno - Modřice, Valtice, Mikulov and Lednice. Next step was to test sewage sludge as a waste that means to evaluate if they exhibit dangerous property (criterion H-14) ecotoxicity. For this purpose sewage sludge with artificial soil in ratio 1:1 were mixed. Sewage sludges showed no ecotoxicity while respecting the application amount established by the regulation. In this case it can be concluded that soils enriched by sewage sludge have positively effect on organisms of soil biota. Adverse results in the case of criterion H-14 testing were obtained. Namely sewage sludge from Brno-Modřice exhibited in the majority of test organisms 100% mortality.

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Session E:

Green chemistry, Green technologies

Posters E-01 – E-06

Poster E-01

BIODEGRADATION OF PHB FILMS IN VARIOUS ENVIRONMENTS

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Polymers are widely used in various industrial fields due to their merits, such as light weigh, resistance to chemicals, resistance to the environment, easy processing. It is difficult for polymers to be treated after use due to their resistance to the environment. When polymers are disposed of in a natural environment, they remain for a long time without degradation. The biodegradable polymers can be classified according to their chemical composition, origin and synthesis method, processing method, economic importance, application. One of the biopolymers class are polyhydroxyalkanoates (PHA). Polyhydroxyalkanoates (PHA) are produced from renewable carbon resources by some microorganisms belonging to the Bacteria and Archaea domains of life. Microorganisms can degrade PHAs under both aerobic and anaerobic conditions, using degradation fragments as source of energy and carbon. Under aerobic conditions PHAs are degraded to carbon dioxide and water as metabolic end products, under anaerobic conditions to water and methane. PHAs are environmentally compatible polymer materials and can be processed into films and fibers [1, 2, 3].

The work was aimed at biodegradability testing of PHB films in various environments. PHB films were tested in liquid media with presence of three species of microorganisms. *Delftia acidovorans*, *Aureobasidium pullulans* and *Aspergillus fumigatus* were selected for biodegradation process based on their PHA-depolymerase activities. Enzyme activity was tested by turbidimetric measurement. Maximum PHB depolymerase activity was observed in case of degradation of PHA by *Aspergillus fumigatus*. Biodegradability testing was also carried out using standard biodegradation test described in the norm IS/ISO 20200. This test was performed under thermophilic conditions. Duration of experiment was determined by complete disintegration of tested material. The process of PHB degradation was completely done in 15 days.

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BIOETHANOL PRODUCTION BY SSF METHOD USING RAPESEED RESIDUE

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The resources of fossil fuels are diminishing and the consumption of crude oil is constantly growing. Also by using, production and processing of oil a huge amount of greenhouse gases are released. This leads to need of finding a new and renewable fuels sources.

Czech Republic belongs to 12 top rapeseed producers in the world with production of 1.532 million tonnes in 2014. During rapeseed processing huge amounts of rapeseed cake are accumulated. It is mainly composed of cellulose 17.35 %, hemicelluloses 31.26 % and lignin 1.13 %. The polysaccharides present in the press cake are a suitable source of sugar monomers. These can be released by acid or enzymatic hydrolysis. The hydrolytic breakdown of polysaccharides is then followed by fermentation of sugar monomers. For this purpose, two strains of yeast *Saccharomyces cerevisiae* and *S. bayanus*, were used for fermentation.

The production of ethanol was determined and evaluated by HPLC/RI method. The highest yield of ethanol, 11.56 g/l, was obtained by applying the SSF method. This included using an enzyme cocktail obtained in cultivation of a specific mould on spent coffee grounds. Using the SHF method, with the step of acid hydrolysis, resulted in lower concentrations of ethanol. This was caused by the development of inhibitory substances such as 5-(Hydroxymethyl)furfural. In addition, the rapeseed press cake contains some antinutrients. To these belong protease inhibitors, glucosinolates, phytic acid and tannins. Their presence slows down the growth and metabolism of yeasts. The concentration of these substances has been lowered by extraction of the substrate in acetone: methanol: water (25:25:50) mixture. Following the extraction process the SSF method was applied and this resulted in higher ethanol yields. The ethanol production was increased by 16.25 % and stopped after a 48 h of cultivation at 13.44 g/l.

In conclusion rapeseed cake, can be used as a suitable substrate for bioethanol production.

Poster E-03

RAPESEED CAKE RESIDUE AS A WASTE SUBSTRATE FOR VALUABLE METABOLITES PRODUCTION

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Carotenoids represent a group of valuable molecules for the pharmaceutical, chemical, food and feed industries, not only because they can act as vitamin A precursors, but also for their coloring, antioxidant and possible tumor-inhibiting activity. Recently, microbiological production of carotenoids prior synthetic production is examined. Microbial production in nowadays is focused on reusing of wastes substrates, because of huge economic impact on the overall economical and therefore environmental situation. Due to increasing demand on biodiesel and oil production is main waste substrate accumulated in a huge amount is rapeseed cake residue. The 1.1 million tonnes in 2012 was produced in Czech Republic, which belongs to 12 top rapeseed producers in the world.

In this work utilization of rapeseed cake by some carotenogenic yeasts strains (*Sporobolomyces roseus*, *Rhodotorula glutinis*, and *Cystofilobasidium capitatum*) was compared. The yeasts were cultivated at 28 °C under permanent lightning and stiring. Two kinds of rapeseed cake residue differs from each other by oil content with various ration with glucose were used as a substrate. Carotenoids, ergosterol and ubiquinone were analyzed by HPLC/PDA and the produced biomass was evaluated gravimetrically.

Better carotenoid production was achieved for rapeseed cake with higher content of lipids. The best carotenoid producer (2x higher production) using rapeseed medium in comparison to control glucose medium was strain *S. roseus* rapeseed medium with glucose (ratio 1:1). But there is a problem with relatively low biomass production and potential pathogenic effect in this strain. Thus the most perspective carotenoid producer is strain *C. capitatum* which had biomass production about 8-10 g/l and pigment production was approx. 1.4x higher on glucose : rapeseed medium (3:1) than in control.

Rapeseed cake can be used as a waste substrate for microbial production of value-added product by red yeasts like carotenoids or cereal biomass enriched by some provitamins and fatty acids for feed purposes.

Poster E-04

RECYCLING OF COPPER USED IN ULLMANN REACTION

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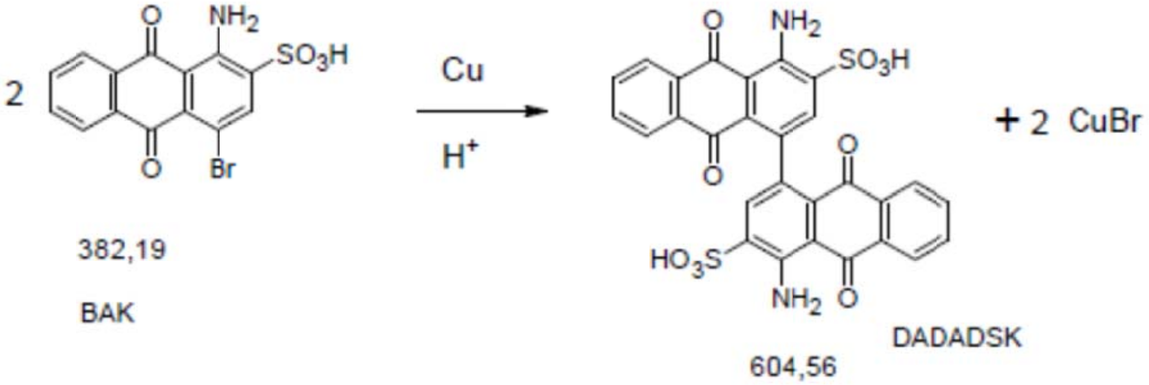
The work describes application of powdered copper in Ullmann type C-C coupling reaction using derivative of bromoanthraquinone as the starting material.

The mentioned Ullmann reaction is essential method used for the preparation of Pigment Red 177, important type of anthraquinone pigment. The reaction scheme illustrates application of copper in the mentioned Ullman reaction:



As could be seen from the reaction scheme, powdered copper is converted to the copper bromide (cuprous slurry). Raw CuBr is isolated as the undesirable by-product and it is contaminated with organic compounds.

We were tested available techniques usefull for the conversion of obtained cuprous slurry to the powdered copper and recycling of this copper powder in the above mentioned Ullmann reaction.

