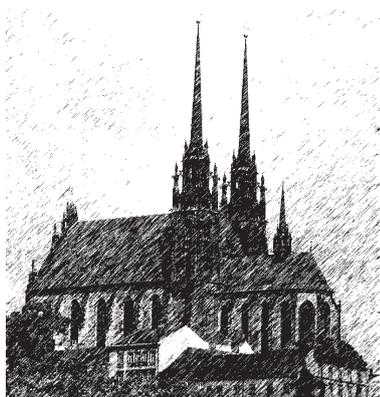


The Seventh European Meeting on Environmental Chemistry
EMEC7

THE BOOK OF ABSTRACTS



Brno, Czech Republic, December 6 - 9, 2006

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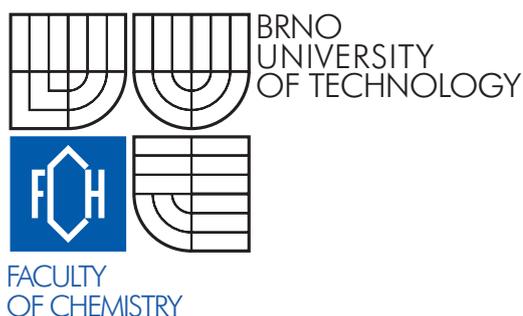
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ORAL PRESENTATIONS

THURSDAY, DECEMBER 7th

ADVANCES AND TRENDS IN THE STUDY OF THE ENVIRONMENTAL FATE OF PERSISTENT TOXIC SUBSTANCES

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INTRODUCTION

Organic substances that are persistent, bioaccumulative and possess toxic characteristics likely to cause adverse human health or environmental effects are called PBTs (Persistent, Bioaccumulative, Toxic substances). 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. Depending on their mobility in the environment, PBTs could be of local, regional or global concern.

Subclass of PBTs so called POPs (persistent organic pollutants) is group of compounds, which are prone to long-range atmospheric transport and deposition¹. The global extent of POP pollution became apparent with their detection in areas such as the Arctic, where they have never been used or produced, at levels posing risks to both wildlife and humans.

In the broader context, we can speak about persistent, toxic substances, which includes all described above and some other types such as for example organometallic compounds, metabolites and degradation products of biotic and abiotic transformations of parent POPs etc.

GLOBAL DISTRIBUTION OF PTS

During the past three decades, analytical data have revealed global contamination of aquatic and terrestrial environments. In large measure, this is the logical consequence of the physical and chemical properties of PTS:

- PTS are highly resistant to chemical and biological degradation. Polychlorinated biphenyls (PCBs) and other chlorinated pollutants, particularly the highly chlorinated ones, have been known for some time to persist in soils, water, sediment and biota for long periods of time.
- PTS are non-polar molecules that can accumulate in fatty tissues. This results in their biomagnification in the higher trophic levels of the food chain.
- Many from various PTS were/are found in pristine areas where there are no known sources of release to the environment, demonstrating that PTS are subject to long-range transport from their initial source.

Researchers have concluded that the major mechanism for this mobility is a cyclical evaporation from soil and water surfaces in which winds lift POPs into the air along with water vapour and dust, eventually depositing them with rain, snow, or adsorbed to particles. With repeated evaporation and deposition, the net result is movement of POPs such as PCBs and some organochlorinated pesticides (OCPs) over long distances in the direction of atmospheric air movements. Models of this mobile behaviour correlate well with the measured POP concentrations in the northern hemisphere.

TRENDS AND ENVIRONMENTAL RE-CYCLING OF POPS

The basic trends of usage and emission to the environment consist from the following steps – they are common for many other POPs¹:

- (1) synthesis and development for use earlier in this century, in this case in the 1930s;
- (2) increasingly widespread use in Europe and North America and other industrialised regions through the 1950s and 1960s;
- (3) concerns over environmental persistence and food-chain accumulation in the 1960s/early 1970s, resulting in restrictions in usage in Europe and North America; and
- (4) reductions in emissions in Europe, North America and other industrialised regions arising from the bans/controls in the 1970s through the 1980s and 1990s.

This general pattern may be unrepresentative of the global emission profile when the chemical is used extensively outside of Europe and North America (following a global shift in the place of manufacture).

These trends in emission have had fundamental implications for concentration trends in air, soil, water and sediments and for magnitude and direction of fluxes between these compartments for POPs capable of dynamic, multimedia exchange^{1,2}. Likely the response to the maximum of emission phase in the 1950s and 1960s has been deposition from the atmosphere to greatly exceed volatilisation to it in the 1940-60/70s and for reverse to have applied in the more recent past. Based on these approaches we can describe the hypothetical responses of the air and the soil compartments to the emission pulse. Air concentration can be expected to respond rapidly to the increasing emission (1940-60s) and to reflect it. However, as the primary sources became controlled/reduced air concentrations initially reduced, but in more recent times may actually have been “maintained” by volatilisation (“outgassing”) of recyclable POP compounds from the terrestrial and aquatic compartments. The time over which they are maintained will be dependent on a number of factors, such as the size of the “reservoir” of compound in the soil/sediment/water compartments, persistence in the soil/sediment compartments, physical-chemical properties of the compound and whether there is free exchange of the compound which has been deposited in the past (i.e. is adsorption/desorption of the POP completely reversible?). For some compounds, which may have entered the soil or water body primarily associated with particulate deposition, outgassing will be limited and concentrations/burdens in these compartments will tend to remain high/increase².

For others, which readily enter the gas phase, outgassing will result in the soil/water body concentration/burden declining. Sediments cores show deposition of POPs to the lakes reflecting the hypothetical emission trend, whilst mass balance calculations, analysis of paired air-water samples and monitoring of air concentrations all provide evidence that volatilisation now exceeds deposition, i.e. the water bodies now act as sources to atmosphere, rather than as sinks. Historical reconstructions of soil and air concentrations for PCBs in the U.K. also suggest a reversal in the long-term net flux². Several researchers have shown atmospheric concentrations of re-cyclable POPs respond to seasonal or diurnal changes in temperature². When this happens, it suggests that the air concentration is “controlled by” secondary re-cycling rather than fresh/ongoing primary emissions (e.g. as for PCBs). In contrast, PCDDs/Fs and PAHs air concentrations are generally higher in the winter than the summer – probably indicating that primary combustion sources are still the principal source to air².

Because of their low solubility in water and their resistance to chemical and metabolic degradation, most PTS are eliminated from organisms very slowly^{1,2}. As a consequence of this persistence, these compounds can accumulate to relatively high levels in biota even at low environmental exposures. Phytoplankton can sorb dissolved DDT, HCB and PCBs directly from the water and it has been

suggested that DDT may be accumulated directly through gill membranes in Arctic char². However, in the aquatic environment the primary route of initial entry into the food chain is through active uptake of PBT-contaminated particulate matter by filter-feeders and plankton and at higher trophic levels dietary uptake is more important than direct absorption. Deposition and degradation processes and the bioavailability of POPs in terrestrial ecosystems are less well understood. However, it is known that PTS can be absorbed through plant surfaces; pine needles have been found to be useful indicators of atmospheric contamination by PTS. For many from them (HCB, HCHs), the indications are that the air/plant/animal contaminant pathways is the major route taken by these compounds into terrestrial food chain, for example in the Arctic.

The resistance of PTS to chemical and metabolic degradation means that they can become more concentrated the further they move up through food chains (biomagnification)¹. Biomagnification can lead to concentrations in top predators many orders of magnitude higher than in the environment. This is especially true of aquatic food chains, which tend to be more complex and longer than terrestrial food chains.

The concept of biotic persistence implies that compounds undergoing biomagnification are unlikely to be transformed at a high rate in living cells¹. It might be expected that PBTs would not tend to exert toxicity following metabolic transformation and indeed, high toxicity is generally associated with metabolically stable compounds such as PCDDs/Fs and co-planar PCBs.

RECETOX LONG-TERM SCIENTIFIC PROJECT INCHEMBIOL - INTERACTIONS AMONG THE CHEMICALS, ENVIRONMENT AND BIOLOGICAL SYSTEMS AND THEIR CONSEQUENCES ON THE GLOBAL, REGIONAL AND LOCAL SCALES

The long-term research and scientific conception of Centre RECETOX, Masaryk University, CR is focused on the study of the environmental fate of persistent toxic substances, their biological effects, mechanisms of these effects and the study of relationships between environmental levels of PTS and their biological effects.

This concept is now main objective of the research project INCHEMBIOL. The plan of this project represents a complex approach to study of interactions among chemical compounds present in environmental compartments and their biological effects, study of the fate of mainly persistent chemical compounds in the environment, their effects on the environment and living organisms including human.

Fate as one for the key words of this project in this concept consists of a summary of transport (from their input in the environment, transport within the environmental compartment, where they are discharged, transport among compartments and long-range transport in the environment) and transformation processes (abiotic and biotic transformations). It also includes study of distribution equilibria, properties conditioning their environmental behaviour, study of the transformation processes and their products.

This complex approach is a part of long-term research activities of the centre RECETOX. It is based on exploration of the causality among chemical (presence of chemical compounds in the environment) and biological (mechanisms of effects on the living organisms) part of the problem of chemical contamination of the environment.

This complex approach requires interdisciplinary, team collaboration of specialists from number of natural sciences and is very demanding on equipment and financial sources.

Project objectives

Next to currently progressive specialized natural science disciplines studying basic chemical and biological processes on atomic and molecular level (such as structural chemistry, molecular biology etc.), **the more complicated naturally existing components (such as atmosphere, geosphere, biosphere, real ecosystems etc.) are still studied very little** and understanding of their structure and function is not sufficient.

Contamination of all environmental components produced from different human activities belongs among very topical problems of current society and the whole planet. This contamination has not only global consequences, such as global warming or increased levels of UV radiation in atmosphere, but direct negative and/or long-lasting (chronic) negative effects of contaminants on living organisms were also shown. It is often unclear to which extension are the processes in atmosphere consequences of anthropogenic activities and to which extension they are results of natural processes of the systems development.

The submitted research plan concentrates on acquirement of new scientific information and experimental data concerned with problem of chemical contamination of the environment with persistent, toxic compounds (persistent, organic pollutants, heavy metals, organometallic compounds). It is necessary to distinguish this contamination from natural migration of the compounds in atmosphere, biosphere and geosphere, and also study its interactions within these environmental spheres.

The basic objective of the research plan is characterization of fate and negative effects of chemical compounds in real ecosystems by interconnection of a few scientific disciplines studying:

- (i) chemical compounds in the environment - fate - transport and transformation, distribution in and among compartments; their determination in different abiotic and biotic environmental components,
- (ii) abiotic processes in the environment - differentiation and migration of the compounds in the atmosphere and geosphere - geology, geochemistry, paleontology and climatology
- (iii) effects of chemical compounds on living organisms – biochemical toxicology, genotoxicology, ecotoxicology, ecological epidemiology;
- (iv) ecologic and human risks combining knowledge of more disciplines for quantification of existing risks

Project INCHEMBIOL proposes to contribute to following research directions:

- ↳ **Fate of chemical compounds in the environment** (sources, physical chemical and environmental-chemical properties, distribution in abiotic and biotic environmental compartments, levels of contamination of environmental components and living organisms, abiotic and biotic transformations) as the basic source of information for evaluation of possible exposure of humans and living organisms;
- ↳ **Study of the impacts of chemical compounds on the living organisms** (on all levels of organization – cell, organism, population and ecosystem);
- ↳ **Evaluation of ecological and human risks** in relation to different types of stressors under real ecosystem conditions.

This long-term project which will be realised during the period 2005-2011 in the following basic parts:

1. **Experimental (laboratory) study**

1A. Chemical compounds properties

1B. Biological effects of chemical compounds, the mechanisms of action

Partial principal studies will be realized in compliance with the research plan:

- Effects of defined priority compounds
- Toxic effects of chiral compounds
- Ecotoxicology of mixtures and effects of different environmental matrices
- Ecotoxicology of environmental processes (transformation, photochemistry as sources of new types of pollutants...)

With the aim to integrate information about ecotoxicology at different levels of biological matter methodologies of the following directions will be interconnected:

- Biochemical ecotoxicology and genotoxicology
- Terrestrial and soil ecotoxicology

1C. Development of new test systems for xenobiotics in the environment

2. **Study of the processes under real ecosystem conditions**

- ↻ **Case study 1:** Fate and impacts of PTS in model systems – use of model ecosystems from the view of the origin of current conditions, impact of principal abiotic factors including rock background and climatic conditions, effects on risk evaluation;
- ↻ **Case study 2:** Bioindication of the stress factors effects under real soil conditions – study of soil biological potential in relation to risk evaluation;
- ↻ **Case study 3:** Bioindication of the stress factors impact under conditions of real aquatic ecosystems on the model of water basins Kníničky (Brno reservoir) and water reservoir Nové Mlýny;
- ↻ **Case study 4:** Natural development of basic parameters of natural environment and their modification by human activity in the area of crystalline rocks - Dolní Rožínka area
- ↻ **Case study 5:** Natural development of basic parameters of natural environment and their modification by human activity in the area of sedimentary rocks – rosicko-oslavanska coal basin area

3. **Risk analysis, critical analysis of information sources and development of information tools**

The basic concept of the INCHEMBIOL Project will be used for the presentations of the advances and trends which is a possible use for the study of environmental fate of persistent toxic substances.

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**EMISSION SOURCE APPORTIONMENT FOR SOIL CONTAMINATION IN
PTOLEMAIDA BASIN - A COMPLEMENTARY APPLICATION OF ORGANIC-
ANALYTICAL AND MICROSCOPICAL METHODS**

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The Ptolemaida basin in North Greece is affected by intensive anthropogenic activities comprising in particular lignite mining, lignite combustion based power production, agriculture, traffic and industry.

The target of this study was not only to point out the level of contamination but more important to differentiate the numerous emission sources with organic-analytical and microscopical methods. Based on screening analysis of cultivated and uncultivated soils, fly ashes and lignite samples the organic-geochemical signature was revealed for different contaminations. The method of fingerprinting was used successfully to distinguish potential sources of pollution, even though the identification of sources was not always effective. However, especially PACs and pesticides dominated the organic pollution as a result of agricultural and pyrolytic emissions. However, a significant contribution of fly ash and lignite derived material to the soil samples was pointed out by white light microscopy in incident mode as well as by REM. Interestingly, the results obtained from both methods were complementary with respect to the information revealed for the different emission sources. Therefore, a combined application of microscopy and chemical analysis revealed a more precious view on the pollution and its sources in the soil environment.

PASSIVE AIR SAMPLING TECHNIQUE AS A TOOL FOR THE LONG-TERM AIR QUALITY MONITORING

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The potential of passive air sampling (PAS) devices to assess the influence of local sources on the quality of surrounding environment was recently investigated as well as their sensitivity to the seasonal variations in the ambient air concentrations of POPs. The fact that PAS showed a very good capability to reflect temporal and spatial fluctuation in POPs concentrations makes them applicable for monitoring on the local and regional scale.

Following the results of those pilot studies, PAS have been employed in the long-term monitoring of the various local sources in the Czech Republic starting 2004, with a number of rural and mountain sites estimating the role of the long-distance transport added to the network in 2005. The steps for extending the program to cover most of the Central and Eastern Europe were taken in 2006. Results of the long-term employment of PAS in the regional monitoring program as well as the unique study employing PAS as a tool for monitoring of decontamination processes and assessment of risks connected with the old burden sanation will be presented here.

LEVELS OF PRIORITY POLLUTANTS IN AMBIENT AIR OF ESTONIA

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Samples of particulate matter (PM) of urban aerosols were taken from different locations in the capital city (Tallinn) and industrial area in Northeastern part of the country. In the sampling episodes quartz and high volume filters were used to collect samples of PM₁₀ and PM_{2.5}. A total of 31 metals (Cd, Ce, Pr, Sm, Pt, Hg, Tl, Pb, Th, U, Mg, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Mo, Sn, Sb, Ba, La) were quantified in PM by inductively coupled plasma mass spectrometry (ICP-MS). The concentration levels of metals were higher for PM₁₀ than for PM_{2.5}. High content of toxic metals (Cd, Pt, Hg, Pb, Cr, Zn) was found in urban areas with intensive traffic whereas alkaline-earth metals and alkaline metals were concentrated in PM in industrial area.

The range of mean concentrations of 16 priority polycyclic aromatic hydrocarbons (PAHs, according to the US EPA List) in PM_{2.5} was quantified from 2.5 to 6.2 ng/m³, including benzo[a]pyrene, 0.1-0.7 ng/m³. The composition of the PAHs fraction varied with the sampling location, i.e. the pollution source characteristics. The domination of PAHs with molecular mass over 252, e.g., in decreasing order, Benzo[ghi]perylene, Indeno[1,2,3-cd]pyrene, Benzo[e]pyrene, Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene and Coronene in a busy traffic and industrial area of Tallinn gives evidence that the non-road transport and treatment of stored fuel of a cargo port are significant sources of emission.

IDENTIFICATION OF PETROLEUM-TYPE POLLUTANTS AND STUDY OF THEIR FATE IN DANUBE ALLUVIAL SEDIMENTS

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Up-to-date results observed in differentiation and transformation studies on petroleum-type pollutants in underground and surface waters are given in this presentation. Water and particulate matter derived from the locality of Pančevo Petroleum Refinery, Serbia (River Danube alluvial formations). It was shown that distributions of *n*-alkanes, steranes and triterpanes, and $\delta^{13}\text{C}_{\text{PDB}}$ values of *n*-alkanes may successfully be used for differentiating the petroleum-type pollutants from native organic matter in recent sedimentary formations. In underground waters, a petroleum-type pollutant is exposed to microbiological degradation which is manifested through relatively fast degradation of *n*-alkanes. Following an almost complete degradation of crude oil *n*-alkanes in underground water, an interesting phenomenon of biosynthesis of novel, even carbon-number C₁₆ to C₃₀ *n*-alkanes may be observed. It was shown that the *n*-alkane distribution observed in an petroleum-type pollutant may depend on the intensity of its previous interaction with water. The fate of petroleum-type pollutants in environmental waters may be predicted through laboratory simulative microbiological degradation experiments by using microorganism consortiums similar to those observed under relevant natural conditions, as well as on corresponding nutrient base.