The cuprous slurry was recycled using two different methods.

The first one is based on the conversion of CuBr to the CuO. CuO is isolated as the paste and reduced to powdered copper in suspension using suitable reduction agent.

The second way is based on the dissolution of obtained CuO in sulfuric acid and reduction of the solution of CuSO4.

Powdered iron, zinc and hydrazine were tested as reductants for the recycling of copper from the above mentioned cupric compounds. The obtained copper powders differ in the particle size and morphology.

Prepared copper powders were tested in Ullmann reaction, the yield of desired coupling product reached 92 %.

Acknowledgement:

The work won prize the company of Synthesia, a.s. 2014 and Karel Velek prize 2014 to congress Waste – Luhačovice.

Poster E-05

UTILIZATION OF WASTE MATERIAL FOR IMMOBILIZATION OF CELLULOSE-DEGRADING ENZYMES

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Great amounts of cellulosic wastes are produced worldwide as residues from agriculture and food industry. Cellulose is a polymer of glucose and it is the most abundant organic material in nature. It is however resistant to decomposition. The degradation of cellulose is done by enzymes and the enzyme system consists of at least three components, an exoglucanase, an endoglucanase and a β-glucosidase. In addition, reducing sugars as end products of enzymatic hydrolysis can be fermented by yeasts or bacteria to other valuable metabolites, e.g. bioethanol, a promising alternative fuel nowadays.

The use of microorganisms and enzymes in order to remove or reduce cellulosic wastes is a real environmental challenge, which could be solved by a focused research concerning efficient methods applied in biological degradation processes [1]. The purpose of this work is to present the possibility of the biodegradation of cellulosic wastes by immobilized enzymes.

Cellulase enzyme of *Trichoderma* was immobilized by using crushed polyethylene terephthalate (PET) bottles obtained from wastes, as carrier. The properties of the immobilized cellulase such as the optimum pH, optimum temperature, thermal stability, storage stability and operational stability were investigated. The obtained results were compared with those of free enzyme and two other commercial carriers (Sorsilen, Eupergit C) and they showed that PET carrier is effective; in addition, this carrier is environmental-friendly (reuse of waste) and economical alternative for many commercial and expensive carriers available.

Acknowledgement:
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LIFE CYCLE ASSESSMENT OF Ni-ALUMINA CATALYST

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Ni-based catalysts are attractive industrial catalysts in many reactions such as hydrogenation, reforming, hydrocracking and oxidative dehydrogenation of light alkanes such as ethane (C2-ODH) and propane (C3-ODH). The oxidative dehydrogenation of ethane (C2-ODH) is an attractive process of the production of ethylene. Ethylene is currently produced by pyrolysis and as a by-product in catalytic cracking. C2-ODH is thermodynamically favoured process and the reaction is not limited by coke formation [1].

In this work we are focusing on the Life Cycle Assessment (LCA) analysis of the production of Ni-alumina catalyst and the efficiency of ethylene production. To fulfil this aim we focused on the separate problems of Ni-alumina catalyst preparation (impregnation, thermal treatment) and catalytic reaction. LCA analysis is for example used to analyse the process of the utilization and production of biofuels. This work contribute to the LCA analysis of heterogeneously catalyse reaction with respect to the catalyst preparation and the catalytic reaction. The system boundaries are set for laboratory production of catalysts. In this work we used data from European reference Life-Cycle Database (EPLCA) for electrical energy and basic input substances. We found a lot of articles on general topics LCA (waste management, recycling materials…)[2, 3], but It is only few works focusing on this topic.

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Session F:

Analytical Methods for Environmental Sciences

Posters F-01 – D-27

Poster F-01

EFFECT OF CONCENTRATION AND TEMPERATURE ON MASS-TRANSFER IN METAL ION-EXCHANGE WITH IDA RESINS

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The dependence of effective diffusion coefficient with concentration and temperature was studied during the ion exchange of copper and cobalt onto a chelating resin. The value of the effective diffusion coefficient determined experimentally shows a large dependence on the concentration of the diffusing cation. The reaction temperature affects both the diffusion process and the chemical equilibrium. Solid metal retention is higher at higher temperature. The Arrhenius equation provides good fit of the effective diffusion coefficient at different temperatures. The calculated activation energy values are in the range of those characteristics for physical processes such as diffusion. The pH and the solution concentration clearly increase the estimated value of the activation energy associated with the diffusion process.

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INTRAPARTICULAR TRANSPORT MECHANISM ON IMINODIACETIC ION EXCHAGER RESINS

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In this work we have performed kinetic studies of metal loading on the Lewatit TP-208 iminodiacetic resin. We have studied the concentration effect on the loading kinetics obtaining that the metal load increases proportionately to its concentration in the external solution. Also it has been concluded that in cases where the concentration of metal in the outer solution is lower, the copper kinetic exchange tends to be controlled by external diffusion, unlike kinetics with more concentrated solutions where the controlling step is clearly internal diffusion.

On the other hand, optical microscopy and SEM/EDX studies have been applied to samples taken from the kinetic assays obtaining some internal fronts of concentration which are optically very sharp but after the SEM/EDX line scan over the radial surface of the particle, trace metals appear in the center of the particle for short reaction times when no heavy metal should be reached the core of the particle.

To explain this phenomenon, a kinetic model of a macroporous ion exchange considering heterogeneous system where the accumulation of solute occurs both in the solid phase and in the fluid of the intraparticle pores is proposed. It is considered a two phase system in which the pores are filled with the external ionic solution, and the solid phase does not suffers solvent flow to/from the pores. Thus, the effective diffusion coefficient of the proposed model is a function of diffusion coefficient in the pore and diffusion coefficient in the gel. Comparing the values of the experimental and the estimated effective diffusion coefficients a good fit of them is obtained.

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Poster F-03

SYSTEMATIC STUDY ON CLEANING PROCEDURES FOR ELEMENTAL ANALYSIS OF HAIR

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Hair is known to accumulate chemicals at higher concentrations than blood, serum or urine. To monitor the environmental burden of the organism (exposure to pollution or accumulation in the body), hair analysis (horsehair, fur, wool etc.) has been recently more widely used to demonstrate the organism intoxication with heavy metals or various organic substances. This matrix is non-invasive, easily available and transportable without any special storage requirements.

Pitfall of hair analysis is a pretreatment step including some cleaning procedures1-3. Although a number of previous studies recommended a wide scale of washing procedures (using of nitric acid, substances as acetone or ethanol, surfactants or chelating agents), any unified procedure (with the exception of the IAEA procedure4) has not existed yet. Preparation steps and their actual testing and optimization bring environmental risk, which has to be minimized if a green analytical chemistry approach is taken into account.

Instead of the one-factor-at-a-time method, optimizing of pretreatment steps can be carried out using of some DOE procedures (design of experiment, e.g. full factorial experiments, Box–Behnken designs, central composite design) with response surface methodologies. These methods are very effective especially in reducing the number of experiments needed for optimizing processes. The DOE, which is built on the analysis of variance, is suitable for evaluating of the effects of several independent variables and their possible interactions between experimental factors5.

The aim of this work was to find a suitable washing procedure used before decomposition and consequential horsehair analysis using inductively coupled plasma optical emission and mass methods. The testing process was divided into two parts. Firstly, the effect of single cleaning media (nitric acid, acetone, Triton X-100, EDTA) was evaluated with the use of statistical methods for the DOE (a full factorial experiment consists of four factors at two levels). The second step dealing with optimization of cleaning conditions (concentration of washing media, time, and agitation support) was assessed using a reduced 2k-p factorial plan.

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Poster F-04

SUPERCRITICAL FLUID EXTRACTION OF ARCTIC BROWN ALGAE

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The research is devoted to supercritical fluid extraction of Arctic brown algae. The object of research were 29 samples of 4 trade brown algae (*Saccharina latissima, Laminaria digitata, Fucus vesiculosus, Ascophyllum nodosum*). Algae have been sampled during the expedition "Arctic Floating University" in 2012 and 2013 years in the White, Barents and Greenland seas. Pigment content in samples was investigated. Chlorophyll content was ranged from 0.01 to 0.05 d.w.% and carotenoid content was ranged from 0.005 to 0.025 d.w.%. The highest chlorophyll and carotenoid content was observed in samples of *L. digitata* and *F. vesiculosus*. While moving of sampling point from north to the south the increasing dependence of total pigment content was observed.

The research objects for the supercritical fluid extraction were samples of *F. vesiculosus* and *L. digitata*, obtained in the Russky Kuzov Island in White Sea. These algae species and sampling point are the most perspective for the future research and industrial processing (from the considered), in terms of pigment content.

The experiment was carried out with ananalytical supercritical fluid system ASFE (Waters, USA). The operating conditions were: supercritical fluid CO_2, fluid flow rate 3-9 ml/min, pressure 10-35 MPa, temperature 40-80 ^{0}C, time 30 - 120 min, algae initial moisture 0-25%, fraction size 0.03 - 2 mm, cosolvent (methanol, ethanol, isopropanol), cosolvent flow rate 10-50% of fluid v/v.

Optimal extraction conditions were established basedon the data of extraction yield and pigment content. The optimal extraction conditions (from the considered) are: fluid flow rate 6 ml/min, pressure 30 MPa, temperature 80 ^{0}C, time 60 min, algae initial moisture 9%, fraction size 0,03 mm, cosolvent - ethanol, cosolvent flow rate 10% of fluid v/v.

Extraction yield, chlorophyll and carotenoid content, amino acid composition, polyphenolic content, fatty acid composition and mannitol content were measured in extracts. The extraction yield of supercritical extract of *L. digitata* was 3.85 % of algae dry weight. The main components are: mannitol 85% (of total extract), free amino acids 2.9%, carotenoids 0,26%, chlorophyll 0.4%, fatty acids 0.5%.

The extraction yield of supercritical extract of f.vesiculosus was 6.81 % of algae dry weight. The main components are: mannitol 4.8% (of total extract), fatty acids 7.0%, chlorophyll 0.66%, carotenoids 0.1%.

Antioxidant activity of extracts also was measured by TROLOX equivalent method. Mass of trolox that equivalent to the antioxidant compounds in extract of *L. digitata* is 5.8 mg (160 mg/g of dry extract) and in the extract of *F. vesiculosus* is 23.1 mg (360 mg/g of dry extract).

The results of this work are shows that Arctic brown algae are perspective source of antioxidant compounds. For today the best and ecological way for the recovery of these components is SFE.

Acknowledgement:
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UPLC-MS/MS METHOD FOR QUANTIFICATION OF EIGHT MAJOR ERGOT ALKALOIDS AND THEIR CORRESPONDING EPIMERS IN FEED

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Ergot alkaloids are mycotoxins produced predominantly by fungi of the *Claviceps* genus, which mainly affect cereals and wild grasses. Ingestion of ergot alkaloids can cause severe health problems in humans and animals. Thus, there is a need for methods that allow determination of these dangerous toxins.

A method based on liquid chromatography-tandem mass spectrometry (LC-MS/MS) has been developed for the simultaneous determination of eight ergot alkaloids: ergosine, ergocornine, ergocryptine and ergocristine and their corresponding epimers as well. Mean recovery, precision, matrix effects and limits of quantification (LOQ) were assessed for cereal and grass matrices within the method validation. Sample preparation based on modified QuEChERS approach was employed.

The presented method was used to inspect various feed samples. Ergot alkaloids were found in 31 out of 113 samples investigated. Ergocornine was the most frequently occurring alkaloid, while the highest levels were observed for ergocryptine, ergocristinine and ergosinine, depending on the product type. The total alkaloid content in positive samples varied from 10.4 µg/kg to 1855 µg/kg.

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Poster F-06

APPLICATION OF OLIGOSACCHARITED HYPERBRANCHED POLY(ETHYLENE IMINE) IN HIGH PERFORMANCE THIN LAYER CHROMATOGRAPHY (HPTLC)

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Impregnation of a stationary phase by organic and inorganic agents in high performance thin layer chromatography may yield higher separation selectivity and resolution. This work is devoted to investigation of new water-soluble polymers such as functionalized dendritic core (poly(ethyleneimine)-PEI) surrounded by oligosaccharide (OS: maltose, lactose and maltotriose) shell as a components of a silica stationary phase for water-soluble vitamins and amino acids determination and as chiral selectors for β-blockers (propranolol, carvedilol, sotalol) enantiomers separation.

Polymers influence (the degree of substitution by oligosaccharide of functionalized dendritic core, weight of core, content in a stationary phase and method of modification) to efficiency of vitamin and amino acid determination and enantio selectivity factors were obtained.

It was established that such polymers can be used as a modifying agent of chromatographic systems for the concentration of vitamins (B2) and amino acids (lysine, tryptophan and glutamic acids) by HPTLC determination.

A large amount of stereogeniccenters presented in the OS shell of polymers indicate that it is possible to use PEI-OS as chiral selectors by HPTLC enatiomers drug separation. The best chiral separation of β-blockers were achieved by using hb PEI polymers with a maltose and lactose shells. The influence of the density (structure A, B or C) and the type (maltose, lactose) of OS shell on the separation selectivity was observed. The highest enantioselectivity factors (α) of propranolol were achieved in the case of maltose shell polymers structure A as a chiral selectors in the stationary phase.

The separation of enantiomers of sotalol was achieved by 1D and 2D eluting with a PEI-Lac modified stationary phase. The cyclodextrines were chosen for TLC determination of the same analytes to compare the potency of PEI-OS as a chiral selector. It was shown that the enantioselectivity factors of separation achieved by the hb polymers as chiral selectors for sotalol and propranolol were 4-5 times higher. It can be explained by a higher content of hydroxyl groups and stereogeniccenters on the polymers surface.

It is of interest that the separation of carvedilol enantiomers was achieved only by using two chiral selectors simultaneously: L-prolin in the mobile phase and PEI-OS in the modified stationary phase. The maximal values of enantioselectivity factors ($\alpha = 6.4$) were attained only with a PEI-Lactose shell (2 mg/ml) stationary phase and L-proline modified mobile phase (3.4%).

All optimized chiral separation conditions of analytes were obtained in the analysis of the drugs which are racemic mixtures.

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Poster F-07

EFFECT OF TEMPERATURE ON THE MIGRATION OF BENZOPHENONE FROM RECYCLED PAPERBOARD USED IN FOOD PACKAGING TO A FOOD SIMULANT

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Because of its wide use in UV cured products, benzophenone is the most studied photoinitiator, being considered as a surrogate, that is, photoinitiator model contaminant, in a significant number of articles. Once the photoinitiators are in the internal side of the package they can migrate to the food by direct contact or by gas phase. In this work, the effect of contact time and temperature on the migration of the photoinitiator benzophenone from recycled paperboard to a food simulant (tylose) has been carried out. For this purpose, small spiked pieces of recycled paperboard have been in direct contact with the food simulant at different times and temperatures into a press until steady state is reached. The increase of temperature from 70 to 110 ºC gives rise to a increase of the migration of benzophenone from 32% up to 55%, whereas at higher temperatures the migration decreases, probably due to the thermal desorption of the contaminant, thus suggesting that the food simulant is not appropriate for high temperature studies. On the other hand, the influence of the presence of barriers films between the recycled paperboard and the simulant has been also studied. Decrease of migration has been observed for all temperatures. Polyethylene film presents the lower effect, followed by polypropylene and finally by metallized polyester, which significantly reduces benzophenone migration (for example, from 46% (in the absence of film barrier) to less than 3% at 100 ºC).

Poster F-08

ELECTROCHEMICAL DETERMINATION OF THE PHOTOINITIATOR BENZOPHENONE IN RECYCLED PAPERBOARD USED IN FOOD PACKAGING

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Photoinitiators are highly photoactive compounds include in the formulations of ultraviolet (UV) curing printing inks and varnishes. The photoinitiators could be present in the food packaging because it is printed with UV light, benzophenone being one of the most commonly used photoinitiators. Several studies have been conducted into the determination of benzophenone in several foodstuffs, most of the methods based on chromatography. In this work, an electrochemical method for the analysis of benzophenone in three types of recycled paperboard used for food packaging has been developed. An square wave adsorptive stripping method for the analysis of benzophenone has been optimized: hydroalcoholic medium (5% methanol, 0.04 M acetic acid/potassium acetate buffer of pH 4.6) at a frequency of 50 Hz, 0.5 V deposition voltage with a deposition time of 120 min, the potential step being 0.1 s. Under these conditions, the limit of detection was found to be 6 µg/L, much lower than that obtained by HPLC with photometric detection. The concentration of benzophenone in three samples of recycled board of different characteristics was analyzed by both methods, after extracting benzophenone from the samples into methanol. The results obtained by the two methods were in agreement. Finally, a risk assessment was made through the calculation of the specific migration limit (SML), in the three cases being lower than the maximum permitted level in food of 0.6 mg/kg stated by the Annex 6 of the Swiss Ordinance (4th ed. 01-12-2012 coming into force 01-04-2013).