NITRO POLYCYCLIC AROMATIC HYDROCARBONS IN THE PARTICULATE PHASE OF ATHENS ATMOSPHERE

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Nitro derivatives of Polycyclic Aromatic Hydrocarbons (NPAHs) are well known mutagens in the atmosphere. Their presence has been related to combustion emissions, mostly by diesel engine, as well as to the secondary transformation of vapor or particulate PAHs during day or night. Following an initial study conducted in the late 90s in Athens, two sampling campaigns have been taken place in a heavy traffic area in Athens center: in the first campaign (2002), selected NPAHs were determined in total suspended particulate phase and in the second (2003-2004), NPAHs were determined in six sized particulate fractions, collected by a cascade impactor. The relation to conventional pollutants and meteorological conditions as well as the diurnal and seasonal variation, were used as a tool for studying origin and abundance of NPAHs in the selected site.

POLYCYCLIC AROMATIC NITROGEN HETEROCYCLES - ANALYTICAL AND DISTRIBUTION ASPECTS

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Polycyclic aromatic nitrogen heterocycles are present in the environment in broad range of concentrations along with polycyclic aromatic hydrocarbons and their derivatives. Successful identification and content determination of PANHs in complex mixtures requires efficient methods of their extraction from environmental samples, suitable preseparation, preconcentration and analytical determination. The very low value of final amount determined in the complex mixture may be result of significant difference in affinity of extracted pollutants both extraction solvent and soil sample. Differences in extraction recovery of PANHs from soil observed using different extraction solvents is presented. Presence of PAH in contaminated soil samples and in organic extracts from often complicate final chromatographic determination due to coelution of separated compounds with similar properties. Separation system enabling effective HPLC separation of PANHs in the mixture of PAHs is presented. Emission of PANHs is connected with their deposition on the surface soil by dry and/or wet way. Static experiments in the system of soil/water were realized to simulate distribution of PANHs in interphases similar to environment. Dynamic arrangement of experiments was made to simulate elution of PANHs by flowing water being in contact with soil. Effect of pH, buffer concentration, temperature and analyte concentration on distribution of PANHs phase both in static and dynamic experiment was investigated.

MODELING OF TRANSPORT PHENOMENA OF PCB CONGENERS THROUGH THE ATMOSPHERE

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Long Range Transport Potential of the toxic contaminants in air, which is exceptionally important field of research, is pushing the studying of transport and spreading phenomena of PCB congeners as well as others persistent organic compounds. In addition, beside to experimental measuring of concentration levels of these contaminants, defining of mathematical model of transport phenomena is necessary for prediction of temporal and spatial coordinates of PCBs migration. The complexity of modeling is caused by the type of PCB's transport through the atmosphere. These toxic components are present in the atmosphere both in gaseous and particulate phases. PCB congeners can be transported over long distances by dispersion of gas molecules or by suspended particulates with strongly adsorbed chemicals.

The aim of this research is to define the simplified model of transport velocity of PCB congeners (ten groups of homologue) based on kinetic molecular theory of gases and Gaussian distribution for modeling the dispersion. The commercial ALOHA software has been used for defining the spatial coordinate. Estimated values are compared with transport velocity of tetra-dioxin and DDT/metabolites obtained with the same method.

Key words: PCBs, transport phenomena, atmosphere, modeling

GCxGC-TOF MS: AN EXTRA DIMENSION FOR THE ANALYSIS ORGANOCHLORINATED ENVIRONMENTAL POLLUTANTS

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Comprehensive two-dimensional gas chromatography (GCxGC) has been attracted attention in recent years because of its great separation efficiency. Unlike “heart-cutting” techniques, in GCxGC the whole chromatograph is subjected to two independent separation mechanisms. In GCxGC, two columns of different selectivity are connected via a thermal modulator, which cuts small portions of the first column eluate, focuses them to sharp zones and sends them onto the second column, where a very fast “flash” separation is performed.

Besides enhanced separation power, this technique provides the advantage of structured two-dimensional chromatograms, in which each compound of a sample occupies a position according to its retention behavior on the two columns with different selectivity (e.g. volatility x polarity).

In the applications, where the confirmation of analyte identity is necessary, mass spectrometry is a desirable detection technique. In GCxGC, extremely narrow peaks (0.1 – 0.2 s) are produced on the second dimension column. Therefore the detection technique used has to be fast enough to describe these narrow peaks properly. In the family of mass spectrometers only time-of-flight MS reaches the acquisition rates needed, since its maximum acquisition rate is 500 Hz, which is cca 10x higher than for other MS detectors.

In this presentation, several applications of GCxGC-TOF MS will be shown for the organohalogenated environmental pollutants. First group of interest are organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs). Classical analysis of these compounds usually comprises parallel dual columns of different selectivity. In GCxGC a non-polar and a polar column are used on orthogonal set-up. In this way, a structured contour plot is obtained, where sample coextracts are situated in the bottom part, in the middle part PCBs are eluted, whereas the OCPs occupy the upper position in the contour plot.

Second group of focus of this presentation are polychlorinated dibenzodioxines and furanes. For the analysis of these compounds usually high-resolution MS detector (magnetic sector) is used. This instrument is very expensive not only as regards its purchase costs but also in terms of operational costs.

In this work the GCxGC-TOF MS has been evaluated for the analysis of dioxins. Using GCxGC-TOF MS the limits of detection reached were below the level of 0.5 pg injected. This can be achieved by focusing of the peak in the modulator and thus the sensitivity is improved compared to one-dimensional chromatography. In the presented work, the quantification data, comparing the results of GCxGC-TOF MS with GC-HR MS will be shown.

CHIRAL ENVIRONMENTAL POLLUTANTS: CHALLENGES AND PITFALLS IN ENANTIOSELECTIVE ORGANIC TRACE ANALYSIS

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According to Lord Kelvin (1904), two equal right handed forms are homochiral and equal right and left handed forms are heterochiral. The right- and left handed mirror images are also called with the scientific name enantiomers. Based on this simple definition of an asymmetric structure a new type of chemistry has developed during the past century with strong implications for our daily life. Many chemicals used in pharmaceutical products, personal care products, pesticides used in agricultural applications are developed as enantiomers. Earlier the role of chirality within biochemical processes was discussed as principal feature of living processes. Today the scientific world has no doubt anymore that chirality is an important factor for life processes. Also in environmental chemistry, the principles of chirality play an outstanding role in understanding biodegradation and transformation processes. New developed techniques for trace analysis of enantiomeric anthropogenic pollutants are today considered as new powerful tools for the environmental risk evaluation of human-made emissions into nature. Within the field of chiral environmental chemistry research, enantioselective separation is both used for enantiomer separation during sampling, sample preparation and chemical trace analysis. Especially enantioselective organic trace analytical methods using gas chromatography or liquid chromatography as separation and mass spectrometry as detection technique for trace analytical quantification of chiral persistent organic pollutants (POPs) has developed into a powerful and versatile tool in environmental chemistry and is currently used by many internationally renowned research groups. However, the correct level determination for single enantiomers using standard analytical procedures including chiral separators like modified cyclodextrin, or other stationary phases, is often hampered by poor separation of the single chromatographic peaks, peak broadening due to non-optimal mobile phases and even instrumental limitations. The combination of ultra trace quantitative chemical analysis and enantiomer separation (into 2 and more enantiomers) still implies a considerable challenge for modern environmental chemistry. Based upon selected examples from gas chromatographic and liquid chromatographic separation methods available in the literature, limitations and challenges in enantioselective trace analysis will be presented and illustrated. Pitfalls but also the potential of this relatively new analytical technique will be discussed in the planned presentation.

DETERMINATION OF CHIRAL ORGANIC COMPOUNDS IN ENVIRONMENTAL MATRICES WITH TWO DIMENSIONAL GAS CHROMATOGRAPHY COUPLED TO TRIPLE QUADRUPOLE MASS SPECTROMETRY

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Two-dimensional gas chromatography (GC-GC) combined with triple quadrupole mass spectrometers (MS-MS) was used for analysis of chiral compounds, which were extracted from soil and air samples of Czech Republic and former Yugoslavia. Air samples were collected using polyurethane foam based passive air samplers. Soil samples were collected at the same sites.

Enantiomeric fraction (EF) values were used to describe enantiomeric signatures. EF values in soil ranged from 0.360 to 0.524 for PCB 95, from 0.220 to 0.597 for PCB 132, from 0.420 to 0.547 for PCB 149 and from 0.478 to 0.535 for PCB 174. In some soil samples were also measured EF values of selected OCPs. EF values for α -HCH ranged from 0.475 to 0.517, for o,p'-DDD from 0.368 to 0.570 and for o,p'-DDT from 0.365 to 0.513.

Ranges of measured EFs values were compared with ranges of values found in literature, and ranges of measured values were approaching those found in literature.

EFs were correlated with the set of physico-chemical and microbiological parameters of the soils in order to better assess the fate of the compounds in the environment. Correlation between EF values and chosen microbial characteristics (such as basal and potential respiration), organic carbon content, fulvic and humic acids content, extractable carbon content, and carbon and nitrogen content was observed. There was no correlation between EF values and pH values.

Air samples were collected at the soil sampling stations in the Czech Republic, former Yugoslavia and Oman using the passive air samplers, and analyzed for POPs. Irrespective of the samples origin, their EF values did not differ significantly from the value of a racemic mixture, and they ranged from 0.49 to 0.51. Since the POPs volatilization from the soils is an important source of these compounds in the atmosphere, it can be expected that EF values of POPs in the atmosphere should correspond to those in the soil. However, the influence of the long-range transport of volatile compounds from other locations as well as continuous mixing of the ambient air layers has to be considered and seems to outweigh local soil sources.

CHARACTERISATION OF DISSOLVED ORGANIC NITROGEN

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The characterisation of dissolved organic nitrogen has received considerable attention in recent years, as its abundance and role in the aquatic nitrogen cycle has become apparent. This study involved the development of a method to identify low molecular weight (LMW) ON compounds (< 1 kDa), which are thought to be both reactive and quantitatively important. Peptides were used as the test compounds and the method comprised extraction of dissolved analytes by solid phase extraction (SPE), followed by elution and analysis by liquid chromatography-electrospray ionisation-tandem mass spectrometry (LE-ESI-MSn).

The method was tested using algal culture waters. The mass analyser was set to acquire data in the full MS mode and then repeated for data acquisition in the data dependent mode (DDMS). Mass spectra and chromatograms of ions from the samples were identified. The DDMS allowed multistage mass spectrometry (collision induced dissociation) to be carried out on those ions that exceeded the threshold ion intensity of 1×10^5 .

Unique ions identified in the axenic cultures included the two amino acids TYR and a modified structure directly related to TYR. Seven peptides were partially sequenced. One whole peptide was sequenced as H-TRP-PHE-OH. A significant loss of data was observed between the unique peptide ions identified in the MS analysis and the ions that underwent CID during the DDMS analysis, because they were below the threshold ion count or co-eluted with a more dominant ion.

HUMAN PHARMACEUTICALS IN SCOTTISH NATURAL WATERS

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In contemporary society, the use of human pharmaceuticals is extensive and widespread. In the UK alone, 3000 active-ingredients are licensed for use as pharmaceuticals and it is estimated that global sales of pharmaceuticals increased by approximately nine percent in 2004. However, recent studies have demonstrated that in general pharmaceuticals are not completely removed during wastewater treatment processes and can find their way into the aquatic environment. Investigations in countries including Switzerland, Norway, Spain and Germany have already revealed the presence of human pharmaceuticals in natural waters ng/l-ug/l concentrations. However, no data are available for Scotland.

The aim of this research was to determine the concentrations of human pharmaceuticals in selected aquatic environment in Scotland. Eleven pharmaceuticals belonging to different therapeutic classes including antibiotics, anti-cancers, analgesics and anti-inflammatories were selected according to their potential to cause a risk for the aquatic environment. Three representative study regions were selected; Orkney (Northern island archipelago), Loch Ness (freshwater lake) and the River Dee (notable salmon river rising in the central highlands with a mouth on the North Sea).

Pharmaceuticals from samples collected from each region were extracted using solid phase extraction (SPE) and analysed with high performance liquid chromatography (HPLC-MS/MS).

Results showed paracetamol, trimethoprim and diclofenac to be present in at least one sample from each area. Highest concentrations were detected in the River Dee including propranolol (anti-hypertensive; 22.0 ng/l) followed by sulfamethoxazole (antibiotic; 11.4 ng/l) and paracetamol (analgesic; 6.9 ng/l). To our knowledge these are the first available data regarding the presence of human pharmaceuticals in the natural waters of Scotland.

ON THE DETOXIFICATION OF BENTHIC BIVALVE CONTAMINATED BY POPs: INSIGHTS FROM EXPERIMENTAL AND MODELLING APPROACHES

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Organisms that have accumulated Persistent Organic Pollutants (POPs) decrease body concentration of toxicants to safe levels when reared in natural environments characterized by low background contamination. Such natural detoxification can represent a cheap and useful strategy for allowing human consumption of natural resources otherwise banned from markets for their health risk. However, successful detoxification is highly depending on chemical properties of pollutants, background contamination, environmental conditions and on biological metabolic processes.

In this work we study the detoxification of the Manila clam (*Tapes philippinarum*) a benthic bivalve of commercial value that is intensively harvested in the Venice Lagoon. Since decades this lagoon has been receiving discharges of pollutants from drainage basin, urban settlements and industrial areas laying on lagoon borders. POPs, which are mainly resulting from industrial activities, have therefore been accumulating in sediments and concentrations of PCCD/F higher than 2500 ngI-TE kgdw⁻¹ have been found in channel sediments of the Porto Marghera industrial zone. Since a positive correlation between sediment and clam toxicity was previously found, for safety reasons the harvesting of *Tapes philippinarum* is not allowed nearby the Industrial Zone. However, Porto Marghera is an important habitat for recruitment and growth of this species and the stock growing in this area represents an attractive opportunity for fishermen that, despite some enforcement, illegally harvest for clams. Specimen illegally caught in highly polluted sediments of Porto Marghera, therefore, might reach consumers with possible consequent threat to human health. The natural detoxification of clam, therefore, might help in reducing human risk while maintaining exploitation opportunities for this resource.

Specimens collected in industrial canals have been reared in areas of the southern part of the Venice Lagoon characterized by low sediment contamination and POPs concentration in clam flesh has been monitored through time both in winter and summer. Experimental data allowed for estimating detoxification rates and half-lives for dioxins, PCB congeners and HCB, thus highlighting main differences among pollutants and effects of physical conditions on the detoxification process. Moreover, an ecotoxicological model was set-up by coupling a bioenergetic model of the growth of *Tapes philippinarum* with a bioaccumulation model. The ecotoxicological model calibrated with experimental data provides inference on major processes involved in accumulation/detoxification of each toxicant and evidenced the role of temperature and metabolic processes in detoxification. Reduced metabolic rates in winter due to low temperature resulted in slower detoxification than in summer, thus detoxification rates and biological half-lives for PCDD/Fs and PCBs estimated in wintertime should be considered more precautionary. The model provides basis for inferring on time needed for reaching toxicity reference level given environmental conditions (water temperature and background contamination) and initial size of specimen giving general value to the study. Findings presented in this work show the potential of natural detoxification, and could represent a solution for the illegal fishing carried out in the Industrial Zone that might be used as nursery area for *Tapes philippinarum*, to be reared in cleaner sediments of the southern lagoon and then consumed safely.

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FIRST RESULTS ON THE ANALYSIS OF SPM SAMPLED IN THE RIVER ELBE BASIN

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In the framework of the German Environmental Specimen Bank (ESB) regularly sampling of suspended particulate matter (SPM) started in 2005. SPM samples are taken on a monthly basis at 5 locations along the river Elbe and at 2 locations from the tributaries Mulde and Saale. Sampling procedure and processing of the material follows strictly the Standard Operation Procedures (SOP) of the ESB. The samples were described in the field and geochemical analysis was applied for sedimentological parameters (grain size distribution, TIC/TOC), some trace metals (Pb, Zn, Cd, Cu) and POPs (EPA-PAH, PCB, HCB, DDX, HCH). Additionally, a non-target screening was performed revealing personal care products like galaxolide, tonalide, linear alkyl benzenes (LABs), flame retardants, di- to pentachlorobenzenes, octachlorostyrene and aryl- and alkylsulfonic acid esters. Compounds like triclosan and its metabolite triclosan-methyl could be quantified. The seasonal variation of SPM contamination and implications for further detailed analysis will be presented.

LIGNITE AND ENVIRONMENT

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Lignite belongs to the class of young coals with a low coalification degree and is traditionally considered and used as a fuel. Because of its low calorific value and production of the greenhouse carbon dioxide during its combustion objections not only to its burning but also to its mining are growing and still more popular within the “green” parties and organizations. However, the traditional view on lignite and its utilization should be changed. The lignite has unique chemical composition, can be used as a versatile raw material for various applications including environment protection technologies and not be lavished in boilers. Our research is focused on potential non-fuel applications of the South Moravian (Czech Republic) lignite, especially on the low-cost technologies, i.e. technologies using the lignite in its natural state. To evaluate real potential of lignite in-land application information of its behaviour especially in aqueous media is necessary. Among other we investigate the lignite as a sorbent, soil remediation agent and as a material preventing and treating desertification. Applications of lignite in the environment, soil call for information on its detailed composition and potential leaching of lignite constituents into the environment, particularly by the action of water or aqueous solutions. This contribution reports on elemental composition of the South Moravian lignite, its leaching in aqueous solutions of various solution chemistries and potential release of both inorganic and organic components from the lignite. In addition, information on the effect of lignite on plant growth are presented.

The lignite was subjected to the organic elemental analysis (contents of C, H, N, S, and O), analysis of other elements, especially metals, by the neutron activation, to the basic tests used in the soil quality control, leaching in water and in both acidic and alkaline aqueous media, and also in aqueous salt solutions. Leachates were analyzed for pH, conductivity, elements, especially metals and selected organic compounds (aromatics).

The moisture contents of the fresh lignite is relatively high, in our sample about 30% (wt.), ash contents was about 20% (dry basis). Combustible matter comprised about 60% (dry, ash-free basis, daf) indicating high level of organic constituents which was also confirmed by petrographical analysis giving 69 vol.% of huminite. Elemental composition (daf): C-65%, H-5.2%, O-27%, N-1.0%, S-1.1%, contents of carbonates was very low (0.12% as CO₂). The lignite contains a plenty of other elements, most of them in trace amounts. Perhaps the concentration of arsenic might cause problems but its solubility even in strong aqueous media has not been detected.

The lignite in general releases negligible amount of organic and inorganic constituents into the water as well is into the acidic or alkaline aqueous solutions. Suspensions of lignite in water or salt solutions are slightly acidic. In aqueous solutions of non-neutral pH it works like a buffer, shifting the final pH to the neutral region. Interestingly, pot tests with several plants revealed suppressing effect of lignite on the uptake of heavy metals by the plants.

Results of our study substantiate efforts to apply lignite as an effective agent in various environment care and protection technologies. Though the lignite mining in the South Moravia is not landscape-devastating, changing our view on it, the lignite can even contribute to landscape cultivation, especially in countries fighting the problem of low soil quality, arid soils or desertification.

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TARGETED AND UNTARGETED MULTI-RESIDUE ANALYSIS OF PRIORITY POLLUTANTS IN SURFACE WATERS USING EXACT MASS GC-TOF

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POPs (Persistent Organic pollutants) are a set of chemicals that are toxic, persist in the environment for long periods of time, and bioaccumulate as they move up through the food chain. POPs have been linked to adverse effects on human and animals' health.

POPs represent a wide range of compound groups with very different polarities. Some of these compounds could be analysed by either LC or GC, e.g. demeton-s-methyl, dimethoate, phenylureas, while others are definitely GC compounds, e.g. Organo-chlorines. The Dangerous Substances Directive (76/464/EEC) lists a number of compound groups which have restricted levels in drinking and surface waters. Many of these compound groups will typically have their own dedicated analysis method that requires specific extraction/clean-up and final analysis. Combining these groups into a single targeted method would allow the laboratory to significantly increase sample throughput. An exact mass Time of Flight instrument allows combining the specificity of exact mass chromatograms extraction, (0.05 Da window) with an efficient quantification on a 4 orders of magnitude dynamic range.

However, a targeted screening approach couldn't permit to access to a global overview of potential pollutants in complex samples. Traditional targeted sample analysis using Quadrupole or Ion Trap technologies result in specific ion selection. By definition this approach is limited to the pre-selected list of compounds. The use of a non "ion selective" Time of Flight instrument allows an efficient untargeted screening in addition to the targeted sample analysis. Moreover, the exact mass information is used as an efficient tool to confirm the library search identification.

APPLICATIONS OF ELECTRON PARAMAGNETIC (SPIN) RESONANCE (EPR/ESR) SPECTROSCOPY IN ECOLOGY

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EPR is a nondestructive method measuring interactions of magnetic field and microwave energy. It is used for determination of free radicals, paramagnetic metal complexes and excited states in gaseous, liquid and solid substances, namely environmental pollutants. In air samples from dwellings there were proved stable organic free radicals and Fe, Mn, Cu and V complexes depending on particular human activities. We proved that extremely long-living radicals are formed by mechano activation. Some of them are ingested causing lung inflammation or even cancer. We also found that ecotoxic compounds are sorbed by humic acids. Moreover, they can be decomposed by ozone in gases and liquids. Moreover it was found that metal complexes of humic acids are useful for identification of particular geologic formations. Beside of it was found that automobile catalysts decompose toxic exhaust gases, but not dangerous free radicals. Free radicals were proved on the surfaces of asbestos and grinded silica. Paramagnetic metal complexes on the surface of archaeological artifacts helped in localization and dating of archaeological artifacts as well as in glass research. Formation of reactive oxygen species on surface of Cyanobacteria and some other plants, increasing with duration of sun exposition. The research was supported by Grant agency of Czech Republic (Grant No 525/06/1757) and Internal Grant Agency (IGA) of Ministry of Health of Czech Republic. (Grant No NR8806-3/2006).

ANALYSIS OF ESTROGENS, GLYPHOSATE AND DEGRADATION PRODUCTS IN WATER USING LC/MS/MS

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Glyphosate [(*N*-phosphonomethyl)glycine] is a broad-spectrum, non-selective, post-emergence herbicide. Glufosinate [Ammonium-2-amino-4-(hydroxymethylphosphinyl) butanoate] also acts as a broad-spectrum contact herbicide.

MPPA [3-(methylphosphinyl)propionic acid] is a structure related compound also in use as pesticide in Europe and the US as well as in Asia. The main degradation product of glyphosate is aminomethylphosphonic acid (AMPA). The determination of these compounds in the low concentration range (0.1 µg/L) is difficult, mainly because of their high polarity and solubility in water. The presented method fully omits enrichment steps – such as SPE - as well as derivatisation of the compounds of interest by using reagent-free Ion Chromatography (RFIC™) high performance liquid chromatographic in line with the highly sensitive mass spectrometer API 4000™ LC/MS/MS. The pesticides of interest were retained on the stationary phase of the LC column and separated from matrix compounds. By using volatile buffers for the anion exchange chromatography a direct coupling to MS/MS is possible. Qualifier and Quantifier MRMs are monitored for glufosinate, glyphosate, MPPA, and AMPA. The method was applied and validated for the determination of dissociated organophosphorus herbicides in various surface water samples and in drinking water down to concentrations of 0.05 µg/L without enrichment.

Another example of sensitive LC/MS/MS analysis is the determination of estrogens in water and soil.

ORAL PRESENTATIONS

FRIDAY, DECEMBER 8th

XENOBIOTICS IN FOOD CHAINS: CONTEMPORARY AND EMERGING PROBLEMS

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In addition to “classic” persistent organic pollutants (POPs), those mentioned below “new” food chain contaminants possessing similar properties have become of concern recently.

Brominated flame retardants (BFRs), chemicals widely used in many products including furniture, textiles and/or electronic equipment to make them fire-resistant, have become of concern at the beginning of 90th. Some of these compounds which are suspected endocrine disruptors are highly bioaccumulative and persistent in the environment. Their widespread occurrence, namely of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), has recently been found not only in Czech aquatic biota and also in a breast milk of Czech women.

Another group of man-made chemicals penetrating into food chains are synthetic musk fragrances. They are widely applied to scent various personal care products, such as perfumes, soaps, creams and also detergents. In recent years, polycyclic musks (PMC) have become the most important commercial synthetic musks due to concern about the environmental distribution and toxicological effects of the nitro musks (NMC) and subsequent reduction in use of these “oldest” synthetic musks. High levels of galaxolide, tonalide and other PMCs were found in Czech rivers with localities downstream Prague identified as the most contaminated. Fish was found as an optimal bioindicator of municipal waste water effluents.

Alike other endocrine disrupting chemicals (EDCs), synthetic steroid hormones may induce abnormalities in reproduction of wildlife, especially feminization of male fish due to their high estrogenic potency. Together with natural 17 β -estradiol and its major metabolites (estrone and estriol), find synthetic estrogens their way in aquatic ecosystem through municipal sewage treatment plants (STPs). One of the most common compounds representing the latter group, 17 α -ethinylestradiol is widely used as a human contraceptive and also for management of many other disorders (menopausal and postmenopausal syndrome etc). Monitoring of these biologically active chemicals in the surface waters has been initiated recently in many counties including CR.

Perfluorooctane sulfonate (PFOS) represents another “emerging” contaminant attracting concerns of (eco)toxicologists since only recently. This fully fluorinated anion, is due to its surface-active properties used in a wide variety of applications such as textiles, carpets, paper, general coating, fire-fighting flaks and in the semi-conductor industry. PFOS can be formed by degradation from a large group of related substances. It has demonstrated toxicity towards mammals and is toxic to aquatic organisms as well. Contrary to the above POPs, PFOS is binding to proteins. Its residues have been reported in birds, fish and mammals and might be a problem in food. Contamination of some fish products at the Czech market by PFOS has been demonstrated in our study

Enormous progress in sampling and analytical strategies has been achieved in recent decade. Regarding monitoring of POPs in surface waters over a longer time period, this may be realized by repeated spot sampling, continuous monitoring, biomonitoring or passive sampling. The latter approach involves the deployment of a calibrated device that uses a diffusion gradient to collect pollutants over a period of days or weeks, followed by extraction and analysis of the pollutants in a laboratory. Among the passive sampling devices, semipermeable membranes (SPMDs) have been currently widely used for lipophilic POPs monitoring. In our study, novel “Chemcatchers” device enabling passive sampling of both polar and apolar pollutants has been demonstrated. To improve efficiency of identification/ quantification process, novel chromatographic techniques have been employed for analysis of components occurring in complex environmental mixtures. The potential of orthogonal gas chromatography (GCxGC) coupled with mass spectrometric detector employing time-of-flight-mass analyzer (MS-TOF) for non-target screening of (semi)volatile POPs has been investigated. Regarding non volatile POPs, developments in LC-MS/MS technique will be shown.

THE TOOLS FOR COMPLEX ANALYTICAL AND TOXICOLOGICAL ASSESSMENT OF CYANOBACTERIAL TOXINS IN CONTAMINATED WATERS

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Anthropogenic release of nutrients into the environment (phosphorus, nitrogen) resulted in massive developments of cyanobacterial blooms in surface waters worldwide. Cyanobacteria and their toxins (cyanotoxins) represent serious ecological, economical and health problem worldwide and World Health Organisation recommends a provisional safety guideline of 1 microgram per liter for one of the cyanotoxins - microcystin-LR, which is now adopted also in the Czech Republic. However, cyanobacteria contaminating surface waters produce a wide range of other toxins than microcystins that are rarely studied. In this report we summarize our research on occurrence of toxic cyanobacteria and cyanotoxins in the Czech Republic. We will demonstrate application of analytical techniques (HPLC or ELISA) along with bioanalytical and toxicological tools for assessment of microcystins as well as other cyanobacterial metabolites. Our results demonstrate significant occurrence and toxicities of both microcystins as well as other (yet unidentified) cyanotoxins in both recreational and drinking water reservoirs in the Czech Republic. The problem of toxic cyanobacteria will also be discussed in the context of other environmental issues such as bioaccumulation and transport of other environmental contaminants in water ecosystems.

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BIOASSAYS AS AN IMPORTANT TOOL FOR EVALUATION OF SPECIFIC TOXICITY MECHANISMS OF COMPLEX ENVIRONMENTAL MIXTURES

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Assessment of the potential effects of contaminants is complicated by their presence in very complex mixtures in different environmental compartments. *In vitro* cell bioassays are useful techniques for the determination of specific toxicity of environmental samples containing mixtures of contaminants. The cell bioassays determine contamination by pollutants that act through specific modes of action. This presentation discusses strategies for the evaluation of dioxin-like activity and endocrine disruptive potential in different types of environmental matrices. Extracts from various types of environmental or food matrices can be tested by these techniques to evaluate their potential for harmful effects and to identify contaminated samples that need further investigation using resource-intensive instrumental analyses. Our results show significant dioxin-like and endocrine disruptive activity in various types of environmental samples, including soil, sediment or air samples, which is not always clearly linked to the measured contaminant concentrations. The evaluated endpoints include dioxin-like activity, (anti)estrogenicity, (anti)androgenicity, interactions with retinoid receptor and effects on steroidogenesis. Widely used are bioassays for detection of interaction with AhR (aryl hydrocarbon receptor) involved in dioxin-like activity, which can lead to various toxic effects including hepatotoxicity, embryotoxicity, teratogenicity, immunotoxicity, dermal toxicity, lethality, carcinogenesis, wasting syndrome and tumor promotion in many species. *In vitro* assays can also detect interaction between xenobiotic compounds and steroid hormone receptors (such as estrogen (ER) and androgen (AR)) that play important role in sexual development and homeostasis. Example of the effective application of the bioassay approach is the evaluation of contaminated sediments from the Ostrava-Karvina region (north eastern part of Czech Republic), where was found high occurrence of intersex large decapod crustacean *Pontastacus* (syn. *Astacus*) *leptodactylus*. This area has been affected by intensive mining and heavy industry. Chemical analyses revealed high concentrations of PAHs. Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were detected as well. Our assessment with *in vitro* cell lines pointed to endocrine disruption as well as unusually high dioxin-like activity. The instrumental and bioanalytical approaches provide different and complementary information. While instrumental analysis is a useful tool to identify the compounds of interest and to evaluate the concentrations of environmental contaminants, it provides little information regarding the integrated biological relevance of a complex mixture of compounds associated with environmental samples such as sediment. Empirical bioassay results and mass balance analyses can suggest the magnitude of contribution of target organic compounds to total specific activity of sediment extracts. Thus, the use of bioassay-based toxicity identification and evaluation (TIE) and mass balance analysis are important approach to assess sediment contamination since the sediment extracts may contain many potentially active compounds, which were not analyzed by instrumental methods. Fractionation of sample extracts exhibiting significant activities, and subsequent reanalysis with the bioassays can identify important classes of contaminants that are responsible for the observed activity and direct the chemical analysis. The bioassay approach can serve as an efficient (fast and cost effective) screening system to identify the samples of interest and to provide basic information for further analysis and risk evaluation. The project was supported by GACR 525/05/P160.

A NEW PRINCIPLE OF XENOBIOTICS BIOIDENTIFICATION IN SURFACE WATER

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The experiments were carried out with using of *Daphnia magna*. The toxicity of organophosphates (Dipterex, DFP, DDVP, Paraoxon, Malathion, Malaixon), carbamates (Aminostigmine, Physostigmine, Sevine), heavy metals (Hg, Pb, Cu, Co, Cd, Cr, As, Al), organochlorines (Aldrin, Dieldrin, Endrin, Aroclor, DDT, Lindane, PCBs etc.) and pyrethroids (Cypermethrin, Fenvalerate, Deltamethrin, Permethrin, Allethrin, Resmethrin, Phenothrin, Kadethrin, Cyphenothrin) was determined. At the first time we discovered that in experiments to *Daphnia magna* some muscarinic cholinoreceptor blockers (atropine, glipine, pediphen etc.) reduced the toxic effect of organophosphates and carbamates. In the case of heavy metals the chelating agents (EDTA, Dithioethylcarbamate, Unithiolum, Sodium thiosulphuricum, L-Aspartic acid) were effective, for certain organochlorine poisonings - anticonvulsive drugs (diazepam, phenobarbital). In the case of pyrethroid-s poisonings the antagonist of glutamate receptor (ketamine), DOPA receptors (haloperidole) and blocker of calcium channel (nimodipine) reduced the toxicity of xenobiotics. As far as these antidotes have a specific treatment action only against definite classes of pollutants, we have elaborated the sensitive express-methods of bioidentification of pollutants.

HEALTH AND ENVIRONMENTAL PROBLEMS OF CHEMICAL WEAPONS DESTRUCTION

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Still existing arsenals of chemical weapons (CW) present not only security threats for possible use in hostilities by state actors or misuse by terrorists but also immanent safety threats to humans and biota due to leakages and possible accidents. The Chemical Weapons Convention (CWC) commits the States Parties (SP) to destroy CW using technologies taking in consideration human health and environmental protection. It does not allow methods, routinely used till the 1970s, such as earth burial, open-pit burning, sea dumping or eventually blasting. Long-term health and environmental threats and some accidents that already occurred in the known localities of the sea-dumped and earth buried arsenals of Nazi-German armed forces in the Baltic Region and adjacent waters and of Imperial Japanese forces in the Far East Region are thoroughly analysed according to the environmental impact of major CW and ammunition types (i.e. sulphur mustard – HD, tabun – GA, arsenicals – DA, DC, DM, arsine oil and chloroacetophenone – CN). At present, there are 180 States Parties (SPs) to the CWC, among them 6 CW possessors (Russia, USA, India, South Korea, Albania and Libya) that have declared altogether about 70 thousand CW agent-tons. Till now, about 20 % of CW agents and about 30 % munitions and containers of mentioned SPs have been verifiably destroyed. The original schedule for complete the destruction, i.e. till 10 years after the CWC entry into force in 1997 will be not managed and the justified exemption by another 5 years in case of both major CW possessors (USA and Russia) has been already agreed. From former (operational after 1946) 65 CW production facilities (CWPFs) declared by 12 SPs, 57 have been certified as destroyed or converted for peaceful purposes. Among remaining 15 countries, that are not yet SPs, the possession of CW is presumed mainly in Israel, Syria, Egypt, Lebanon and North Korea). Beside (former) CW arsenals, also so called non-stockpile agents exist, i.e. old and abandoned CW that can be occasionally found mainly on battlefields of WW-I and elsewhere. Any possible operations and handling with CW envisaged by the CWC as well as their verification are summarised and assessed taking into account the health threat they pose. CW and toxic armament waste to be destroyed and applied technologies (both developed and under current use in operational CW destruction facilities – CWDF) are reviewed. System of health safety and environmental protection of the CW demilitarisation operations, i.e. destruction/disposal to non-toxic solid salts and scrap metal, stems from the extraordinary high toxicity of super-toxic lethal agents in man and biota. Problems of currently utilised Russian and US standards for maximum allowable workplace concentrations and general population limits and possibilities of the determination by available analytical instrumentation are discussed.

EFFECT OF THE PRESENCE OF INORGANIC IONS ON THE FORMATION OF DRINKING WATER DISINFECTION BY-PRODUCTS

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Chlorination is the most common method of drinking water disinfection all over the world. However one of its serious drawbacks deals with the formation of toxic organohalogen by-products. Natural humic substances and anthropogenic organic pollutants are the main precursors of these toxicants. The reaction of aquatic chlorination depends on a number of parameters. The present work throws light upon the influence of several inorganic anions on the formation of disinfection by-products in the aquatic chlorination reaction of two organic substrates often present in natural water.

Reactions of the selected model compounds with the chlorinating agents were conducted during 24 hours at constant stirring in the dark at 20°C in deionized water solutions at equimolar ratio of 1-methylnaphthalene to active chlorine and at 1:20 ratio of benzyl alcohol to active chlorine. In all the experiments concentration of 1-methylnaphthalene was 10^{-4} M and that of benzyl alcohol – 10^{-3} M. Besides chlorination with common sodium hypochlorite in water, the same reactions were studied in the presence of Br^- , I^- and Cu^{2+} ions. Inorganic anions were added in equimolecular to 1-methylnaphthalene quantities and in 5-fold quantities to benzyl alcohol. Active chlorine content was determined by iodometric titration before each experiment. Sodium hypochlorite reagent solutions were prepared by dilution of concentrated stock solution (5%, Fisher). Various GC/MS techniques have been used for the qualitative and quantitative analysis of aquatic chlorination of the selected substrates.