Poster F-09

VOLTAMMETRIC DETERMINATION OF SYNTHETIC ANTIOXIDANTS USING LINEAR SCAN VOLTAMMETRY WITH A GOLD DISC ELECTRODE

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Typical lubricating oils contain various additive compounds, such as detergents, dispersants, corrosion inhibitors, antioxidants, anti-wear, and extreme-pressure agents. The quality of oil is negatively affected by oxidation processes which are in relation with the presence of oxygen, higher temperatures and pressures, as well as of catalytically acting agent. However, a proper addition of antioxidants may significantly decrease the degree of that unwanted oxidation, although the total resistence against oxidation processes can not be achieved [1, 2].

There are various instrumental techniques allowing one to determine these antioxidants, including spectrophotometry [3], liquid chromatography [4]; herein, in combination with electrochemical detection [5], or a mass spectrometer, and gas chromatography. On the other hand, the advantages of synthetic antioxidant electrochemical determinations have been claimed. Electrochemical methods represent a suitable alternative because of the relatively low costs of instrumentation, possibility of miniaturization, and particularly the fast and sensitive performance of analysis. However, it is known that overlapping of electroanalytical responses in mixtures of synthetic phenolic antioxidants is sometimes strong, generally preventing their simultaneous quantification.

The most common phenol-type antioxidants include Butylated hydroxytoluene (BHT), butylated hydroxyanisol (BHA), tert-butylhydroquinone (TBHQ), propyl gallate (PG) and pyrogallol (PA). In practice, a mixture of two or more antioxidants is found to be more effective than the use of a single compound. Since these substances are chemically similar, analysis becomes difficult at trace concentrations without prior separation.

In this work, a new method has been suggested for determination of synthetic antioxidants in petroleum products when using linear-sweep voltammetry in combination with a gold disc electrode. Samples of biodiesel were analyzed direct in supporting electrolyte (isopropanol containing 0.1 mol/ L sulfuric acid) without any special sample treatment and samples of oil had to be extracted with 96% ethanol. The method proposed can be characterized as relatively simple, quick, and capable of being carried out with satisfying accuracy and precision. Also, contrary to other techniques, it does not require expensive instrumentation and the operational costs are minimal. Based on the results of analyses of spiked and real samples, it seems that the method developed can be recommended for practical analysis in the laboratories of oil refineries and similar industrial service stations. The electroanalytical method proposed has enabled the determination of antioxidants in real samples of biodiesel and oils with satisfactory results and prospects for practical analysis.

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XRD ANALYSES OVER THE CEMENTS TO CONFIRM THE BIOCHEMICAL ORIGIN OF CEMENTED SANDS

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Coastal cemented sands are sedimentary rocks resulting from the in-situ precipitation of $CaCO_3$ in the intertidal zone, prevailingly at low latitudes where evaporation rates and the saturation of carbonates in marine waters determine such phenomenon. Conversely, in the studied temperate latitude locations, the mentioned parameters do not explain the occurrence of the amalgamated structures, whereas the high anthropogenic influence of the area could have promoted variations of the local physicochemical properties inducing the cementation.

In order to ascertain the mineralogical crystalline habit of the compounds integrating the cements, selective destructive analyses were conducted by X-ray diffraction (XRD) spectrometry over the cements to confirm the results derived from non-destructive techniques such as Raman spectroscopy or SEM-EDX analyses. For that purpose, open air exposed and not exposed samples obtained by core drilling in two emplacements were selected.

Based on the dual/wave particle nature of X-rays, $CaCO_3$ polymorphs like orthorhombic aragonite and trigonal calcite with different amounts of Mg accounting for the presence of $Ca(Mg)CO_3$ were identified on the cements, as well as, other mineral phases associated to the framework grains (e.g. natural compounds such as trigonal quartz (SiO_2) or phyllosilicates and anthropogenic compounds like akermanite-gehlenite ($Ca_2Mg(SiO_7)$-$Ca_2Al\ (AlSiO_7)$) silicate tetragonal series or cristoballite (SiO_2) assumed to be part of scoriaceous or slag waste thrown away to a submarine disposal area located 4 miles north of the target coastal zones).

Moreover, relative percentages of carbonate mineral abundance based on the relative intensity ratio (RIR) and magnesium contents (% mol $MgCO_3$) were quantitatively estimated. Indeed, the presence of Mg in calcites arise from the substitution of Mg^{2+} for Ca^{2+} and depending on the Mg content two types of calcites are discerned. This fact in accordance with the existence of some amorphous carbonaceous phases, contributes on the elucidation of the role of the microbiological processes and the organomineralization activities in the first steps of the cementation processes.

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Poster F-11

DEVELOPMENT OF HPLC-DAD METHOD FOR DETERMINATION OF IMIDACLOPRID IN POLLEN FROM AUTONOMOUS PROVINCE OF VOJVODINA

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After the EU ban on the use of the neonicotinoids in flowering crops that honeybee might visit, there has been an increased interest on determination of the neonicotinoids residues in honeybee products such as pollen. Imidacloprid is currently the most widely used insecticide in the world and can be applied by soil and tree injection, application to the skin of the plant, broadcast foliar, ground application as a granular or liquid formulation, or as a pesticide-coated seed treatment. Recent research suggests that widespread agricultural use of imidacloprid and other neonicotinoids may be contributing to honey bee colony collapse disorder, the decline of honey bee colonies in Europe and North America. The objective of this study was to develop HPLC-DAD analytical method with QuEChERS sample preparation procedure for the analysis of neonicotinoidimidacloprid in pollen samples. The optimized method was validated to fulfil the requirements of SANCO/12495/2011 for the sample pretreatment procedure providing results for accuracy (R 70-120%), repeatability and within-laboratory reproducibility (RSD <20%), limit of detection (LOD, 2.5 $\mu g\ kg^{-1}$) and quantification (LOQ, 5.0 $\mu g\ kg^{-1}$). Matrix effects were compensated by the use of matrix-matched calibration. For the first time, pollen samples collected from Autonomous Province of Vojvodina were analysed discovering the presence of imidacloprid, therefore implicating the necessity of ongoing control of this type of food.

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DETERMINATION OF SELECTED PERFLUOROALKYL SUBSTANCES IN SEWAGE SLUDGE BY UPLC-MS/MS

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Perfluoroalkyl substances (PFAS) are environmental contaminants of anthropogenic origin. They comprise a large group of compounds including perfluorosulfonates (PFSAs) and perfluorocarboxylic acids (PFCAs). These chemicals have unique physicochemical properties and therefore they are widely used in industrial applications, especially as surfactants. These persistent substances have been reported in a wide range of environmental matrices including water, biota and sludge [1]. In the Czech Republic, there are currently no legislation limits for PFAS content in sludge intended for application in agriculture as a fertilizer. The aim of the present study was (i) optimization of preparation procedures for PFAS in sludge samples, and (ii) to carry out screening of selected PFAS in sewage sludge collected in Czech waste water treatment plants.

Three extractions techniques were compared within optimization: accelerated Soxhlet extraction, pressurized liquid extraction and the Powley method [2]. The last method showed sufficient efficiency, the lowest matrix effect and minimal background. Two approaches were tested for extract clean up: liquid-liquid extraction with hexane and dispersive solid phase extraction with graphitized carbon. Samples were analysed by ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC-MS/MS) with negative electrospray ionization. Data acquisition was performed in multiple reaction monitoring mode (MRM). Five PFCAs and perfluorooctanesulfonate were determined in sludge samples. The method limit of quantification was 0.1 $\mu g\ kg^{-1}$. Requirements on trueness and precision given in the Commission Decision 2002/657/EC were fulfilled for all tested PFAS [3].

PFAS screening was carried out on 41 sewage sludge samples in 2013–2014. Perfluorooctanesulfonate (0.74–390.26 $\mu g\ kg^{-1}$), perfluorodecanoic acid (0.42–46.90 $\mu g\ kg^{-1}$) and perfluorooctanoic acid (0.47–21.04 $\mu g\ kg^{-1}$) were present in all sludge samples. These results corresponded to previously published data [4, 5]. The continuous collection of data on the occurrence of PFAS in sewage sludge and the optimization of the method to analyse long-chain PFAS will be the subject of future study.

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Poster F-13

VITAMIN D IN THE SELECTED FOODS

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Vitamin D intake is currently very actual theme. It is known that sunlight stimulates synthesis of vitamin D3 (cholecalciferol) in human organism (UVB rays transform 7-dehydrocholesterol into pre-cholecalciferol). Dietary intake of vitamin D2 (ergocalciferol), and D3 is important in periods and areas where sunlight is not intensive enough.

The monitoring of vitamin D in the Czech foods was organized1. Some myths from internet and magazines about vitamin D2 in food of plant origin were first reviewed2, 3. Fungi and yeast, especially after UV irradiation4, are often presented as the rich source of vitamin D2.

Food samples were purchased during March and September 2013. 10 samples including wild grown (*Boletus sp.*) and cultivated fungi (champignon (*Agaricus bisporus*), oyster (*Pleurotus ostreatus*), shiitake (*Lentinula edodes*), Jews ear (*Auricularia auricula*) and chanterelles (*Cantharellus cibarius*), 8 samples of yeast (4 fresh and 4 dry) some other samples were collected and analysed by LC-MS/MS method.

Average content of vitamin D2 in all kinds of mushrooms was 167 ± 180 µg/100 g dry matter (d.m.). The highest content was detected in shiitake and Jews mushrooms (267 and 637 µg/100 g d.m.). Average content of ergosterol was 2.37 ± 1.61 mg/g d.m. Effect of natural sun irradiation was tested on sliced champignons. Concentration of vitamin D2 increased 22 times after 3.5 hours of sun drying. No sample of yeast contained vitamin D2, content of ergosterol was 3.43 ± 1.61 mg/g. Yeast exposed to UV irradiation, dose of 2017 J/m^2, caused production 931 µg of vitamin D2/100 g. The other food didn't contain any measurable quantity of vitamin D2. Ergosterol was detected in the range of values 295 – 3025 µg/kg (except avocado). Experiments concluded that mushrooms exposed to natural sun irradiation can be a considerable source of vitamin D2 whereas other tested food does not play any important role in covering of daily needs of vitamin D for typical Czech consumers (DRI-AI = 5 – 15 µg/day).

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Poster F-14

HOW TO DEVELOP A CERTIFIED REFERENCE MATERIAL FOR ENVIRONMENTAL ANALYSIS: THE EXAMPLE OF MERCURY IN FISH

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Chemical pollution of surface water poses a threat to the aquatic environment and also to human health. On the European Union's level, the Water Framework Directive (2000/60/EC (WFD)) together with its daughter directives establishes a framework for EU action in the field of water policy and lays down a strategy against the pollution of water. That strategy involves the identification of priority substances among those that pose a significant risk to, or via, the aquatic environment at Union level. A list of environmental quality standards (EQS) for 45 priority substances and certain other pollutants was adopted. However, the EQS for most of the priority substances are so low that measurement of such concentrations is a challenge for the analysts. The analytical methods need to be improved or new ones developed. Furthermore, validation of each method is required. A main part of this process includes the use of certified reference materials (CRMs) in order to check the trueness of the method.

To help the laboratories to prove and improve their measurement capabilities, IRMM offers to its customers more than 800 certified reference materials, about 140 of them related to the environment. Recently, the Institute started the development and production of the certified reference material ERM-CE101 "Mercury and other trace elements in fresh-water fish". A new approach was used for the material processing resulting in a fish paste, a matrix which is very similar to the real fish samples. With this approach the main problem of the commonly produced freeze-dried powders - the difference in the matrix compared to the analysed routine samples - was vastly overcome. The reference material is stable if stored in a refrigerator at 4 °C. Its homogeneity, stability during transportation and during shelf life are guaranteed. The CRM is intended to support the laboratories responsible for the water monitoring under the Water Framework Directive as well as all laboratories dealing with fish analysis.

This presentation provides an overview of the different stages during the production of a certified reference material. As an example, the choice of the raw fish material used for the production of ERM-CE101 "Mercury and other trace elements in fresh-water fish" and its processing are presented. At the end, a short explanation on how to compare a measurement result with the certified value is given.

Poster F-15

A LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC-MS/MS) METHOD FOR THE DETERMINATION OF MONOHYDROXYLATED POLYCYCLIC AROMATIC HYDROCARBONS METABOLITES (OH-PAHS) IN HUMAN URINE

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitously present in the environment and associated with a variety of adverse health effects. In the exposed organisms PAHs are rapidly hydroxylated in the liver and then undergo conjugation, typically to the glucuronides, which are excreted in urine. Biomonitoring of PAH metabolites is an important approach for evaluation of human exposure and body burden of these pollutants, but it is quite complicated. PAHs occur almost exclusively as a complex mixture of several hundred compounds, and except for naphtalene, all potentially carcinogenic PAH are higher condensed substances (more then 4-ring systems), the amounts of which in the complex mixture are far lower than those of the lower condensed PAH. Although urinary 1-hydroxypyrene has been the most commonly used biomarker for PAH inhalation exposure, pyrene itself is not carcinogenic. Therefore, it seems more appropriate to monitor biomarkers of carcinogenic benzo[a]pyrene, but due to its trace levels in air compared to pyrene and predominantly elimination of its metabolites in feces, recently hydroxylated metabolites (OH-PAHs) of abundant gas-phase PAHs such as naphtalene and phenanthrene have gained attention as biomarkers of PAH exposure.

Within our study the analytical procedure consisting of enzyme digestion (β-glucuronidase from *Helix pomatia*) followed by solid phase extraction (sorbent C18) and final determination by ultra-high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) was developed and validated for the simultaneous determination of 11 OH-PAHs in urine. The spectrum of analytes included major 2-, 3- and 4-rings metabolites, namely 1- and 2-hydroxynaphtalene; 2-hydroxyfluorene; 1-, 2-, 3-, 4- and 9-hydroxyphenanthrene; 1-hydroxypyrene; 3-hydroxybenzo[a]pyrene and 6-hydroxychrysene. Target compounds, especially hydroxyphenanthrene isomers, were successfully chromatographically separated using the PFP (pentafluorophenyl) stationary phase. In order to achieve the lowest quantification limits (LOQs) required for real-sample analysis, MS/MS and ionization parameters (capillary voltage, ionization temperature etc.) were extensively tested. Finally, the method was successfully validated: the recoveries for all target compounds ranged from 70 to 120% with relative standard deviations lower than 25% and the LOQs were in the range of 0.025-0.125 ng/ml of urine. In the next phase of our pilot study, the method will be used for the analysis of urine samples obtained within the project Impact of air pollution to genome of newborns (No. 13-13458S).

Poster F-16

DETERMINATION OF VOLATILE ODOUR COMPOUNDS IN SELECTED SPECIES OF MICROALGAE

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Microalgae and cyanobacteria represent some of the oldest living organisms, and their biomass has a potential for use as food, feed, biodiesel production and waste water remediation. However, blooms and scums of cyanobacteria can also occur in various fresh and brackish water environments, causing musty odour and production of harmful toxins. In this work, we investigated selected species of *Spirulina spp.*, *Anabaena spp.* and *Nostoc spp.* originating from Serbia, which were previously proven to be non-toxic. *Nostoc* and *Anabaena* strains were cultivated under laboratory conditions in synthetic mineral broth, with (+N) and without added nitrogen (-N) while *Spirulina* strains were cultivated in mineral SOT broth. The aim of this study was to determine the chemical profile of volatile organic compounds produced by these organisms. The results show that unbranched alcanes represent the main group of volatile compounds in these species, but also that several other important odour-causing compounds, such as methyl-isoborneol, β-ionone and β-cyclocitral were present in all of the tested samples. It was shown that tetradecane and 6,9-heptadecadiene were characteristic for *Spirulina*, and 2,2,6-trimethyl-cyclohexanone was present in all *Anabaena* strains regardless of the presence of nitrogen in the growing media, but not in *Spirulina* and *Nostoc* samples. *Nostoc* strains were characterized by the presence of 8-methyl-heptadecene (2S7B) and 3-octadecene (2S9B), which were not present in *Spirulina* and *Anabaena* strains. Geosmin, as one of the main compounds responsible for earth-like odour was not detected in any of the samples, which can be important for potential future use of these microalgae.