A dramatic increase of the degree of transformation was confirmed for both substrates with addition of the inorganic ions, especially Cu^{2+} . For example in the case of benzyl alcohol the conversion rate has changed from 3% to 98% (Table 1). More reactive 1-methylnaphthalene brought to the formation of about 20 products, including new organohalogen compounds. The conversion rate of 1-methylnaphthalene increased notably with addition of any of the studied ions. Copper was again the most efficient while Br^- and I^- led to similar conversion rates. However if bromides addition resulted in the formation of bromoderivatives as the main products, iodides addition brought to the dramatic increase of the levels of organochlorines (similarly to copper). Besides that the levels of products with modified methyl group were considerably higher in the case of copper ions and especially in the case of iodides. Taking into account the ability of iodine and copper to promote radical reactions, a radical mechanism of the formation of these compounds may be assumed.

Table 1. The products (micrograms) of aquatic chlorination of benzyl alcohol

Compound	Substrate[S]	[S]:[Cl]=1:20	S]:[Cl]=1:20 + Br^-	S]:[Cl]=1:20 + I^-	S]:[Cl]=1:20 + Cu^{2+}
Benzyl alcohol	6300	6100	3700	5900	130
Benzaldehyde	-	150	780	190	1500
Benzoic acid	-	-	2100	40	4700
Conversion degree		3.2%	42%	7.0%	98%

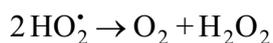
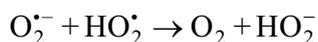
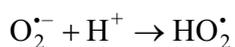
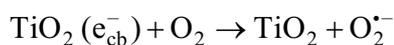
PHOTOCATALYTIC DISINFECTION OF WATER ON TiO₂ LAYER

M. Veselý, M. Veselá, P. Dzik, J. Chomoucká, J. Chovancová

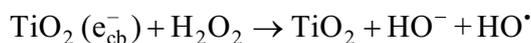
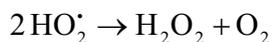
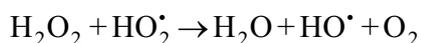
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Titanium dioxide photocatalyst attracts a great attention as material for photocatalytic sterilization, especially in the food and environmental industry. Photocatalytic reactions with TiO₂ are used for organic compounds oxidation, metal reduction, disinfection of various surfaces and waters. As the photogenerated active oxygen species are formed at the irradiated TiO₂ surface, this system can be utilized for microbes deactivation instead of the conventional methods such as ultraviolet irradiation, heat treatment or chemical disinfectant dosage.

In water solution, microorganisms in contact with irradiated TiO₂ surface are damaged by the action of hydroxyl radicals and active oxygen species generated on such surface. In the presence of O₂ the main way of the HO[•] formation on TiO₂ surface is expressed by equations:



Superoxide anion and its protonated form subsequently dismutate to yield hydrogen peroxide or peroxide anion. Those species can form hydroxyl radical.



However, the understanding of the photochemical mechanism of the biocidal action largely remains unclear. It is supposed that this process can lead to the changes of outer membrane permeability, which enables the reactive species to easily reach the cytoplasmic membrane. The structural and functional disorders of cytoplasmic membrane lead to the loss of cell viability and cell death.

A photocatalytic flow reactors usage is reported, especially for organic compound degradation and water sterilization. This process is used not only in laboratory scale, but in solar pilot-plants, too. A typical photocatalytic flow reactor is designed as a system of parallel glass tubes, connected together by knee fittings permitting the studied suspension to circulate through the whole system.

Most of published experiments with anti-microbial effect on titanium dioxide are focused on bacteria. But there are many places contaminated by yeasts, drinking water or water in swimming pools. Therefore we have focused our experiments on yeasts. They are easily observable and can be as dangerous as bacteria.

We have prepared a thin TiO₂ layer inside of glass tubes by sol-gel process using titanium tetraisopropoxide. We have diluted the aliquots of *Hansenula anomala* or *Candida tropicalis* cultures by sterilized water to obtain a suspension containing from 500 to 3000 CFU.ml⁻¹. These suspensions were circulated through irradiated flow reactor. We used a survival ratio for a reaction efficiency expression, defined as a ratio of number of viable cells to total number of cells. An optimal flow rate through reactor tubes was determined by calculation of survival ratio at various flow rates. It was found that at the used experimental conditions the cells of *Candida tropicalis* were more sensitive to oxidative attack than cells of *Hansenula anomala* and kinetic calculations were performed.

WATER QUALITY AND TROPHIC STATE INDEX OF THE PALIĆ LAKE (SERBIA)

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Palić Lake, a shallow lake typical for Pannonian plain, is located in the northern part of Serbia (Vojvodina Province) near Serbian-Hungarian border. The lake serves as a collector for the processed municipal waste waters from the lagoons for active sludge water treatment, but as well it is the lake for recreation. The lake itself was in a very bad condition during last century's late sixties, totally polluted and highly eutrophic. It was dried out in 1971 and re-established in 1977. From that time until now the water quality was regularly monitored every month.

Among monitoring results, the most important, for Trophic State Index (Carlson's TSI) determinations, according to the US-EPA Ambient Water Quality Criteria Recommendations (2000), were the following parameters: total phosphorus, total nitrogen, chlorophyll-a and Secchi disk transparency.

Regarding these recommendations it was concluded that the lake water quality is constantly belonging to hypereutrophic from the very beginning of its re-establishment in 1977. The total phosphorus varied from 200 to 21200 µg/L, total nitrogen varied from 500 to 164900 µg/L, chlorophyll-a varied from 0 to 3777 µg/L and Secchi disk transparency varied from 0 to 250 cm. The corresponding TSI values are well over 70 indicating to hypereutrophic state of the Palić Lake. This should provoke concern and it requires immediate action.

CONTINUOUS TREATMENT OF SELENIUM CONTAINING WASTESTREAMS USING BIOAUGMENTED BIOREACTOR SYSTEMS

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The importance of selenium in environmental research is related to the fact that it shows only a marginal line between the nutritious optimum (as an essential element) and toxic effects upon exposure. The environmental fate of selenium compounds varies greatly in dependence of its complex speciation. A huge variety of both anthropogenic and geogenic aqueous waste streams call for an efficient low-tech cleanup solution.

Compared to adsorptive or precipitative techniques, the bioreduction of selenate is very promising, as combining a separation and a detoxification step. Therefore different bioaugmented Upstream Anaerobic Sludge Blanket Reactor (UASB) systems were tested towards their removal capacity for selenate. Bioaugmentation can be defined as techniques for improvement of a remediation system via the introduction of specific competent strains or consortia of microorganisms. In this study, immobilized microbial cells have been investigated, as in this way microbial growth rates are decoupled from washing-out rates. Anaerobic granular sludge previously tested towards selenium bioreduction (1) was used to inoculate two continuous bioreactors with a working volume of 0.46 L, operated at a superficial upflow velocity of 1 m h⁻¹ and a hydraulic retention time of 6 h. Lactate was used as carbon source at an organic loading rate of 5 g COD L⁻¹ d⁻¹. *Sulfurospirillum barnesii* immobilized in polyacrylamide gel beads was added to one of the reactors. A third reactor was inoculated with gel beads solely.

During bioreduction of selenate not only elemental selenium can be formed, but also different other selenium species, that might show an even higher toxicity. Therefore the most frequently described selenium species were analyzed species specifically via Ion- and Gas-Chromatography (3). These species include selenate, selenite, dimethylselenide and dimethyldiselenide. The formation of elemental selenium was investigated by XRD. During the reactor run, the removal efficiency from the liquid phase for total selenium was lower in comparison with dissolved selenate. As neither selenite nor dimethylselenide or dimethyldiselenide were detected, an unknown selenium species was indicated to be present. The nature of this species is currently investigated by LC-MS. The gap in the selenium balance clearly underlines the importance of species-specific selenium analysis.

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REMOVAL OF TOXIC OXY-ANIONS FROM WATER STREAMS: A THERMODYNAMIC STUDY

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Water, and especially pure water, is a very limited natural resource. In many cases there is not enough water supply of appropriate quality for industrial and home use. Many pollutants in water streams have been identified as toxic and harmful for human health. Among them, heavy metals, arsenic, chromates, etc. have been considered of high priority. Toxic metals removal from water streams have been studied quite extensively and many efficient removal methods have been proposed and applied. Among them sorption/ion exchange methods predominate. However, arsenic, chromium, boron, selenium, exist in water streams mainly as oxyanions and possess negative charge. The usual sorbents, which are effective for cation removal are not efficient enough for oxyanions. Therefore, new sorbents are needed for effective removal of oxyanions from water streams. The removal of toxic species from water streams by sorption methods is affected greatly by the solution chemistry and, therefore, the distribution of the various species in the solution. Surface charge, is an important factor in sorption and is defined by the solution pH and the species distribution. As a rule, cations are better removed by negatively charged sorbents while anions by positively charged ones. Most of the toxic species hydrolyze in water streams creating various species; from simple hydrated cations or anions to complexes with natural or synthetic organic or inorganic ligands, or are attached to colloidal inorganic or organic matter. It is obvious from the above that, a thorough understanding of the solution chemistry is a great aid in the selection of effective sorbents. In this contribution the removal of oxyanions from water streams, as presented in the recent literature is overviewed. Then the chemical speciation of water solutions containing the above mentioned oxyanions in various ratios is calculated with the aid of computer programs (Mineql Plus, Visual Minteq, Geochemist Workbench, etc.). The effect of solution pH, total concentration of each species studied, and the presence of other species in solution is calculated and presented in the form of thermodynamic speciation diagrams. Electrochemical diagrams (correlating pH to Eh) are also calculated and presented. The conditions of solid phase precipitation (when it occurs) are clearly given. Surface reactions between the ions present on the sorbent surface and the chemical species in solution are also discussed. Finally, some experimental sorption data are presented, which show a good agreement between the calculations and the experiments. Guidelines are given for the selection of effective materials for the removal of oxyanions from water streams.

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ENVIRONMENTAL METALLOMICS

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Heteroatoms present in typical biomolecules integrated by C,H, N and O play important roles in the behaviour of small (amino acids, oligopeptides) and large molecules (nucleic acids, polysaccharides, and proteins). The distribution of metal and metalloid species among the cell compartments is considered as the “metallome”, and “metallomics” (1) is the application of analytical approaches to decipher the metallome.

A Metallomics Analytical Approach (MAA) has been proposed for this purpose (2), which considers the combined use of three main instrumental components: (i) a separation technique (SEC, HPLC, CE) for target species isolation from the matrix, “selectivity component”; (ii) an element (ICP-MS), for element quantification, “sensitivity component”; and (iii) a molecule-specific detector, based on MS, for biomolecules characterization, “structural component”.

MAA has important possibilities in environmental studies (3), because many metalloproteins are used as markers of organism exposure to contaminants. Several examples about use of MAA in this field is considered, such as metal uptake mechanisms in hyperaccumulating plants, characterization of metallothioneins in organisms under stress, and presence and structure of arsenic species in marine organisms.

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NEW PERSPECTIVES IN SPECIATION MODELLING APPLIED TO ENVIRONMENTAL SYSTEMS

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The use of computer programs for the calculation of the distribution of the species formed in aqueous systems is not new, e.g. a model for seawater was developed more than 40 years ago. However, nowadays the technique is potentially more available due to the advances in computer technology and, at present, speciation modelling can be considered as a routine tool in many fields. This has led to the false impression that any system can be modeled and computer models are too often used as black boxes. The reality is that these models have evolved very little over the years and that they present today almost the same limitations as 30 years ago. Some of these limitations, in particular those related to the quality of the equilibrium constant values used, and issues associated with the role of natural organic matter have been largely discussed in the past. More often ignored are the limitations imposed by the lack of adequate analytical methods for the quantification of the mineral and macromolecular ligands present in natural aquatic systems. The new perspectives opened by the recent development of methods that allow the quantification of inorganic colloids (V. Chanudet and M. Filella, 2006. A non-perturbing scheme for the mineralogical characterisation of colloids in natural waters. *Environ. Sci. Technol.*, 10, 485-490) and of refractory organic substances (V. Chanudet, M. Filella and F. Quentel, 2006. Application of a simple voltammetric method to the determination of refractory organic substances in freshwaters. *Anal. Chim. Acta*, 596, 244-249) will be discussed in this communication.

CO-ADSORPTION OF CARBOFURAN AND LEAD AT SILICA/INTERSTITIAL WATER. SPECIFIC ROLE OF WATER, KINETICS OF DESORPTION AND POSSIBLE IMPACT ON ENVIRONMENT

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Despite its extremely weak adsorption at the water/silica interface, carbofuran can induce the coadsorption of metallic salts such as lead nitrate, and thus enhance their adsorption. We quantitatively studied this phenomenon with a depletion method and under concentration conditions close to the environmental ones. Heavy metal salt was found to positively adsorb, whereas carbofuran relative adsorption is generally slightly negative. Frequently, focussed on pollutants, authors forget that one of the main components of polluted systems is water. This explains why one may measure pollutant negative adsorptions whereas this pollutant is present on the surface. Particular emphasis will be put on this specific behaviour at silica/solution interfaces where water exhibits co-pollution by ions and organic compounds such as carbofuran.

Coupled with desorption kinetics data related to the silica / solution interfaces and adsorption data concerning water / air interface, the possible impact on environment is discussed, in terms of transfer between several compartments.

SPECIATION OF CADMIUM IN SOIL SOLUTION FROM HYPERACCUMULATING PLANT ALPINE PENNY-CRESS

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Environmental monitoring and speciation of heavy metals (HMs) in soil solution is very important for ecological assessments as well as for understanding of relations between plant and soil. Exposure of plants to metals is primarily through the aqueous phase of soil, soil solution. Several plant and soil properties affect the composition of soil solution. In this case, composition of soil solution including concentration of potentially toxic metals in the solution and speciation of these elements, i.e. distribution of the elements among their various physical and chemical forms, and possible oxidation states (free ions, complexes, ion pairs, and chelates in solution), may influence the reactivity, mobility, and bioavailability of the elements. Several methods for HMs speciation were developed (i.e. diffusive gradient in thin films and electrochemical speciation).

The soil solutions were obtained with suction cups from pot experiment with *Thlaspi caerulescens* L. (alpine penny-cress) planted in two types of soil from two localities in the Czech Republic (Píšťany (Fluvisol) and Příbram (Cambisol)). The soil solution was drawn-off at the end of vegetation period at the same time when the plant biomass was harvested. The soil solution was analyzed by the anodic stripping voltammetry (ASV) and the cadmium ionic species were detected in unchanged pH (in 10^{-3} mol L⁻¹ NaClO₄ base electrolyte). The total contents of Cd were measured by GF-AAS (Table 1) and verified by ASV in pH 2 (in 10^{-2} mol L⁻¹ HNO₃ base electrolyte). The pH depended ionic fractions in pH 3 were determined by ASV (in 10^{-3} mol L⁻¹ HNO₃ base electrolyte). The analyses by ASV in different pH amount the speciation during changeable pH (Table 1). The diffusive gradient in thin film technique (DGT) was used for theoretical estimation of available portions of cadmium in the soil solution (C_b , Table 1) and for characterization of diffusion circumstances in the Diffusive Boundary Layer (F). For conception of Cd plant uptake was established daily available content (DAC) of Cd, which is Cd hypothetically accumulated by 1cm² passive root area (substituted by resin in the DGT device) in 24 hours.

Table 1 Comparison among total content of Cd in soil solution (measured by GF-AAS), real ionic portion of Cd in unchange pH and in pH approx. 2 and aprox. 3 (measured by ASV) and with available Cd portion determined by DGT, n=4.

Method	GF-AAS	ASV (HNO ₃) 0.1 mol L ⁻¹	ASV (HNO ₃) 0.01 mol L ⁻¹	ASV (NaClO ₄) 0.01 mol L ⁻¹	DGT (C_b)
Locality	$\mu\text{g L}^{-1}$				
Píšťany	0.892	0.843	0.284	0.061	6.65E-06
pH	± 0.070	± 0.068	± 0.009	± 0.001	$\pm 1.51\text{E-}06$
		1.94	3.07	6.76	6.76
Příbram	1.798	1.741	1.281	1.105	2.61E-05
pH	± 0.120	± 0.080	± 0.077	± 0.060	$\pm 1.19\text{E-}06$
		1.98	2.99	6.39	6.39

The ionic portion of Cd measured in original pH is the real Cd²⁺ content in real soil solution, the ionic fraction is incomparable with C_b , the C_b concentration stem in physical speciation compare to chemical speciation using pH changing. DGT technique allows theoretical estimation of physical properties of interface between soil solution and root cell: the Cd flow through the DBL, $F^{\text{Píšťany}} = 2.23\text{E-}10 \pm 5.07\text{E-}11 \mu\text{g cm}^{-2}\text{s}^{-1}$, $F^{\text{Příbram}} = 8.74\text{E-}10 \pm 3.98\text{E-}11 \mu\text{g cm}^{-2}\text{s}^{-1}$; $\text{DAC}^{\text{Píšťany}} = 1.92\text{E-}05 \pm 4.38\text{E-}06 \mu\text{g cm}^{-2}$, $\text{DAC}^{\text{Příbram}} = 7.55\text{E-}05 \pm 3.44\text{E-}06 \mu\text{g cm}^{-2}$. The physical and chemical views give us the theoretical description of HMs uptake by the plant.

Financial support for these investigations was provided by the GACR project No. 521/06/0496.

SPECTROPHOTOMETRIC DETERMINATION OF NITRITE IN CURING MEAT SAMPLES USING N,N-DIMETHYL-P-PHENYLENEDIAMINE DIHYDROCHLORIDE-RESORCINOL AS DIAZOTIZING-COUPLING AGENTS

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A rapid and sensitive method for the determination of nitrite ion based on the diazo-coupling reaction was studied. Nitrite was reacted with acidified N,N-dimethyl-p-phenylenediamine dihydrochloride to yield a water-soluble and colorless diazonium ion, which subsequently coupled with resorcinol to form an azo dye in alkaline medium, having maximum absorption at 472nm. The calibration graph showed that Beer's law is obeyed over the concentration range of 0.05-3.0µg/ml of nitrite, with the detection limit of 0.01µg/ml and the molar absorptivity was 3.06×10^4 l/mol. cm. The precision and the accuracy were acceptable depending upon the values of relative standard deviation and error percentage. The influence of common interferences was studied and the method was applied for the determination of nitrite ion in cured meat samples. The results were agreed with those obtained by the NEDA standard method.