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Poster F-17

POLYCYCLIC AROMATIC HYDROCARBONS, SULFUR- AND OXYGEN HETEROCYCLES RELEASED BY PYROLYSIS OF COAL FROM BOGOVINA EAST FIELD, SERBIA

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The Bogovina Basin is a northeast-southwest elongated tectonic depression, (length of 25 km, width of 2.5 km) and located 220 km southeast of Belgrade. It is divided into two coal fields: West (exhausted deposit) and East field, with coal reserves estimated at 2 Mt [1]. The basin itself is of Oligocene to Upper Miocene age, with two coal seams in East field formed in slightly alkaline depositional environments during Lower Miocene [2].

One subbituminous and one bituminous coal sample were collected from fresh working faces in the underground mine Bogovina East field. Bitumen was extracted from the pulverized coal samples by Soxhlet's extraction and bitumen-free residues were pyrolysed. Pyrolyses were performed in an autoclave under a nitrogen atmosphere, for 4 hours at two temperatures: 250 and 400 °C. Aromatic fractions were isolated from bitumenes and liquid pyrolysates using column chromatography and subsequently analyzed by gas chromatography-mass spectrometry.

Great number of polycyclic aromatic hydrocarbons was formed during pyrolysis, including n-alkyl-benzenes, nonalkylated and alkylated naphthalenes, biphenyls, fluorenes, phenanthrenes, anthracenes, fluoranthenes, pyrenes, benzofluorenes, phenyl-naphthalenes, benzophenanthrenes, benzanthracenes, triphenylenes, chrysenes, terphenyls, phenyl-fluorenes, benzofluoranthenes, benzopyrenes, perylenes, binaphthyls, phenyl-phenanthrenes and phenyl-anthracenes.

Moreover, a variety of polycyclic aromatic sulfurheterocycles was produced, such as nonalkylated and alkylated benzothiophenes, dibenzothiophenes, naphthothiophenes, phenyl-benzothiophenes, benzonaphthothiophenes, phenanthrothiophenes, anthrathiophenes, benzo-phenanthrothiophenes, benzophenalenothiophenes, pyrenothiophenes, triphenyleno-thiophenes, chrysenothiophenes, phenyldibenzothiophenes, phenylnaphthothiophenes, naphthylbenzothiophenes, dinaphthothiophenes and dibenzobenzodithiophenes.

Among polycyclic aromatic oxygen heterocycles, nonalkylated and alkylated dibenzofurans, benzonaphthofurans, phenyl-dibenzofurans, dibenzobenzodifurans and benzoxantenes were identified.

The vast majority of these compounds were produced by complex reactions on sulfur- and oxygen-rich coal macromolecular matrix, such as thermal and catalytic cracking, defunctionalisation, isomerisation, alkylation/dealkylation and others. Many of these are considered to be highly toxic and carcinogenic substances, classified as persistent organic pollutants. They can be produced by incomplete combustion of fossil fuels or – as simulated in this study – in high-pressure industrial processes.

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SPECIATION OF SOME SELECTED HEAVY METALS IN COAL BOTTOM ASH FROM OKABA COAL, ANKPA, NIGERIA

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Speciation of coal cotton ash from Okaba in Kogi State Nigeria was carried out using flame atomic absorption spectrometry. Results of this research showed that the elements studied (Cr, Fe, Cu, Ni, Pb, Cd and Zn) were all observed in at least three fractions of the sequential extraction procedure. Pb showed more presence in the exchangeable fraction (80±0.03 μg/g) which is a serious problem to plants and human due to weathering activities in the soil. Most of the elements with high concentration in the residual fractions were found to be thermally stable and of low volatility (Cu and Zn). Chromium occurred mostly as a reducible fraction (80±0.02 μg/g) while Fe occurred mostly as bound to carbonate species. Cadmium was generally low in all the fractions analysed. This trend may be attributed to high volatility of Cd species. Similarly, Ni had a distribution in all the fractions with the highest in the reducible fraction (39±0.01 μg/g) and lowest in the carbonate bound fraction (24 ±0.01 μg/g). The exchangeable fraction of the elements studied is consistent with previous studies of coal bottom ash speciation. The ash matrix may also have contributed to a significant rise in the concentration of Ni at the exchangeable fraction thereby leading to significant variations in metal concentration over the ash particle.

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Poster F-19

DETERMINATION OF ANIONIC SURFACTANTS BY CAPILLARY ELECTROPHORESIS

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Surfactants are widely used compounds because of their characteristic properties. People use them daily in products of personal care, laundry detergents, cleaning agents, etc. Anionic surfactants belong to the most widespread surfactants.

This study deals with the optimization of method for determination of selected anionic surfactants (Sodium Dodecyl Benzene Sulphonate, Sodium Octyl Sulphate and Sodium Dodecyl Sulphate) by capillary electrophoresis (CE) and subsequent determination of these analytes in samples of common domestic cleaners.

The parameters of the optimised CE method for determination of SDBS are following: a capillary of 50 cm of effective length and 75 μm I.D.; buffer: 10 mmol/L phosphate pH 6.8 in 30% (v/v) acetonitrile; separation voltage 25 kV; UV detection (200 nm). In order to determine SOS and SDS by indirect detection an addition of SDBS to buffer was required.

The “common” and “environmental friendly” washing up liquid, dishwasher powder and laundry gel were analysed and the contents of anionic surfactants were compared.

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Poster F-20

MASS SPECTROMETRY IN EVALUATION OF SEED DORMANCY LEVELS IN LEGUMES

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Timing of seed germination is one of the key steps in plant life cycles. It determines the beginning of plant growth in natural or agricultural ecosystems. Germination is driven by ability of a seed to develop in appropriate conditions. However, not only convenient conditions ensure development of all present individuals in a given set of seeds. The property describing the percentage of seeds which remain inactive in appropriate conditions is dormancy. The level of dormancy is therefore a key element for reproduction of plants from the environmental point of view as well as for efficient production of crops in agriculture. Crop production will be decreased if the dormancy levels of seeds are too high, while yield loss due to pre-harvest sprouting occurs if the seed dormancy levels are too low. Legumes are suitable model plants to study the changes of seed in the first stages of germination [1]. The objective of this study is to develop an effective methodology to distinguish dormant legume types (crop wild relatives) from non-dormant (agriculturally utilizable) ones. Matrix assisted laser desorption ionization high resolution tandem mass spectrometry (MALDI-HRTMS) appeared to be a useful technique to directly study of chemical composition of pea seed coat tissue. The obtained spectra (raw data) further inspected by principal component analysis (PCA) allowed classification of seed samples with respect to dormancy. Compounds present in seed coat tissues influencing the dormancy level were taken out from raw spectra, tabulated and elucidation of their chemical structure is now in progress.

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Poster F-21

THE RELEASE OF PGEs FROM GASOLINE AND DIESEL AUTOMOBILE CATALYSTS AS FUNCTION OF pH

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Motor vehicles represent an important source of highly dispersed environmental contamination. The catalysts wear down chemically and physically during combustion. As a result, platinum group elements (PGEs) can be emitted with exhaust gases in particulate form. The PGEs were identified in the air, road dust, soils and waters. In our research, we focused on leaching behaviour of PGEs from gasoline and diesel automobile catalysts. While catalysts for gasoline engines contain a mixture of Pt-Pd-Rh, catalysts for diesel engines are composed only of Pt. We used dust from two crushed gasoline and two crushed diesel catalysts (new and aged). The dust of gasoline catalysts contains a significant concentrations of Pt (700 $mg.kg^{-1}$), Pd (11 000 $mg.kg^{-1}$) and Rh (700 $mg.kg^{-1}$). And the dust of diesel catalysts are composed of Pt (3 900 $mg.kg^{-1}$) and they contain negligible amounts of Pd and Rh (< 0.5 $mg.kg^{-1}$, < 0.1 $mg.kg^{-1}$, respectively).

To evaluate leaching of PGEs from dust we used pH-stat leaching test according to the European standard CEN/TS 14997 [1]. The concentrations of cations: PGEs (Pt, Pd a Rh), K, Na, Ca, Mg, Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, La and Ce were determined by inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS), and anions: F^-, Cl^-, SO_4^{2-} and NO^{3-} by high-performance liquid chromatography. The calculation of species in leachates was carried out in PHREEQC3 [2].

The leaching of PGEs from catalysts showed a strong dependence on pH. Generally, the highest concentrations were released under acidic conditions. The leaching of PGEs was higher for Pt in diesel catalysts and for Pd and Rh in gasoline catalysts. The PHREEQC3 simulations indicated neutral hydroxyl complexes $Pd(OH)_2^0$, positively charged hydroxyl complexes $PtOH^+$, neutral and negatively charged hydroxyl complexes of Rh. The chloride complexes of PGEs occur under very acidic conditions (pH 2). They are not significant at environmentally relevant pHs. Positively charged species can be absorbed on negatively charged surface of HFO or clay minerals during transportation. The neutral hydroxyl complexes of Pd or Rh may be mobile in the environment.

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RAPID AND SENSITIVE VOLTAMMETRIC ANALYSIS OF PESTICIDES USING SILVER SOLID AMALGAM ELECTRODE

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Pesticides are substances which are used because they exhibit toxicity to certain organisms. Although their effect should be selective, they are often also poisonous to other species, usually to a lesser degree. They may be harmful, even in low concentration, as well to humans either in acute poisonings or after chronic exposure and they have toxic effects on some non-target organisms in the environment. Thus, the investigation of possibilities of their analytical detection and determination has still been important. Voltammetry represents very sensitive, rapid and relatively cheap analytical technique suitable for pesticide analysis. The silver solid amalgam electrode (AgSAE), either the type introduced by Novotny and Yosypchuk [1, 2] or partly different type based on the dental amalgams introduced by Mikkelsen and Schroder [3], represent an intermediate stage between mercury electrodes and solid electrodes. They combine advantages of both above-mentioned types. The AgSAE introduced by Novotny and Yosypchuk was used in experiments described in this contribution.

Within this work, the voltammetric behavior of herbicides triasulfuron, picloram and metamitron as well as of insecticides pymetrozine and imidacloprid has been studied on AgSAE with different surface modifications, and the voltammetric methods for its determination have been proposed. Differential pulse voltammetry in connection with AgSAE has been applied for development of sensitive methods of determination for investigated compounds and the relevant statistical parameters (e.g. LOD, LOQ or RSD) were calculated. All results obtained using AgSAE were compared with those achieved with classical hanging mercury drop electrode (HMDE), which could be replaced by the amalgam electrodes in the area of electroanalytical chemistry especially due to the toxicity of mercury. New proposed methods were successfully applied for analysis of practical samples of pesticide preparations and spiked river or dam water with good accuracy. It was proved that silver solid amalgam electrode represents an environmentally acceptable alternative to mercury electrodes in pesticides analyses.

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Poster F-23

VOLTAMMETRIC BEHAVIOR OF INSECTICIDE IMIDACLOPRID ON SILVER SOLID AMALGAM ELECTRODE

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Imidacloprid (IMI, 1-(6-chloro-3-pyridylmethyl)-N-nitro-imidazolidin-2-ylidenamine)) belongs to the most widely used insecticides in the world. Its major uses include agriculture, arboriculture, home protection, etc. IMI is a systemic insecticide chemically related to the tobacco toxin nicotine. It is used to control sucking insects by the effect on several types of post-synaptic nicotinic acetylcholine receptors in the nervous system. IMI belongs to a class of chemicals called neonicotinoids. The symptoms of the exposure include apathy, incoordination, labored breathing, emaciation, and convulsions.

In the literature electrochemical techniques for IMI determination using mercury electrodes, carbon electrodes or electrodes with variously modified surface have been describe [1, 2]. Silver solid amalgam electrode represents very good alternative to mercury electrodes. It has been utilized in three surface modifications: polished (p-AgSAE), mercury meniscus modified (m-AgSAE) and mercury film modified (MF-AgSAE) silver solid amalgam electrode [3].

In this study the m-AgSAE was used to investigate the electrochemical behavior of the insecticide. All obtained results were compared with those achieved on hanging mercury electrode (HMDE). The parameters of differential pulse voltammetry (DPV) for IMI determination were proposed and also the conditions of regeneration of working electrode surface were optimized. Britton-Robinson buffer of pH 10 (m-AgSAE) and pH 9 (HMDE), respectively, served as a supporting electrolyte. It was found that IMI provides two irreversible cathodic signals corresponding to the insecticide reduction using both tested electrodes. Whereas it has been proved as a diffusion-controlled process the accumulation of IMI was not observed and the method of adsorptive stripping voltammetry could not be used for increasing of sensitivity of IMI determination. The value of LOD for determination of IMI was calculated as 36.2 nmol/L (m-AgSAE) and 2.6 nmol/L (HMDE), respectively. The proposed new method was successfully applied for determination of the insecticide in practical samples of pesticide preparation and spiked river water.

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Poster F-24

DEVELOPMENT OF ANALYTICAL METHOD FOR THE DETERMINATION OF ORGANOPHOSPATE FLAME RETARDANTS AND PHTHALATES IN DUST

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Nowadays, the occurrence of various contaminants in dust is continuously monitored, especially in the indoor environment, where people typically spend most of their time. The exposure via household air and dust represents potential hazard mainly for infants and toddlers, who can put various dusty objects in their mouths. One of the most emerging groups of indoor pollutants are phthalates and organophosphate flame retardants (OPFRs). These compounds are added to the large amount of consumer products and building materials. Phthalates are mainly use in plastic industry as plasticizers while OPFRs are apply to different materials in order to reduce the risk of subsequent development of a fire. However, these contaminants can have potential negative effects on the human organism including neurotoxicity, potential carcinogenicity and several compounds can act as endocrine disruptor.

The aim of the study was to develop and validate the simple and fast analytical method for the simultaneous determination of phthalates (n=8) and OPFRs (n=9) in indoor dust. The identification/quantification of target analytes was realized with gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) operated in the electron ionisation mode (EI). For the method development and validation experiments, the standard reference material of dust (SRM 2585) was used. Although, that for these compounds their concentrations in SRM 2585 are not certified, there is a plenty of similar studies, which published the amounts of phthalates and OPFRs in this matrix. For the isolation of phthalates and OPFRs ultrasonic extraction with organic solvent was optimized. Sample was extracted with nonpolar solvents (ethyl acetate, dichloromethane and acetone) and their mixtures. The extraction efficiency of ethyl acetate was significantly higher compared to other tested solvents/mixtures (13 of total 14 presented in SRM 2585). The results of validation experiments, which were performed on the SRM 2585, were in accordance with published values. The obtained repeatabilities (expressed as relative standard deviation) were lower than 20%. The limits of quantifications were in the range of 5-50 ng/g. Finally, the newly validated method was successfully applied for the monitoring of phthalates and OPFRs in dust samples collected in Prague households.

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Poster F-25

DETERMINATION OF LINEAR MUSK COMPOUNDS IN ABIOTIC MATRIX

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Synthetic musk compounds are artificial organic compounds with a smell similar to the odor of a natural musk. The most recently discovered and also the least known group of artificial musks is linear musk compounds. These substances are now often used in cosmetics, personal care products, detergents and various cleaning products. They have leaked into all the major environment components, especially into the hydrosphere. There has been great attention drawn to synthetic musk compounds in the last few years due too of their environmental impact.

The topic of this research is to identify twelve linear musk compounds (linalool, 2-cyclohexylethanol, fresco menthe, citronellol, HSA, isobornyl acetate, arocet, aroflorone, allyl cyclohexyl propionate, lilial, isoamyl salicylate and hexylcinnamic aldehyde) in waste water samples. The samples were taken at three different waste water treatment plants (WWTP Brno-Modřice, WWTP Luhačovice and WWTP Hodonín) with a different equivalent number of inhabitants.