NITRATE AND NITRITE AS PHOTOCHEMICAL SOURCES OF HYDROXYL RADICAL AND NITROGEN DIOXIDE IN NATURAL WATERS

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The photochemical production of reactive radical species ($^{\circ}\text{OH}$, HCO_3° , $^{\circ}\text{Cl}_2^-$, $^{\circ}\text{NO}_2$) on irradiation of natural water components is an important environmental sink of water-dissolved organic compounds, including pesticides and pharmaceuticals [1]. Nitrate, nitrite and DOM (dissolved organic matter) are the main sources of $^{\circ}\text{OH}$ radicals in natural waters. Nitrite usually prevails over nitrate as $^{\circ}\text{OH}$ source, although DOM plays on average the most important role [2,3]. The results concerning hydroxyl sources and sinks on irradiation with simulated sunlight of surface lakewater samples collected in the Piedmont region (NW Italy) will be presented, together with a quantification of the relative role of nitrate, nitrite and DOM as $^{\circ}\text{OH}$ sources, and of DOM and inorganic carbon as sinks. The reaction transforming benzene into phenol was employed for the quantification of both the photochemical formation rate of $^{\circ}\text{OH}$ and the steady-state $[^{\circ}\text{OH}]$ under irradiation. The results indicated that DOM is both the main source and sink of hydroxyl radicals in the studied samples, and that the steady-state $[^{\circ}\text{OH}]$ is therefore independent of DOM. The steady-state $[^{\circ}\text{OH}]$ values obtained in the present study, referred to 22 W m^{-2} sunlight UV intensity, are in the 10^{-16} M range.

Nitrate and nitrite can also produce the nitrating agent $^{\circ}\text{NO}_2$, the former on photolysis and the latter because of oxidation by $^{\circ}\text{OH}$. It is possible to assess the relative role of nitrate and nitrite as $^{\circ}\text{NO}_2$ sources from the concentration values of nitrate and nitrite in a given water sample, the photoproduction rate of $^{\circ}\text{OH}$ (and of $^{\circ}\text{NO}_2$ as a consequence) by nitrate, and the steady-state $[^{\circ}\text{OH}]$ [3]. Nitrate tends to prevail over nitrite as $^{\circ}\text{NO}_2$ source in surface water samples, while they play a comparable role in atmospheric waters [4]. Furthermore, the steady-state $[^{\circ}\text{NO}_2]$ levels thus assessed would cause the conversion of typical phenol into nitrophenol levels in a few days in surface waters, and often in a few hours in atmospheric hydrometeors [3,4]. Coherently, detectable levels of phytotoxic and suspected mutagenic nitrophenols are formed on irradiation of benzene-spiked natural waters samples in the presence of nitrate levels $> 0.10 \text{ mM}$ [2,3].

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ICP-MS DETERMINATION OF MICROELEMENT COMPOSITION OF HUMAN TOOTH TISSUE BIOMINERAL PHASE

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Main components (Ca, P) and major trace elements (Na, Mg, Cl, etc.) composition of tooth enamel had been studied earlier, but there are very few articles dedicated to investigation of its microelement composition. Nevertheless bone and tooth biomineral phase is known for ability to accumulate from environment some trace elements, particularly heavy metals. Chemical composition and properties of tooth biomineral component reflect physiological peculiarities of organism functions and can give important information for ecological monitoring of residence region.

In many regions of Russia pathological process in hard tooth tissue of different etiology (increased abrasion, decreased caries and non-caries resistance, etc.) are closely connected with negative ecological situation, especially in Urals region. Thus research of human tooth hard tissue biomineral phase microelement composition is very important and actual scientific problem.

The most promising method for micro-trace analysis of human calcified tissues is high sensitivity multi-element ICP-MS analysis. However there are three main problems associated with the analysis of tooth hard tissues. These are:

- the low concentration of the elements accumulated, and thus application of high-purity reagents and glassware and up-to-date analytical equipment
- interferences from the large amounts of hydroxyapatite and organic component (for example, tooth enamel contains up to 2 % wt. and dentine up to 30 % wt. of organic compounds) present in the matrix
- lack of suitable reference materials for quality assurance.

The aim of present work is to develop analytical method of sample preparation which would allow to realize ICP-MS microelement analysis of human tooth hard tissue layer-by-layer and experimental investigation of its peculiarities.

Teeth of different degree of integrity were studied – intact, carious of various depth and localization and also with increased abrasion.

Sample preparation included acid etching of tooth enamel by 2 ml 3M HClO₄ during 3-5 minutes. After that tooth was dried and weighed and procedure of acid etching repeated until enamel was dissolved. Remained dentine was mechanically separated to fragments and dissolved in HClO₄.

All measurements are carried out with use of ICP-mass-spectrometer ELAN 9000 (PerkinElmer). 99,998% purity Ar, MilliQ water and purified acids were used through the experiment. Sample introduction was managed by pneumatic cross-flow nebulizer. Instrument was optimized for maximum sensitivity of ions M⁺ and minimum signal from M²⁺, MO⁺ and background ($m/z = 220$).

Introduced multi-stage dissolution scheme of tooth enamel was applied to analysis of human teeth with increased abrasion. Dissolution speed of inner enamel layers increase as their degree of integrity decrease probably due to matrix crystal structure disturbance. Groups of trace elements concentrating in intact and affected enamel in different ways were separated; element incorporation features depend on a degree of tooth tissue integrity. Obtained data were subjected to correlation and factor analysis in order to reveal element accumulation and distribution regularities.

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INVESTIGATION OF POLLUTION LEVEL, VERTICAL AND PLANAR DISTRIBUTION OF SOME HEAVY METALS IN THE TISA RIVER SEDIMENTS

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In this work, sediments of the River Tisa are studied to assess their environmental pollution levels for some major heavy metals (Zn, Cd, Pb, Ni, Cu, Fe, Mn and Cr) and to obtain the information of vertical and planar distribution of the studied elements.

Sediment samples were collected at 32 locations: 24 samples of the River Tisa (surface and lower - laying river sediments), and 8 samples of tributaries and pools. The modified Tessier method [1] was used in order to extract the metals from the sediments.

A comparison between metal concentrations in the Tisa River sediments to its tributaries showed that larger concentrations of Zn, Cd, Pb, Cu, Mn and Cr are found in the Tisa sediments, while Ni and Fe concentrations are found to be larger in the sediment of tributaries. The average metal concentrations in the surface sediment layer were higher than in the deeper layers (about 20%), which indicate the accumulation of metal pollutants from adjacent land sources and normal sedimentation processes, particularly in recent years.

Pearson correlation and factor analysis [2] were performed in order to get information about the relationships and behavior of heavy metal. Factor analysis of the elemental data (Fig.1) identified two major groups of heavy metals: (a) Cu, Cr, Zn, Pb, Cd, and Mn and (b) Fe and Ni, which may indicate the different origins or different concentration controlling factors of heavy metals in sediments.

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BIOACCUMULATION OF HEAVY METALS IN SOME FAUNA AND FLORA FOUND IN IJAW AREA OF NIGER DELTA OF NIGERIA

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Bioaccumulation of heavy metals in fauna and flora in the Ijaw area of the Niger Delta of Nigeria were investigated. The fauna-molluscs and crustacea, and flora *Hibiscus esculentus* and *Vernonia amygdalina* were selected for this study. Results show that Molluscs and crustacea accumulate considerable amounts of heavy metals. Higher levels of all the metals determined Hg, Pb, Cr, Cu, Ni, and Zn were observed in the shells than in the fleshy tissues. *Hibiscus esculentus* and *vernonia amygdalina* also accumulated these heavy metals. The mercury levels in the roots of *Hibiscus esculentus* and *Vernonia amygdalina* is $0.010 \mu\text{g/g} \pm 0.00$, while the stem $0.17 \pm 0.03 \mu\text{g/g}$ and leaves $0.25 \pm 0.02 \mu\text{g/g}$ was recorded for the v. amygdalina. The H. esculenta fruit has lead levels of $0.22 \pm 0.03 \mu\text{g/g}$. The levels of Cu, Ni, and Zn are generally higher than those of Hg, Pb and Cr in all the samples analyzed. There is a growing concern about the physiological and behavioral effects of environmental trace metals in human population. The toxicity of lead at high levels of exposure is well known but of a major concern is the possibility that continual exposure to relatively low levels of these heavy metals through the consumption of these fauna and flora may entail adverse health effects.

Key words: Heavy metals, industrial effluents, molluscs, crustacea, *Hibiscus esculentus*, *vernonia amygdalina*, toxicity and bioaccumulation.

EVALUATION OF NANOMETER THICK MERCURY FILM ELECTRODES FOR SCANNED STRIPPING CHRONOPOTENTIOMETRY

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Stripping chronopotentiometry (SCP) has been proposed as an alternative to more conventional stripping techniques, in order to minimize the problems caused by adsorption of species onto the mercury electrode. SCP was recently applied to micrometer thick mercury film electrodes (MFE). The results pointed out some advantages of SCP at the MFE, compared with the hanging mercury drop electrode however, the preparation procedure of the MFE is complex and often presents low reproducibility¹.

The present work evaluates the potentialities of thin mercury film electrodes (TMFE) plated onto glassy carbon in thiocyanate medium for SCP. The present mercury films were very reproducible, stable and present a homogeneous distribution of small size mercury droplets².

SCP curves were easily obtained for Pb concentrations of 1.2×10^{-8} M. In the scanned deposition potential mode (SSCP) the experimental result is a transition time vs. deposition potential curve. SSCP yields information on the metal complexation via the potential shift (using an equation similar to the DeFord-Hume formulation). The ability of the TMFE to perform reproducible SSCP curves was evaluated being the metal speciation parameters for labile complexes determined³.

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ORAL PRESENTATIONS

SATURDAY, DECEMBER 9th

THE CANADIAN APPROACH TO REMEDIATION OF PETROLEUM CONTAMINATED SOIL AND RELATED ANALYTICAL METHOD

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The Canada-Wide Standard for Petroleum Hydrocarbons in Soil (PHC CWS) was developed by the Canadian Council of Ministers of the Environment (CCME) as a means to promote the consistent measurement, assessment and management of contamination from release of both crude and refined sources. The standard acknowledges that petroleum hydrocarbons have widely varying physico-chemical properties that govern both their effects in the environment and the analytical approaches appropriate to their determination. Prior to the development of the PHC CWS there was no consistency in Canada in the measurement of these substances so results could not be properly compared between sites or among laboratories.

An Analytical Methods Technical Advisory Group (AM TAG) was formed to assist CCME in identifying a reliable and scientifically sound analytical method for determining PHC in soil. The resulting reference method combines both prescriptive and performance-based procedures to address the extraction, purification and determination of the four CCME PHC fractions (nC6-<nC10, nC10-<nC16, nC16-<nC34, C34+). Some of the key prescribed elements include the solvent systems to be use; the quality assurance/quality control parameters and single lab validation results.

CHEMICALLY INDUCED PHYTOEXTRACTION OF LEAD FROM SMELTER-IMPACTED AGRICULTURAL SOILS

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Chelant-enhanced phytoextraction of heavy metals is an emerging technological approach for a non-destructive remediation of contaminated soils. The main objectives of this study were (i) to assess the extraction efficiency of two different synthetic chelating agents (EDTA, EDDS) used for desorbing Pb from two studied multi-metal contaminated agricultural soils originating from a mining and smelting district and (ii) to assess the phytoextraction ability of maize (*Zea mays*) and poplar (*Populus* sp.) after the chelant application. EDTA was more efficient in desorbing and complexing Pb from both soils compared to EDDS, removing as much as 60% of Pb from soil. The PHREEQC-2 thermodynamic modelling showed that the majority of Pb is present as [Pb-EDTA]²⁻ complexes (> 99%) after the EDTA application. Maize exhibited better results than poplar in Pb uptake from a more acidic (pH ~ 3-4) and more contaminated (up to 1360 mg Pb kg⁻¹) agricultural soil originating from the smelting area. This was predominantly due to the high contents of Pb (365 ± 44 mg kg⁻¹) in maize biomass after the application of 9 mmol EDTA kg⁻¹. On the other hand, poplars proved to be more efficient when grown on the near neutral (pH ~ 6) moderately contaminated (up to 200 mg Pb kg⁻¹) agricultural soil originating from the mining area, mostly due to their higher biomass production. The addition of EDTA led to a significant increase of Pb content especially in poplar leaves, proving a strong translocation rate within the poplar plants.

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THE EFFECT OF SINGLE AND SPLIT EDTA APPLICATIONS ON THE EFFICIENCY OF HEAVY METAL PHYTOEXTRACTION USING *ZEAMAYS*

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Induced phytoextraction of heavy metals using chelating agents and agricultural crops could present an environmental-friendly and cost-effective remediation technique for agricultural soils contaminated with heavy metals originating from smelting industry. The chelating agent ethylenediaminetetraacetic acid (EDTA) proved to be efficient in increasing the mobility and phytoavailability of heavy metals in soils. However, phytotoxicity and possible groundwater contamination through heavy metal leaching are the possible drawbacks of EDTA application. Therefore, there is the need to optimise the agronomic practices to enhance the phytoextraction efficiency together with minimising the risks associated with heavy metal leaching.

Samples of an agricultural soil (0-20 cm) contaminated by smelting industry were collected from the Příbram area, Czech Republic. The effect of single and split applications of EDTA disodium salt (3, 6, 9 mmol kg⁻¹ and 3×1, 3×2, 3×3 mmol kg⁻¹, respectively) on heavy metal solubility and phytoavailability was evaluated. Split applications were applied in ten days intervals.

In a batch incubation experiment, the highest single dose (9 mmol kg⁻¹) of EDTA resulted in an increase of total water-soluble concentrations of Pb by 148-times, Cd by 203-times, Cu by 63-times and Zn by 23-times compared to the control. Thereby the total water-soluble fractions were increased to 64% of total Pb, 32% of total Cd, 41% of total Cu and 18% of total Zn. Split applications of EDTA resulted in lower, but more constant water-soluble heavy metal concentrations, especially in the case of Pb.

In a pot experiment, high initial water-soluble heavy metal concentrations resulted in phytotoxic symptoms observed on *Zea mays* (especially following higher single doses of EDTA). Split doses caused less phytotoxic effects. The phytotoxic effects resulted in a significantly decrease of plant biomass production. Decrease was higher following single doses compared to corresponding split doses. Cd, Cu, Pb and Zn concentration in the plant shoots were significantly increased by EDTA applications (especially that of Pb with a 23-fold increase in the treatment amended with the highest single dose). Single doses of EDTA were generally found to be more effective in increasing heavy metal concentrations in shoots of *Zea mays* compared to corresponding split doses. The higher metal uptake resulted in higher remediation efficiency (although biomass was lower following single doses compared to split ones).

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HEXAVALENT CHROMIUM ADSORPTION ON EXHAUSTED COFFEE WASTE

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Chromium is released into the environment from different anthropogenic sources e.g. electroplating, leather tanning, textile dyeing and metal finishing industry. In aqueous systems, chromium occurs in both trivalent and hexavalent forms, the latter being of particular concern because of its greater toxicity. Conventional processes used to remove hexavalent chromium are adsorption on activated carbon, reverse osmosis, or chemical processes such as reduction of hexavalent chromium into trivalent chromium, then its precipitation as chromium hydroxide. Recently, the use of low-cost sorbents has been investigated as a replacement for current costly methods of removing heavy metals from aqueous solutions. During the last years, we investigated the potential of some vegetable wastes from industrial processes to be used as metal sorbents.

One of these wastes is exhausted coffee waste generated in the soluble coffee production process. In the present work, this sorbent is investigated for hexavalent chromium removal from aqueous solution. Batch experiments were designed to study the influence of contact time, initial pH and metal concentration on Cr(VI) sorption on exhausted coffee wastes. Pseudo-first and pseudo-second order models and Langmuir and Freundlich isotherm models were used to describe sorption kinetic and equilibrium data, respectively.

Results showed that metal sorption is pH dependent and maximum sorption was found at initial pH 3. The equilibrium process was described well by the Langmuir isotherm model with maximum sorption capacity of 13 mg of Cr(VI) per gram of exhausted coffee waste. Good correlation coefficients were obtained for the pseudo second order kinetic model. Results put into evidence that the sorbent is able to reduce Cr(VI) to its trivalent form. In summary, exhausted coffee wastes a part from being a suitable low cost sorbent for hexavalent chromium, has the advantage of converting Cr(VI) to the less toxic Cr(III), so, this sorbent can be used for the removal of chromium from wastewaters through a cost-effective and environmentally friendly process. Furthermore, the potential of using the studied wastes as cheap reducing agent for the reduction of Cr(VI) to Cr(III) deserves to be investigated.

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ARE PLASTICS IMPORTANT IN THE TRANSPORT OF HYDROPHOBIC CONTAMINANTS?

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Plastic is of great environmental significance due to the vast amount produced, and the considerable portion that ends up in the environment. Weathering of abandoned plastics leads to fragmentation and hence increased surface area; the resulting microscopic plastic fragments are becoming an integral component of marine sediments. Accumulation of hydrophobic contaminants on the surfaces of plastic debris has been proposed for decades. However few comprehensive studies have investigated the interactions between such compounds and plastics.

Using phenanthrene as a model compound, we have investigated uptake by a range of plastics, and subsequent desorption under different conditions. An emphasis has been placed on in vitro desorption designed to mimic gut conditions in the lugworm *Arenicola marina*, an important detritivore at the base of the food chain. Experiments assessed the potential transport of contaminants to the organism (and hence higher up the food web) via plastics. The extent of uptake varied by more than an order of magnitude between plastic types, and greatly exceeded that of a number of natural sediments (polyethylene >> polypropylene > polyvinyl chloride (PVC) >> sediment). Desorption rates spanned several orders of magnitude with more rapid release from sediment than from plastics (sediment >> polypropylene > polyethylene > PVC). This indicates that exposure time is likely the most significant factor governing transport of contaminants to organisms by plastics.

CATALYTIC CONVERSION OF POLYETHYLENE INTO GASOLINE-RANGE FUELS

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Rapid growth of polymer production becomes a significant ecological problem. Since biodegradation of polyethylene, polypropylene and other widespread polymers is very slow their wastes contribute to a contamination of environment. Various approaches are developed to minimize polymer wastes or to recycle them. Among the latter techniques degradation of waste polymer into a mixture of lower hydrocarbons, which can be used as a fuel, is considered to be an environmentally benign. The procedure requires appropriate catalysts, application of available and cheap raw materials for catalyst production is crucial for the process to be used on a large scale. Clay minerals seem rather attractive and essential source of the raw materials.

Montmorillonite-containing clay minerals of Belgorod region are used for catalyst preparation. Catalytic experiments were carried out in nitrogen flow under atmospheric pressure at 400°C.