At the first, a working method was optimized, then applied on real waste water samples. Solid-phase microextraction (SPME) technique was used for the extraction of analytes. Gas chromatography–mass spectrometry (GC/MS) was then used for identification and quantificaton of the studied compounds.

Concentration of selected musk compounds was determined in the range of units to hundredths ng.ml^{-1} in waste water. The highest concentration of linalool and citronellol were determined in all selected waste water treatment plant. The efficiency of cleaning process in waste water treatment plant was calculated from experimental data, in the range of 69.45 – 96.71 %. Despite the high efficiency of the cleaning process surface waters have been contaminated.

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Poster F-26

DETERMINATION OF NONYLPHENOL AND ITS ISOMERS IN WATERS

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This work was focused on the issue of nonylphenol, which is a degradation product of surfactants. Nonylphenol belongs to a group of chemicals called alkylphenols. Found its application in a wide range of industrial applications. The most common occurrence of nonylphenolethoxylates (NPnEO) in the environment is in waste waters and industrial and municipal water. Considerable amount of the total consumption of nonylphenolethoxylates is used in the textile industry as surfactants in dyeing and other adjustments of the textile materials. Nonylphenol however most often arises in wastewater treatment plants predominantly during the microbial degradation of nonylphenolethoxylates used in industry. It is a substance highly bioaccumulative, toxic predominantly to aquatic organisms. In addition, also belong among the substances known as hormone disruptors. In our work nonylphenol was determined in samples of wastewater originating from waste water treatment plant Brno-Modřice. The solid phase extraction (SPE) for the isolation of the analyte and purification of the extract was used. The final determination of analytes using the gas chromatography with tandem mass spectrometry with time of flight analyser (TOF) was performed. All steps of the preanalytical and the analytical procedure were optimized.

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Poster F-27

EFFICIENCY OF TWO ANALYTICAL METHODS FOR THE DETERMINATION OF SELECTED ORGANOCHLORINE PESTICIDES AND PCBS IN FOOD SAMPLES

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Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) belong to food and environmental contaminants and they are included in the group of persistent organic pollutants (POPs) due to their high lipophilic character and resistance to degradation. POPs, according to the Stockholm Convention, should be completely prohibited or widely limited.

Determination of OCPs and PCBs is a very difficult and complex issue because of the need to isolate and accurately identify and measure minute quantities in large number of various matrices. Many analytical procedures for analysing these compounds, based mainly on gas chromatography, were proposed for a wide variety of sample types [1].

The aim of this study was to evaluate the efficiency of two analytical methods (GC/2xECD and GC-QqQ-MS/MS) for the determination of selected 27 organochlorine pesticides and 9 polychlorinated biphenyls in 25 various food samples, representing the average food basket of the Czech population, including meal, vegetables, fruits, bakery and dairy products, fish, eggs, potato and cereal products, tea, spirits. Samples were collected within the Environmental Health Monitoring Programme of the National Institute of Public Health in Prague [2].

ECD detector has always been one of the few devices capable of detecting organochlorine pesticides and PCB congeners. It was decided to compare it with tandem mass spectrometry, which has become one of the most powerful tools in simultaneous quantification-confirmation of these organic compounds due to its high selectivity and sensitivity [1, 3].

Currently it is not possible explicitly to say that the method GC-QqQ-MS/MS or GC/2xECD is more or less effective for the target analytes. Obtained results, mainly LOQ, were better for analysis of PCBs and some OCPs by GC-QqQ-MS/MS but for the most of OCPs the better method was GC/2xECD. Improving of the resolution and decreasing of the LOQ for the GC-QqQ-MS/MS method is the subject of further research.

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Session G:

Emerging contaminants

Poster G-01

Poster G-01

EMERGENT SUBSTANCES AS CHEMICALS THAT CAN ALTER ENDOCRINE SYSTEM

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Chemical substances are present in all compartments of environment and in all spheres of human existence as an inseparable part of modern life. Significant number of these everyday substances, recently named emerging substances (EmS), managed to stay unrecognized due to the fact that they occur at very low doses and are, therefore, not included in routine monitoring programs at EU level and whose fate, behaviour and (eco)toxicological effects are not well understood. The dominant physicochemical characteristics particularly specific for EmS are: stable structure, low/non degradability, lipophilicity and hydrophilicity with log Kow in the range of 0.03 to 10.6, bioconcentration/bioaccumulation, biomagnification and protein interaction, toxicity, eco/toxicity, and acute but rather chronic effect. Most of the emerging substances are endocrine disruptors, with suspected teratogenic, mutagenic and carcinogenic consequences in low and sub low doses. Low doses effect and non-monotonic response in relation to dose are observed in the picomolar to nanomolar range, which is well documented as a characteristic of endocrine disruption chemicals (EDC). There is now substantial evidence that low doses of EDCs have adverse effects on human health as well as on the wildlife. EDCs can alter the metabolism of natural hormones in different ways. EDCs can change the amount of hormone that is available for binding to the receptor, they can have agonistic or antagonistic role. EDCs can change the transport of the hormone, or have the effects that are different from known endocrine action. The traditional thinking in toxicology still does not adequately recognize the effects occurring at low doses, which is still a phenomenon very hard to define since different concentrations can be considered to be low dose. Regardless of that fact, recent epidemiological studies show a clear link between environmentally relevant low concentrations and disease incidence which indicates a responsibility to deal with this issue at a higher level.

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Company Presentations

DIRECT ANALYSIS OF CONTAMINANTS IN WATER USING ULTRA-SENSITIVE LC-MS INSTRUMENTATION

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Analysis of water represents a challenge from the analytical point of view. European drinking water directive defines the maximum limits of pesticides in drinking water to 0.1 ug/l (for individual pesticides and relevant metabolites) and 0.5 ug/l for the sum of pesticides. The limits for other contaminants, such as hormones and pharma substances are not yet defined in EU legistation. The monitoring of these compounds in waste, surface and drinking water is being realized to assess the presence and risks of these contaminants for cosidering their future implementation in the legislation.

The use of modern pesticides of polar and less stable character implies the move from traditional GC-MS methods to LC-MS instrumentation that is able to cover not only the polar pesticides, but also the above-mentioned pharma compounds. To achieve sufficient limits of quantification with respect to EU legislation requirements, the classical sample preparation approaches to sample involve loading of large volume of water (typically 100 – 1000 ml) to SPE cartridge, elution by organic solvent, concentration step. With the development of LC-MS instrumentation towards more sensitive techniques, today, much simpler sample prep is possible, such as online SPE or even direct analysis.

In this presentation, two applications will be demonstrated: i) targeted and ultra-sensitive determination of hormones in drinking water using UHPLC coupled to a triple quadrupole instrument. ii) screening of pharmaceutical drugs residues in water using UHPLC – QTOF instrument.

QUICK, RELIABLE AND SENSITIVE ANALYSIS OF ENVIRONMENTAL CONTAMINANTS IN DIFFERENT MATRICES USING AGILENT GC–MS INSTRUMENTS

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The number of environmental contaminants which undergo the legislative control or are included in the monitoring programs of the European Food Safety Authority and other international bodies as the U.S. Environmental Protection Agency and the U.S. Food and Drug Administration still increases, as a consequence, the demand for high throughput, selective, sensitive and non-expensive analytical methods arises as well.

In this presentation, implementation of various GC–MS systems for the analysis of different types of environmental contaminants will be introduced. Emphasis will be paid on speeding up the whole methodologies while maintaining or improving the reliability and sensitivity of the whole analysis. Both target and non-target GC–MS approaches will be shown. Determination of known substances using GC–MS/MS together with extensive Agilent compounds databases as well as non-target screening of environmental samples contamination using Agilent GC–QTOF MS system will be demonstrated. Different high-end tools connected with GC–MS instruments including backflush technology, retention time locking, self-cleaning ion source and many others will be present on the following real case studies:

Case study #1: “Determination of persistent organic pollutants (POPs) in fish tissue using the Agilent 7000 Triple Quadrupole GC–MS & 7200 GC–QTOF MS”

Case study #2: “High sensitivity GC–MS/MS analysis of nonpolar organic compounds (PCBs, PBDEs, pesticides and PAHs) in water using the Agilent 7000 Triple Quadrupole GC–MS”.

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GCMS-TQ8030


ASI-L
TOC-L


LCMS-8040


UV-1800

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