Original clay minerals were shown to have low activity in the process. Catalyst samples leached by acids were proved to be much more active catalysts in high-density polyethylene degradation. Catalytic degradation of the polymer resulted in the products other than those of pure thermal degradation. Only over the catalysts leached with nitric or sulfuric acids liquid products dominated; the product range was typically between C₅ and C₃₀. In other cases catalytic conversion resulted in solid products.

XRD results confirm that the materials leached with acids are slightly amorphized. One can conclude that optimum treatment causes decationation and slight amorphization. An essential increase of a content of amorphous phase has a negative influence on a yield of liquid products. On the other hand acid sites are considered to be responsible for the catalytic degradation of ethylene but they also accelerate carbon deposition. Thus optimum catalyst is probable one possessing optimum surface acidity.

Up to 30% of gasoline fraction was obtained over optimum catalyst. Octane number of the fuel corresponded to 79–80.

Montmorillonite clay is proved to be a cheap and available raw material for a preparation of catalyst of polyethylene conversion into liquid gasoline-range products.

TRACE METALS INFLUENCE ON METHANOGENIC ACTIVITY OF ANAEROBIC GRANULAR SLUDGE

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The lack of trace metals in wastewater (e.g. wastewater generated by condensation processes) can cause serious problems during its anaerobic treatment. It has already been well documented that metals such as cobalt, nickel or zinc are essential for growth of methanogens and therefore it is crucial issue to ensure supply of these metals into the anaerobic reactor (Zandvoort et al., 2006).

Our research has been focused on the phenomenon of trace metals limitation in the system of Up-flow Anaerobic Sludge Bed reactor (UASB), where the granular anaerobic biomass is employed. The effect of trace metals (Co, Ni, Zn, Se, W, Mo etc.) limitation has been described – the changes in methanogenic activity, metabolic pathways and evolution of microbial community of anaerobic granules were mainly studied. Breakdown of methanogenic activity as the consequence of Co (Ni) limitation (60 and 130 days, respectively) as well as restoration of the process after metal supplementation were documented (Zandvoort et al., 2004).

The metals dosing strategy (form of metals, time schedule etc.) is very important for the full-scale reactor operation. Therefore, the chemical mechanisms of the metal exchange between solid and liquid phase and also the mechanisms of bacterial uptake are extremely important for the overall process. Therefore, the effect of chemical speciation on metal uptake was studied.

Especially the free metal ions (Me^{z+}) are important for bacterial uptake. There were published several studies showing that only free ions can be transported cross the cell membrane (directly or using some kind of transporters). Therefore, the influence of the free cobalt concentration was studied (mainly for the toxic concentrations). For this purpose the Donnan Membrane Technique (DMT) has been used (Weng et al., 2001).

The aim of this presentation is to present the role of trace metals in the system of UASB reactors treating methanolic (synthetic) wastewater. The results of long-term lab-scale reactors treating this wastewater under metal (Co, Ni, Zn) limitation will be shown. The impact on methanogenic activity as well as on the composition of the microbial community will be presented. The principal of DMT will be explained and results from our cobalt-speciation experiments will be shown.

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COUPLING OF THE PHOTOCATALYTIC AND MICROBIOLOGICAL DEGRADATION PROCESSES FOR THE ORGANIC POLLUTANTS DESTRUCTION

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This research contributes to studies of new degradation techniques for purification of wastewater, groundwater, watercourse and drinking water containing different toxic and hardly biodegradable organic pollutants.

The subjects of this paper are the methods that are coupling photo catalytic and microbiological degradation of methyl-tertiary-butyl-ether (MTBE) dissolved in water. The effects of concentrated solar radiation simulated with sodium lamp (SON T UV400), titanium based catalysts, Fenton reagents and microorganisms have been investigated in lab experiments, and their efficiency compared. The degradation methods have been investigated in the slurry catalyst circular photo-reactor's system that provided uniform distribution of the photo catalysts and microorganisms.

Finally, the best results of their methods showed that it's possible to find an optimum of synergetic effects of concentrated solar radiation, type of microorganisms as well as distinct catalyst systems, leading to the determination of the effective systems for different toxic organic compounds from real sources.

EFFECTIVE CARBON RATE A NEW FACTOR FOR VALUATION OF BIOMASS ENERGY

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The need of fossil energy sources and greenhouse effect are growing problems. This inspires the use of biomass in energy industry. In the latest time there was only one factor to evaluate the different processes – energy efficiency.

Our studies point it out: through these processes a great amount of carbon atoms coming from biomass change to carbon dioxide. Beside, through used energy production is also generated carbon dioxide. There is a further decrease in efficiency if through the consumption of engine fuel produced of the new elementary substance the emission of other noxious materials would grow. Typical example for this is the bio diesel, where consumption generates a significant growing in CO and NO_x emission. The specific CO₂ value of NO_x in greenhouse effect is enormous high.

In life cycle evaluation of individual processes the following should be measured. How much is the amount of excess carbon dioxide and other greenhouse gas equivalent produced in consumption, and how much is the rate of carbon changed into carbon dioxide in energy production (engine running, generation of electricity, etc.). This is the effective carbon rate. Considering all these the priority list of BAT (Best Available Technology) would change definitively, that must be also evaluated.

In our study we introduce an evaluation method, where we can follow up the gross carbon dioxide „production” of the elementary substance from exploitation of row material up to energy production. Especially interesting data can be won about biogas and bio-ethanol, where a striking amount of carbon-dioxide is generated in phase fermentation of biological row material, and finally as well as in technological phase of concentrate to usual composition.

The presentation demonstrates the mass and energy flowchartings in the produce of bioenergetics. We have calculate the arising greenhouse gases from these date and convert its into carbon dioxide. With these date we can calculate the effective carbon-dioxide mass, which originates in the energy production step.

We make a comparison between the biogases, bio diesel, bio ethanol, bio fuel by syngas and biomass burning processes.

The results of investigations refer to errors of technologies. Some of favourite process makes a height percent carbon dioxide from carbon in the parts of technologies (for example biogas production). These processes are good for the treatment of toxic waste, but not important energy production.

The goal of our investigations is draw the attention to the really environmental friendly energy making processing.

OZONATION OF CHLORPYRIFOS AND CHLORPYRIFOS-OXON

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Over the last decade, a growing interest has been paid to ozone reactivity in relation to the elimination of pesticide residues. The behaviour of organophosphorus pesticides towards the ozone was studied, and a cycloaddition of ozone to P = S double bond was proposed. Consequently, the formation P = O before the breakdown of the molecule is expected. Chlorpyrifos, a member of diverse family of organophosphorus compounds (OP) is the only OP insecticides authorized for use in plant protection for the next years. It has been skipped from the large investigation of ozonation during the last years and it was thus selected together with its oxon analogue chlorpyrifos-oxon for additional studies. We have noticed that chlorpyrifos is completely transformed into chlorpyrifos-oxon under ozone treatment during first half minute of the experiment, whereas the formed oxon is than after 2 h of ozonation under same conditions still 20% of the initial amount. With the use of different analytical techniques, such as GC-MS and LC-MS, we were able to monitor the formation of several ozonation products, but the formation of oxon seems to be the predominant way in chlorpyrifos ozone treatment, since chlorpyrifos-oxon was very stable to the treatment applied. Chlorpyrifos-oxon, unfortunately, is known to be a potent acetylcholine esterase (AChE) inhibitor. The use of ozone for treatment of OP polluted waters represents a serious threat if the stable by-products are not adequately monitored.

LOW COST BIOSORBENTS FOR THE REMOVAL OF COPPER FROM SYNTHETIC AND INDUSTRIAL WASTEWATER.

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Growing environmental concerns and regulatory pressures mean that novel, cost efficient techniques are required to remove contaminants such as heavy metals from natural and waste waters. The use of biosorption technology, utilising natural materials or industrial and agricultural wastes to passively remove metals from aqueous media has been investigated as a possible alternative to conventional remediation methods. While numerous biosorbents have been proposed, the evaluation of their performance has been conducted under a wide range of conditions including pH and ionic strength. Consequently it is difficult to compare and contrast the performance of different biosorbents or to assess their potential relative to conventional sorbents such as ion-exchange resins or activated carbons.

We present results from an intercomparison of three low cost, biosorbent materials, crab carapace, peat and the macroalgae *Fucus vesiculosus* with an ion-exchange resin and an activated-carbon for their ability to remove copper from synthetic and industrial wastewater.

Data from batch equilibrium and column studies shows that removal efficiencies for crab carapace and *Fucus vesiculosus* to be >90% and comparable to the ion-exchange resin for both synthetic and industrial wastewaters. Results will also be presented that demonstrate that copper concentration, pH, point zero charge and matrix effects all effect removal and uptake efficiency and that biosorption follows pseudo second order kinetics.

On the basis of these results, we indicate the potential of these biosorbents to be considered as viable alternatives to commercial sorbents for the removal of metals from aqueous media in industrial applications.

POSTER PRESENTATIONS

1. RISK ASSESSMENT, BIOINDICATORS

POSTERS No. 1 – 10

CONTENT OF POLYCHLORINATED BIPHENYLS IN BLOOD OF HUMAN POPULATION OF VOJVODINA (NORTHERN SERBIA)

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Polychlorinated biphenyls (PCBs) are known human carcinogens, and contemporary epidemiological studies have shown that most human carcinoma are related to the living and working environment. Entrance pathways for toxic contaminants into the human body include respiratory system, digestive system or skin. Due to lipophilic characteristic, PCBs bioaccumulate in the tissues with high lipid content and have toxic effects on central nervous system and parenchymatous organs, especially liver. This paper presents the levels and distribution of polychlorinated biphenyls in organisms of humans. The content and distribution of PCBs was determined in samples of blood and adipose tissue collected in Spring 2005 from random donors of both genders and different age during vascular and abdominal surgical procedures the Clinical Center of Novi Sad, Serbia. The quantitative data were determined by ultrasonic extraction of PCBs from human material and gas chromatography (GC/ECD). In all investigated samples PCB residues were detected, of which more abundant were PCB congeners with higher molecular masses.

Poster No. 2:

DOSE RESPONSE CURVES DATA PROCESSING

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We can find dose-response experiment in the wide range of biological branches. Unfortunately, data processing approaches are not uniform. There are differences between recommendations of toxicological agencies in Europe and in the United States.

This paper reviews available problem solutions and shows recommendation. Problem solution was implemented into the developed software ADRIS for dose-response data processing. Implemented algorithms and calculations copy U.S. EPA recommendations.

RISK ASSESMENT AND ESSENTIALITY OF TRACE AND MAJOR ELEMENTS IN PLANT – SOIL SYSTEM

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The majority of medicinal herbs contain macro and micro nutrients in concentrations that are generally not harmful. However, numerous plants have an ability to accumulate some elements in relatively high and for human toxic concentrations, but mechanisms of adaptation strategy of plants for specific elements are still unknown. On the other hand, plants are part of food chain. The aim of this work is the determination of nutrients and toxic metals in herbal drugs that originate from plants of the family Asteraceae: Chamomillae flos and Millefolii herba. Calcium, K, Mg, Fe, Mn, Zn, and Cu as essential, and Cr, Pb, Cd, and Ni as toxic elements, were also determined in soil samples where analyzed plants were cultivated under strongly controlled conditions. This is of special importance having in mind a dynamic system and complex equilibrium between those environmental compartments. Additional importance arises from the fact that soil might be a very significant source of influence when pollution is detected. All samples were prepared following standard EPA procedures microwave-assisted decomposition. Atomic spectroscopy methods such FAAS and GFAAS were applied for measuring. Investigated herbs are often used as supplement therapy of different disorders and illnesses. Therefore, it is highly important to evaluate the possible risk of their usage in human medicine. The amounts of all tested elements have been compared with Recommended Dietary Allowances (RDA) and Safe Daily Dietary Intakes (SDDI) recommended by WHO.

Poster No. 4:

USING MACHINE LEARNING METHODS IN ENVIRONMENTAL RISK ASSESSMENT – OVERVIEW

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In a past few years evolution in Machine Learning (ML) techniques was significant. And the number of fields where ML is employed is still continuously growing. One of these field is Environmental Risk Assessment (ERA). The nature of many problems from the field (ERA) is "machine learning-friendly". The goal of this paper is to describe how and on which problems ERA use ML. To give a short overview of the works which were already done and give some notes about focuses of the future possible scientific researches.

Big impact on this 2 jointed fields had the Fourth International Workshop on Environmental Applications of Machine Learning in 2004 which was held in Slovenia and also the scientific journals Ecological Modelling and Science of the Total Environment.

SAFETY OF TRANSPORT OF DANGEROUS SUBSTANCES

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Transport of dangerous substances can be a potential hazard for the population, their property and the environment. Road - accidents in hazardous materials transportation have increased 95 % in the last 30 years. There are available statistics which demonstrate that there are an increasing number of road accidents in Europe (including those relating to the transport of dangerous substances and the increasing costs related to these accidents).

Transport of dangerous substances is, due to this increasing number of accidents, a very real problem. As an example of main causes of accidents the ADR accident frequency in 2003 and 2004 will be used. Accident registration has been launched in 2000 in the Czech Republic by the traffic police. Data from 2000 – 2002 are not very precise because of administration faults. Data registered since 2003 are more precise and data from 2005 are not complete yet.

The Czech Republic is one of the countries with the largest accident frequency and high number of deaths of people during accidents. Reasons for accidents are mostly the same when considering small cars or trucks. The main reason is human error – poor attention of drivers and their reactions. Substances included in the group of flammable substances (according with European ADR directive) constitute the most frequently transported dangerous materials on the roads. A risk assessment for dangerous substances is performed using different kinds of methods. In order to propose and create methods for the safe transport of dangerous substances it is first; necessary to perform an extensive analysis of the existing situation. Methods must also be focused, made relevant to different localities and the industry that applies there, there must be better control systems on the routes (there is often the transport of unmarked dangerous goods and substances; tachometers are still not always good used or are falsified) etc. More strict penalties could be applied. We recommend re-establishing the system of precise routing during transport of dangerous substances. The experience of drivers is crucial and each company (transporting substances according to ADR) should have a duty to prove drivers crime sheet regarding accidents and other offences. Decontamination of accidents is mostly very difficult or not possible because of different conditions (wind direction and intensity, atmospheric stability etc.) and the type of contamination (soil, surface water, ground water etc.). Risk, health and environment hazard during transport of dangerous goods seems to be lower because of tank cubature, but damage could be unexpectedly large when we consider for example an accident in a highly populated area. There is possibility to improve the situation through our preparedness, self-education, and interest regarding the problem. To protect the population against dangerous substances it is necessary to work out effective methods for accident prevention or in emergency situations and to learn from previous incidents. Therefore a project has been established with the aim of a comprehensive treatment of transport of dangerous substances in the Czech Republic. The partners participating in this project are the Faculty of Chemistry (Brno), the Centre for Road and Public Transport (DEKRA Prague), Public Administration (Czech Government) and other institutions. Some of mentioned results in the poster are presented for the first time and data used are taken from different sources.

THE PREVENTION PROCESS OF MAJOR CHEMICAL ACCIDENTS AND RISK ASSESSMENTS

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Already in the period of the former Czechoslovakia important accountable norms have been accepted and subsequently introduced into technical and technological work experiences. It can be reminded the earlier norm CO-51-5 included in sum 12 main industrial toxic substances.

The prevention problems of the major accidents are supported already since middle 80s of the 20th century by several prestigious international projects of the OSN, the EU and trade unions. In terms of the membership of the Czech Republic in these international organisations the projects are considerably supported on the part of the state and industrial concerns' union syndicates. As the most important projects regarding this subject can be considered programs APELL, Responsible care, Correct experience, and also Czech project Secure concern from the perspective of the Czech Republic. Another extended method of the prevention support have been, and are being standard and certificate systems implemented in the scope of quality, environment and labour protection, e.g. series of norms CSN EN ISO, for instance CSN EN ISO 9 001 (quality management system), CSN EN ISO 14 001 (environmental management system) or 18 001 OHSAS (*Occupation Health and Safety Assessment Series* for health and safety management systems).

In the course of the existence of the Czech and Slovak federal republic (in 1992) it was imposed to the Ministry of Industry and Trade to draught a national act concerning the major industrial accidents prevention and disposal. The act preparation responsibility during its processing was transferred to the Ministry of Environment. The act was prepared and passed as the act no. 353/1999 Sb., with effect from January 2000.

It is a surprising fact that even 10 years after the European directive SEVESO II legalization (1996), this effectual norm wasn't complemented with a method for demanded risk analyses (eventually with individual methods of risk analyses for a particular subject of interests, as it is demanded by the Czech national act: persons – livestock – environment – property), so far from the convenient and freely distributed software tool.

According to the Czech national legislation it is necessarily required to analyse and assess impacts of accidents to persons, livestock, environment and property. The method choice or selection of the risk analyse depends according to Czech legislation on the risk analyse executor. Even the last amending the law (act no. 59/2006 Sb.) have not changed anything. It is a serious consequence for the crisis process management and accident planning; mainly it is not possible to compare particular observers and their subjects and establishments containing dangerous chemical substances.

As an available example of the preparation for the risk analyse methodology is possible to mention above all the renew methodology of the International Atomic Energy Agency: IAEA TECDOC 994 (1998), which could be after improvements the ground for the discussed effectual execute norm. The mentioned publication collectively solves all subjects: permanent emission analyse and assess of the stationary sources, dangerous chemical substance analyse, chemical substances analyse from stationary sources, dangerous chemical substance transport, dangerous waste analyse, etc.

Poster No. 7:

POLYMERIC BARRIER MATERIALS AND THEIR EVALUATION

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Barrier properties of the polymer construction materials against the highly toxic agents and industry harmful substance are the phenomenon, which adjudicate about the quality of every protection means. By selection of the suitable polymer materials for the protection means it is needed to know not only their physical and chemical properties, but primarily their resistance against the permeation of this agents by short time and longtime contamination in the gas and liquid phases. For comparison of the barrier materials from view of the resistance against the harmful substances, it is necessary the suitable methods for their evaluation. In presentation there are stated the basic information about the selected barrier materials and are described the new methods for evaluation of their barrier properties.

POST-CONFLICT ENVIRONMENTAL ASSESSMENT IN AFGHANISTAN

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Decades of conflict and violence coupled with drought and earthquakes have had devastating impacts not only on people of Afghanistan, but also on natural environment, once pristine and rich in biological diversity but now suffering from years of overexploitation of natural resources and habitat loss. Afghanistan is at a crucial point in its tumultuous history. Since 1973, the country has changed regimes frequently, and has been led by eight different leaders. Instability and war has caused widespread devastation, insecurity, displacement, poverty and severe environmental degradation. After the tragic events of 11 September 2001, Afghanistan received unprecedented international attention, and the events drew strong support for the required humanitarian, political and military actions and solutions needed to put Afghanistan on the road to peace, stability, recovery and development.

It is tragic to see how many people have left Afghanistan due to war and drought-related issues. Apart from the conflict, environmental degradation has been an important force driving people to find a better future elsewhere. The lack of water resources has led to the collapse of many livelihoods, and most of the country is subject to an alarming degree of land degradation propelled by poverty, population growth and the need to survive. The country had also been robbed of its precious forest resources by Afghan and non-Afghan timber mafia and smugglers. The net result of the degradation is widespread desertification and erosion, and increased vulnerability to environmental disasters. Now is the time to take stock of the current conditions, develop systems for the sustainable use of resources and look for ways to rehabilitate degraded ecosystems.

The scope of UNEP's post-conflict environmental assessment in Afghanistan has included such vital environmental issues as pollution hotspots in the urban environment, surface and ground water resources, deforestation, waste and sanitation, air quality, and desertification. Environmental improvements cannot be made without proper institutional arrangements. Therefore there has to be addressed issues like environmental impact assessment, framework environmental laws, regional co-operation and Afghanistan's participation in international environmental conventions.

The UNEP work in Afghanistan has been financially supported by the governments of Canada, Finland, Luxembourg and Switzerland. The close link between humanitarian and environmental needs in Afghanistan has been recognized in both the United Nations Immediate and Transitional Assistance Programme (ITAP) for Afghanistan in 2002 and in the Transitional Assistance Programme for Afghanistan (TAPA) in 2003.

Environmental experts were also seconded to participate in the UNEP mission by FAO, the United Nations Development Programme (UNDP), and the United Nations Economic Commission for Europe (UN-ECE). UNEP also had close co-operation with the United Nations Educational, Scientific and Cultural Organization (UNESCO), which carried out a special water mission to Afghanistan with one expert from UNEP. The United Nations Office for Project Services (UNOPS) provided operational support for the field missions, including contracts, transport and communications equipment, while the United Nations Assistance Mission to Afghanistan (UNAMA) provided overall support and security. Good co-operation was achieved with the United Nations Office for the Co-ordination of Humanitarian Affairs (OCHA), including the Joint UNEP-OCHA Environmental Unit. Invaluable technical assistance was provided throughout the assessment by UNOSAT, the Afghanistan Information Management Service (AIMS), and the UNEP World Conservation Monitoring Centre and by the UNEP Global Resource Information Database (GRID-Geneva).

DETERMINATION OF TOLUENE AND XYLENE IN WHOLE BLOOD OF RESIDENTS NEAR A PETROCHEMICAL PLANT

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Organic solvents such as toluene and xylene are distributed in the environment because of their wide industrial use in production of plastics, paints, glues and also as intermediate in the production of other chemical substances(1). These solvents can be emitted into the environment by the petrochemical plants. Due to the toxicity and the adverse health effects of toluene and xylene, the determination of these compounds in air has been the subject of many researches (2), but less is known about the concentrations of these compounds in human body. In this work, the blood levels of toluene and xylene in the residents near a petrochemical plant was investigated. Blood samples were collected from the residents who had no special exposure to toluene or xylene. Toluene and xylene were separated from blood samples by purge and trap method. The liberated toluene and xylene were collected on the tenax and analyzed by head space gas chromatography. Table 1 summarizes some of the results obtained from this investigation.

Table 1:

Concentrations of toluene and xylene in the blood of the residents of the city of Isfahan as ($\mu\text{g/l}$)

Sample	Toluene	Xylene	Sample	Toluene	Xylene
1	0.34	0.37	3	0.62	0.47
2	0.31	0.32	4	0.58	0.48

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THE USE OF BIOINDICATION FOR THE EVALUATION OF THE ENVIRONMENT

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The systematic monitoring of negative changes in the ecosystems requires suitable plant and animal species whose reaction to the presence and/or the effects of pollutants occurring in the environment will be similar to that of crop plants and domestic animals. Bioindicators are known to contain substantially higher levels of some pollutants, as compared to air, water, and soil. It is assumed that the biological effects of toxic substances occurring at the level of the ecosystem precede chemical reactions in individual organisms. It can also be assumed that the concentrations of pollutants, which initiate chemical reactions, are lower than those that would induce a life-threatening event in the target organism or measurable degradation in the ecosystem. The indicator should have the ability of "timely warning", i.e. its biochemical response should predict the effects produced at higher levels of the biological system and should prevent them, it should be specific for a particular pollutant or a group of pollutants, it should provide the concentration-dependent response for a particular pollutant, with regard to the typical level of such a pollutant.

Plant bioindicators are used in the Czech Republic in environmental studies of agrarian ecosystems where they can yield information for both conventional monitoring and biomonitoring. The most frequently used plant species are alfalfa, cereals, and oil plants. The level of contamination in plants is strongly linked with soil contamination, which is predominantly caused by dry and wet atmospheric deposition. However, findings indicating the presence of increased levels of PCBs are predominantly of a local character, being associated with a particular source of pollution. In the past, the fertilization of soil using PCB-containing sludge from wastewater treatment plants and various industrial accidents were major and frequent sources of soil contamination. Most studies investigating the possibilities of the transfer of PCBs from soil into plants have arrived at the same conclusion that the transfer of hydrophobic pollutants from soil is poor, probably due to their low stability.

Bioindicators of animal origin are an effective tool for the monitoring of environmental contamination of agrarian ecosystems, which are known to contain considerably higher concentrations of some organic pollutants than other matrices, such as air, water or soil. Small terrestrial mammals are also used in the monitoring of terrestrial ecosystems in some countries. The major objective of this study was to test the suitability of small terrestrial mammals for chemical monitoring. The best animal bioindicators are the following species: brown hare, roe deer, pheasant, common partridge, wild ducks, small rodents and fish. The examination of blood performed in some of the test organisms is very useful particularly for the determination of stress imposed on an organism.

Indicator PCB congeners were monitored in the matrices of selected bioindicators of animal origin that occurred in the site where Delor 106 was used during the manufacture of paints and varnishes from 1970 to 1985 and where there was a factory for the preparation of precoated gravel using a technological procedure requiring Delor 103. It was shown that game, small ground-living mammals, fish and the bodies of dead bees can be employed as sensitive indicators of the pollution in a particular ecosystem. The lowest concentrations of PCBs were found for PCB 101 and 118, while the highest concentrations of PCBs were detected for PCB 138 in all of the materials mentioned above.

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2. GREEN CHEMISTRY

POSTERS No. 11 – 16

ROOM TEMPERATURE IONIC LIQUIDS: HOW “GREEN IS GREEN”? – A REVIEW

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Ionic liquids are highly solvating non-coordinating medium in which a variety of organic, inorganic and polymeric compounds are able to dissolve. They are outstanding good solvents for a variety of compounds and their lack of a measurable vapor pressure, good thermal stability, high ionic conductivity, wide range of liquidus temperature, low melting point and a large electrochemical window make them a desirable substitute for volatile organic compounds (VOCs). As this solvent is employed more and more as a substitute for the traditional organic solvents in chemical reactions, only little data are available with regard to their toxicity and ecotoxicity. This, in addition to many other factors have contributed to the snail rate commercialization and large scale utilization of ILs. This review therefore tends to x-ray the many applications and potential benefits of ILs, the environmental, safety and health issues involved in their large scale usage and some of the factors that cast some doubts about the ‘greenness’ of these solvents.

Keywords: Ionic liquids, applications, environmental, safety and health issues, green chemistry, barriers to commercialization

THE ANTIOXIDANT EFFECT OF LIGNITE HUMIC ACIDS AND THEIR SALTS ON THE THERMO-OXIDATIVE STABILITY OF WATER SOLUBLE POLYMERS

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Thermal and oxidation stability of polymer materials is an important physico-chemical property which can restrict or enlarge the application areas of products. The material behavior may be profoundly modified by the addition of compounds acting as antioxidants. Various classes of stabilizers (hindered phenols, hindered amines, triazines, organic sulphites, organic phosphites, elementary selenium, etc.) have been reported.^{1,2} They assure longer preservation of the initial structure by acting as oxygen scavengers. Depending on the degradation process(es), one or more stabilizers may be used to minimize degradation. In formulating stabilizer systems, proper dosage is important, as over-dosage can be detrimental.

Humic substances are natural products of microbial degradation of dead plant tissues and animal bodies. Lignin-derived compounds, i.e (poly)phenols, are considered to be one of main constituents of humic acids' chemical structure and they are supposed to be responsible for their antioxidant effect. The potential of humic substances as antioxidants has already been demonstrated for PVC, however, the experimental arrangement is disputable since humic substances were not incorporated directly within the polymer structure.³ Nevertheless, in the case of positive influence of humic acids on the polymer system stability, they can represent nature-friendly agent with reasonable price and potential especially in environmental and agricultural applications.

The aim of this work is the investigation of the potentiality of lignite-extracted humic acids as antioxidants in polymeric matrix.

Humic acids and their Na^+ , NH_4^+ salts were tested at different concentrations for their stabilization effect on poly(vinylalcohol) (PVA). For the stability evaluation simultaneous differential thermal analysis and thermogravimetry techniques have been used. As a measure of stability the onset of degradation and weight loss up to 50% of the original weight have been evaluated.

All measured samples showed at least a slight effect on the stability of polymer under study. Humic acids showed a positive effect on the thermo-oxidative stability of PVA. On the other hand the presence of humic acids supported the faster degradation and resulted in lower char weight. The same results, but with lower efficiency on PVA stability showed records after the addition of NH_4^+ and Na^+ salts. Moreover, higher concentrations of Na^+ salts (5-10%) showed even the prooxidation effect causing destabilization of investigated polymer.

Further, the optimal concentration of HA and its salts to maximally increase the thermo-oxidative stability of PVA have been found around 2%.

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FERTILIZERS WITH GRADUAL EFFECT COATED BY CELLULOSE ETHERS

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Our research is specialized in a monitoring and testing the influence of coating substances cellulose-based on physico-chemical properties of an industrial fertilizers. We evaluate especially the solution rate and strength and therefore shelf life fertilizers with such surface treatment. We used a type of fertilizer NPK as a base. This mass was put into a laboratory disc-type granulator after the size modification, where was distributed coating dilution by glass jet. There was used these kinds: AC – acetylcellulose, EC – ethylcellulose, CMC – carboxymethylcellulose and its sodium salts, OC – oxycellulose, HPMC – hydroxypropylmethylcellulose, MHEC – methylhydroxyethylcellulose. After the application of water solutions, samples slowly ran dry than of organic solutions. Solution rate comparison of particular samples and comparison with uncoated fertilizer is stated on fig. 1 and the strength comparison on fig. 2.

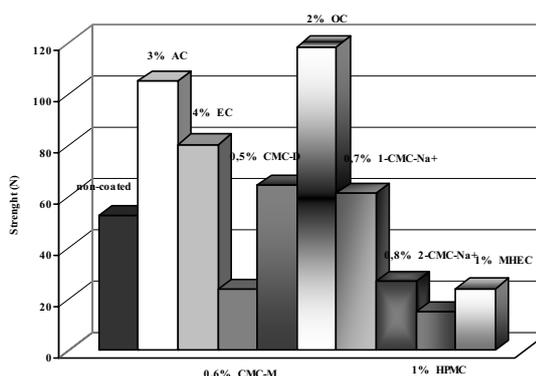
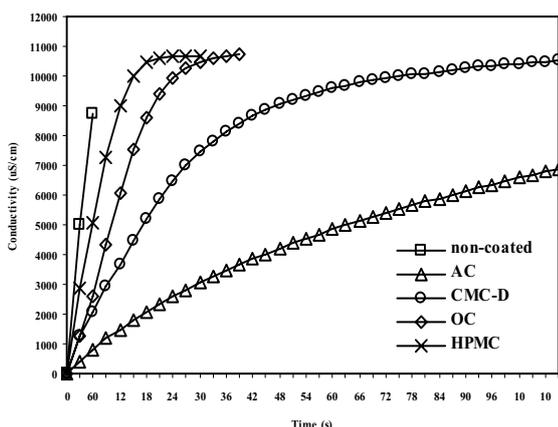


Fig. 1: Solution rate comparison of the samples Fig. 2: Strength comparison of the samples

Analytes with surface treatment shows higher strength and slower dissolving than uncoated pellets. We reached higher strength in conjunction with slowing down of loosening nutrients with growing percentage by weight of coating substance.

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SCREENING OF FUNGAL SPECIES FOR HYDROLYTIC ENZYMES INVOLVED IN STRAW DEGRADATION

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The wastes of animal and plant nature represent an important source of raw materials for biotechnology. The main part of phytomass is composed of saccharides (cellulose, hemicellulose, starch, pectins) lipids, proteins, nucleic acids, lignin etc. One of the most decisive factors, influencing the protection of environment, are microorganisms, because they also play an important role in human life. The community of different microorganisms is able to decompose all natural organic substances.

Within experimental work the degradation of cellulose substrates using fungi under different cultivation conditions was investigated. As a substrate the desintegrated wheat straw with particles 0,3 – 0,5 mm, modified wheat straw, CMC and colored wheat straw with adsorbed green dye was chosen. As microorganisms *Aspergillus niger* F 8189, *Botrytis cinerea* F 314, *Cladosporium herbarum* F 445, *Fusarium avenaceum* F 503, *Mucor plumbeus* F 443, *Rhizopus stolonifer* F 445 were tested.

By cultivation *A. niger* the cellulase activity by all tested substrates was detected. The highest value was achieved on CMC in noncarboneous medium. Other high activities of cellulase were detected by cultivation *M.plumbeus* on glucose medium with wheat straw. It was also found out that by degradation of wheat straw irreversible sorption of cellulase on its surface occurs.

Acknowledgements

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THE PRODUCTION OF ENZYMES ON VARIOUS AGRICULTURAL WASTES

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Plant cell wall consists of biopolymers, such as cellulose, hemicellulose, lignin and pectin. These biopolymers are degraded by many microorganisms, and particularly by filamentous fungi, with the support of extracellular enzymes. Currently the production of enzymes on various agricultural wastes, such as straw has been investigated. The microbial enzymes belong between the most important products obtained for human need. Number of enzymes found its use in various branches of industry, environment and food technology.

Within this work the influence of cultivation conditions on production of hydrolytic enzymes onto modifying straw by cultivation of *Aspergillus niger* was studied. Wheat straw particles with size about 0,3-0,5 mm were selected as the substrate. As the method of cultivation the solid state fermentation was chosen and realized in differently shaped and sized cultivation vessels. During the cultivation test, the tubes with diameter 1,5 cm and Petri dishes with diameter 9 cm were used. For the purpose of this study especially manufactured glass column with diameter of 4 cm was also employed. The cultivations were performed at laboratory temperature (22 °C) and in thermostat at temperature 29 °C. The enzyme degradation of cellulose and pectin was monitored. Consequently, the change of both proteins and reducing sugar concentrations was followed.

COATED FERTILIZERS REDUCING SOIL CONTAMINATION

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The nutrients of fertilizer that are not consumed by the cultivated plants can be metabolised by soil microorganisms. This process is slow and cannot prevent the washing out of easily soluble nutrients to deeper soil horizons. Coated fertilizers by oil matrices or water repellents were used to save fertilizer consumption and minimize environmental pollution.

Studies on the possibility of using plant oil-based materials (linseed and rapeseed oil) and industrial water repellents (SK fert F20A, linseed oil varnish) as a coating for NPK granular fertilizers were performed.

Two types of different granulated fertilizers were used for experiments – mixed fertilizer NPK-Mg (8-10-12-2) and comprix fertilizer NPK (15-15-15).

The mentioned coating materials were sprayed by means of a glass laboratory sprayer on granules of fertilizer in a laboratory plate granulator. Influence of the structure and weight of the coating on the speed of nutrient release from the fertilizer (Fig.1) and strength and caking of granules were studied after drying of the product.

The application of these materials leads to slower dissolution of the nutrients from the granules of the fertilizer, to improvement of its strength and also to the caking elimination.

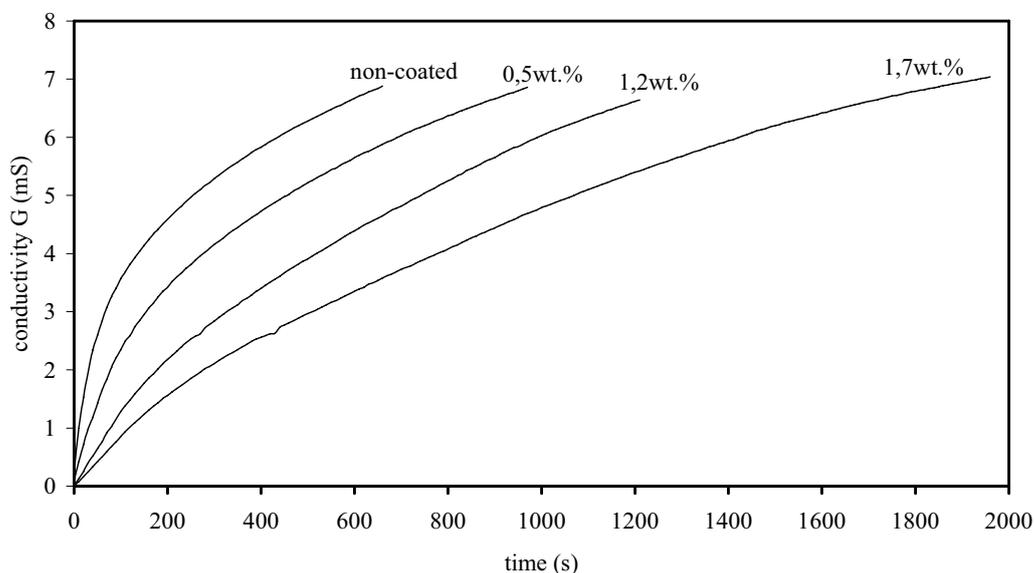


Figure 1: Effect of different thickness of coating on the release rate of the fertilizer NPK-Mg (8-10-12-2) coated by industrial water repellents SK fert F20A

This work was supported by the project MSM 0021627501 of the Ministry of Education, Youth and Sports of the Czech Republic and by the project FT-TA/037 of the Ministry of Industry and Trade of the Czech Republic.

3. SOIL CONTAMINATION, DEPOLLUTION TECHNOLOGIES, MODELLING

POSTERS No. 17 – 33

CATALYTIC EFFICIENCY OF BIRNESSITE ON PCP REMOVAL BY GRINDING A CONTAMINATED SOIL

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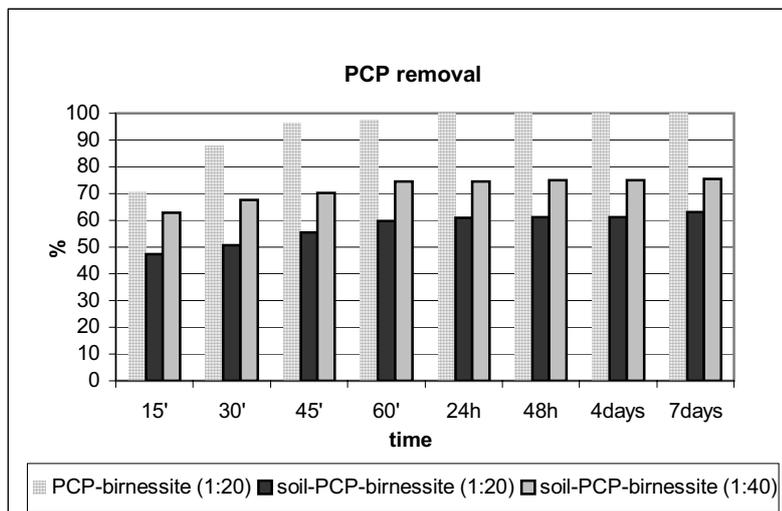
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Mechanochemical treatments conducted by grinding polluted dry solid material in mills at high energy have attracted attention on the use of this method for the degradation of organic pollutants. The aim of this work was to evaluate the catalytic efficiency of different amounts of birnessite in degrading pentachlorophenol (PCP) in the presence and in the absence of soil using a planetary ball mill.

According to this scope, different experimental setups were adapted: 1) milling of PCP and birnessite in 1:20 ratio (binary system); 2) milling of PCP, birnessite and soil (ternary system), using a constant concentration of PCP and varying the amount of birnessite (xenobiotic-oxide ratio of 1:20 and 1:40). The mechanochemical reactor was a planetary ball mill with two zirconium pots (45 cm³) in which fourteen zirconium balls (10 mm diameter) were arranged. The pots were situated on a rotating disk, which enabled the pots and the disk to rotate in opposite directions. The planetary ball mill was operated applying a high rotation speed (700 rpm) for different milling times (15-min periods with a 15-min cooling step after each period). Afterwards, grinded mixtures were incubated at 30°C in capped porcelain cups for periods ranging from 24h to 7 days. After each time of milling and after each incubation period, aqueous and organic extracts from grinded mixtures were analyzed by HPLC-DAD, HPLC-IC and DPSAV to determine residual PCP, Cl⁻ and Mn²⁺ ions, respectively.

In the binary system, results showed that the whole amount of PCP was already removed at the end of the mechanochemical treatment. In the ternary system, it was observed that the higher the amount of birnessite added, the higher the PCP removal.



The release of Cl⁻ and Mn²⁺ ions, observed in all interactions, suggests a redox reaction mechanism involved in PCP degradation. The amount of PCP removed, as well as the amount of Cl⁻ and Mn²⁺ ions released in ternary interactions, were lower than in the binary ones. This observation could be due to the dilution effect of soil, which prevented the direct contact between PCP and oxide, as realized in binary system.

These results show that the grinding treatment could be an effective technology for the removal of organic xenobiotics in soils.

RISK OF COPPER ACCUMALATION IN SOILS AFTER REPEATED SEWAGE SLUDGE APPLICATION

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Sewage sludge use in agriculture represents a risk of soil contamination with heavy metals. The aim of the study was to assess the risk of copper accumulation in soils after repeated application of sewage sludge on arable land. Precise field experiments conducted since 1996 at four sites with different soil and climate characteristics were used for the investigation. Potatoes, winter wheat and spring barley have been growing in a crop rotation and anaerobically digested sewage sludge was applied once in a three year period (before potatoes plantation) at two different application rates (single ~ 8 t DM.ha⁻¹ and triple ~ 23 t DM.ha⁻¹ depending on sludge nitrogen content). Results from years 1996-2005 (three completed crop rotation cycles) are presented here. Three applications of sludge during this period resulted in following total addition of copper to soil: single application rate added 5851 g Cu.ha⁻¹ and triple rate added 17 556 g Cu.ha⁻¹. Copper content in soil increased by 3-16 % depending on the locality and sludge rate. From the total amount of sludge borne copper, only small portion was removed by harvests of crops. The uptake and removal of heavy metals by crops differed depending on soil properties. The highest total removal was obtained on soil with the lowest pH (cambisol Humpolec) and reached 5.41 % of Cu added by single application rate and 1.95 % of Cu added by triple rate (Tab. 1). From the three crops planted, the highest removal was found in potatoes followed by wheat and barley. These results showed that the risk of copper accumulation in soils is high, especially when high application rates of sludge are used.

Tab. 1: Copper input-output relationship at control a sewage sludge treatments (1996-2005)

Treatment	Total Cu addition to soil (g.ha ⁻¹)	Total Cu removal by harvests of crops							
		Luvisol Hněvčeves		Cambisol Humpolec		Cambisol Lukavec		Chernozem Suchdol	
		g.ha ⁻¹	%	g.ha ⁻¹	%	g.ha ⁻¹	%	g.ha ⁻¹	%
control	—	158,07	—	242,21	—	140,57	—	201,90	—
sludge 1	5851,40	248,52	4,25	316,39	5,41	208,90	3,57	230,65	3,94
sludge 3	17555,55	272,97	1,55	342,56	1,95	263,23	1,50	235,19	1,34

This work was supported by FRVŠ 2351/2006/G4 and NAZV QF 4063 projects.

THE UTILIZATION OF INTERCALATION PROCESS AS SUITABLE MODELLING METHOD FOR THE STUDY OF INTERACTION METALS - SOILS

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The intercalation process is very suitable method for the study of metals distributing in soils. The expandable layer silicates such as smectites can be use for the study of interactions soil – metal ions, the organic compounds, complexes etc. Montmorillonite can adsorb heavy metals via two different mechanisms: (1) cation exchange in the interlayers resulting from the interactions between ions and negative permanent charge and (2) formation of inner-sphere complexes through Si–O and Al–O groups at the clay particle edges. Both mechanisms dependent pH because in acid conditions (pH < 4) most silanol and aluminol groups are protonated; therefore, in particular for the latter, an acidification can lead to an increase in mobility of metals bound to soil. This contribution is focused on the intercalation of montmorillonites by hazardous metals Pb, Cd, Sn, Al. The intercalation of montmorillonites by Pb and Cd is type of simple cation exchange and the determined exchanged amounts of Pb²⁺, Cd²⁺ were in the range 0.8 – 1.2 mmol/g MMT, according to the type of montmorillonites. In the case of intercalation of montmorillonite by Sn and Al, the strong influence of pH (measured in range 0,8 -2,5 for Sn and 1,5 -4,1 for Al), due to formation various types of ion and complexes, was confirmed by the determined amounts of metal cations and interlayer cations for intercalation process. The finding of useful sample preparation and separation method was also prerequisite for the successfully intercalation process and determined of metals cations and interlayer cations too. The factors (pH, concentration of Cl⁻, ion forms) were studied in this work too. The method ICP-OES and AAS were used for the determination of cations.

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POLYCYCLIC HYDROCARBON PATTERNS IN THE UPPER ODRA RIVER BASIN AS A KEY TO PROVENANCE ASSESSMENT OF FOSSIL AND RECENT SEDIMENTARY ORGANIC MATTER

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Polycyclic aromatic and saturated hydrocarbons show characteristic patterns in shallow sedimentary profiles in the Odra river basin and adjacent lakes. These are related to the variable proportions of the recent organic matter; weathered outcrops of Tertiary and Carboniferous rocks, and human induced municipal and industrial waste in the fine-grained sediments. A set of characteristic compounds has been identified to differentiate among the mentioned sources. The recent natural organic matter is poor in aromatics and enriched in unsaturated hydrocarbons. Tertiary organic matter studied in borehole core samples has a contribution of marine algae biomarkers. Carboniferous coals and siltstones from mines display several marginal marine, deltaic, and lacustrine facies types, all of them typical by high thermal maturity indicated by phenanthrene, sterane, and hopane isomer ratios. The present analyses serve as a reference for the natural background patterns, which usually interfere, at least partly, with the contaminants in a specific geological setting.

BIODEGRADED PETROGENIC SUBSTANCES IN BILLABONG SEDIMENTS AS EVIDENCED BY MOLECULAR FOSSILS

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Extractable organic matter in fine-grained sediments of a blind stream branch of the Morava River provides information on potential environmental contamination. The sediments consist of stratified mixture of mud, silt, sand, and organic matter. The total organic carbon content (TOC) ranges from 1.6 to 3.3%, the darker layers mark the seasonal peaks in bioproductivity. The analysis of total non-polar extractable matter shows patterns dominated by n-alkanes with maximum on C₂₉ and with a strong preference of the odd-numbered homologues. Such pattern is typical for deciduous plant debris and leaf waxes with no diagenetic overprint. The observed n-alkane series is associated with an unresolved compound mixture (UCM) occurring in the C₁₅₋₄₀ range. The relative proportion of the UCM in the total extractable matter increases with depth and attains maximum at 0.8 m where it indicates possible petroleum-related contamination. GC-MS analysis of the molecular fossils shows hopane, sterane, and phenanthrene patterns of a thermally mature organic matter similar to that in crude oils generated from source rocks at temperatures over 100 °C. The absence of crude oil-like n-alkanes in the rock extract is understood as a result of microbial degradation of petroleum related compounds, which removed the easier degradable volatile n-alkanes and left behind the polycyclic saturated hydrocarbons as a more resistant residue. The biomarker fingerprint suggests further details on the genetic relationship to the oils naturally occurring in deep reservoirs of the Vienna Basin and adjacent West Carpathians.

ORGANIC CONTAMINANTS IN SEDIMENTS AND SOILS FROM AN INDUSTRIAL AREA IN NORTH GREECE

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In the present study sediment samples and soils have been collected and analysed in order to give a comprehensive view on organic pollution in the coastal industrial area of Kavala city, Northern Greece. The dominant anthropogenic activities affecting this area are a) operation facilities of petrogenic hydrocarbons, b) a phosphoric fertilizer industry, c) fishery plant and d) agriculture activities in the surrounding area. Offshore the principal activities are three production treatment platforms and submarine pipelines right-of-way connecting the platforms. In 2003, 10 marine sediments from Aegean Sea were collected from a distance between 500 m and 1000 m from the coast and a depth of approximately 5 m and 10 m, correspondingly. Additionally, 20 samples (terrestrial sediments and soils) from the effected area were collected. The samples have been extracted by a sequential solvent procedure using an overhead-shaking method and fractionated by liquid chromatography on silica gel using mixtures of solvents with increasing polarity. Finally, the analytical procedure included detailed GC/MS non-target screening analyses which revealed a wide variety of substances including e.g. PAHs, hopanes and steranes, chlorinated aromatics, DDT-group substances, etc. In summary, individual organic contaminants as well as groups of well-known compounds are discussed in order to give a comprehensive view on the pollution in the area or to identify compounds appropriate for source apportionment.

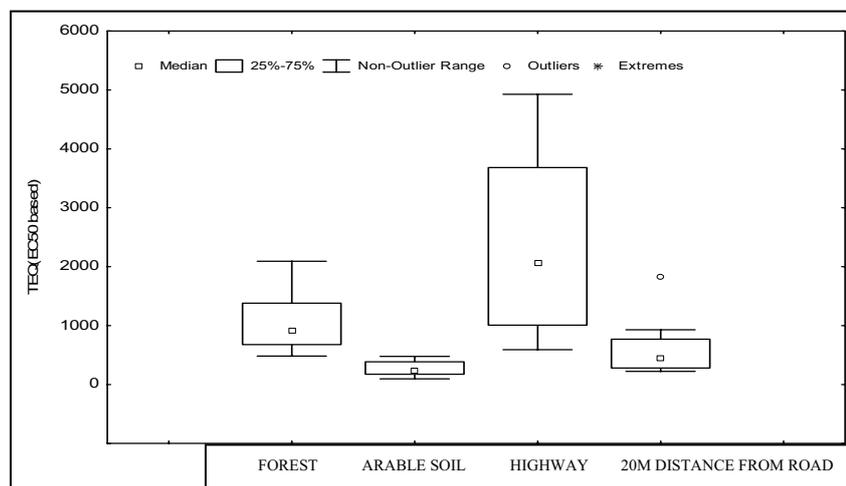
ENDOCRINE DISRUPTIVE AND DIOXIN-LIKE ACTIVITY OF THE THE TRAFFIC-CONTAMINATED SOIL OF SAMPLES

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Diffuse pollution of surface soils with traffic-produced contaminants can be a significant issue along the highways with heavy road traffic. This study investigated the potential of road traffic to produce contaminants with specific modes of action by testing soil sampled along a major highway on a battery of in vitro bioassays. Samples were collected in different distances from the highway – just next to the road and from 20m distance and reference samples were taken from arable and forest soils. Arylhydrocarbon-receptor activation (dioxin-like activity) was assessed in the H4IIE.luc-assay, using a stably transfected H4IIE hepatoma cell line containing a plasmid for the luciferase gene under transcriptional control of dioxin-responsive elements. In addition, samples were examined for hormonal activities using recombinant yeast bioassays, which stably express human androgen or estrogen-alpha receptor.

The greater dioxin-like activity corresponded to elevated PAHs concentrations in the samples taken directly next to the roadside compared to the samples from 20 m distance. The significant contribution of nonpersistent compounds such as PAHs to the observed activity was confirmed by decrease of the activities after sulphuric acid treatment. However, there were also significant activities in the treated samples, confirming the contribution of persistent fraction to activities of some samples. Significant difference was also found between dioxin-like activities of arable and forest soils in the reference area. Samples of forest soil elicited higher dioxin-like activity than arable soil. This may be caused by redistribution of pollutants during ploughing, or by higher content of organic matter in forest soils.



The yeast bioassay showed no significant estrogenic or androgenic activities in any of the collected samples. On the other hand, the assays showed antiestrogenic and antiandrogenic activities in the soil extracts with no clear gradient with distance from the highway. The results document that traffic can be an important source of compounds with specific mechanism of action. This study was supported by GACR 525/05/P160 and by the project INCHEMBIOL MSM0021622412.

Poster No. 24:

INFLUENCE OF SOIL TYPE ON ACCUMULATION AND DISTRIBUTION OF SEVEN MOST TOXIC CHLORINATED BIPHENYLS IN CARROT ROOTS

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The extreme persistence of PCB in the environment and their ability to bioconcentrate in the food chain makes them great environmental and human health risk. The aim of this study was to investigate during two vegetation seasons the accumulation and distribution of seven most toxic PCB congeners (IUPAC No. 28, 52, 101, 118, 138, 153 and 180) in carrot roots (*Daucus carota* L. var. Nantes) grown on spiked soils (same amount of each PCB congener) with different physical and chemical characteristics. Results showed that the concentrations of the sum of PCB congeners (PCB7) in edible parts of carrot were significantly higher in the first experimental year. And also differences in PCB accumulation between treatments were observed only in the first year. The highest value $1280 \pm 130 \mu\text{g PCB7.kg}^{-1}$ was found in carrot roots planted on the soil with the lowest soil organic matter content. The differences in accumulation of individual congeners were more obvious in the second year of plantation in terms of higher accumulation rate of more chlorinated biphenyls whereas the effect of soil type was not significant.

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CHEMICALLY INDUCED PHYTOEXTRACTION OF LEAD FROM SMELTER-IMPACTED AGRICULTURAL SOILS

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Chelant enhanced phytoextraction of heavy metals is an emerging technological approach for a non destructive remediation of contaminated soils. The main objectives of this study were (i) to assess the extraction efficiency of two different synthetic chelating agents (EDTA, EDDS) used for desorbing Pb from two studied multi metal contaminated agricultural soils originating from a mining and smelting district and (ii) to assess the phytoextraction ability of maize (*Zea mays*) and poplar (*Populus* sp.) after the chelant application. EDTA was more efficient in desorbing and complexing Pb from both soils compared to EDDS, removing as much as 60% of Pb from soil. The PHREEQC-2 speciation modelling showed that the majority of lead is present as (Pb-EDTA)₂-complexes (99-100%) after the EDTA application. Maize exhibited better results than poplar when extracting Pb from the more acidic (pH ~ 3-4) and more contaminated agricultural soil originating from the smelting area. This was predominantly due to the high contents of Pb (365 ± 44 mg kg⁻¹) in maize biomass after the application of 9 mmol EDTA kg⁻¹. On the other hand, poplars proved to be more efficient when grown on the moderately contaminated agricultural soil originating from the mining area. The addition of EDTA led to a significant increase of Pb content especially in poplar leaves, proving a strong translocation rate within the poplar plants.

POSSIBILITIES OF MODELLING OF METAL IONS TRANSPORT IN NATURE

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Humic acids (HA) play important role in soil and natural water chemistry. They can form stable complexes with heavy metals which influences their toxicity in environment. This contribution is aimed at modeling of metal ion transport and their immobilization. Use of HA in gel state makes possible to prepare it in defined size and shape, which is necessary for mathematical modelling of observed processes¹⁻³. Copper was used as a model metal for experiments due to high affinity to HA and stability of formed complexes.

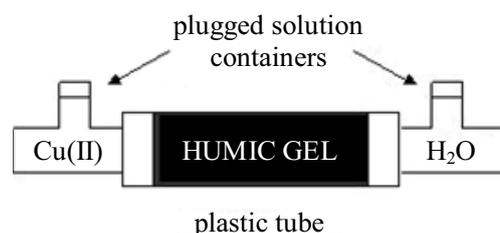


Fig. 1. Scheme of the apparatus used in diffusion experiments

Diffusion experiment was divided into two parts. In the first one diffusion coefficient of copper(II) ions in humic gel was determined by the stationary diffusion from saturated copper(II) chloride solution. Obtained value ($7.96 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$) has to be considered as „effective“ one, including also immobilization of copper(II) ions in HA structure. Experimental procedure and computing are described in previous works¹⁻³. Non-stationary diffusion was studied in second part. Humic gel was packed into plastic tube and copper ions solution and deionized water were filled into side containers (see Fig. 1). Diffusion flux as well as concentration profiles in gel were also measured by the same methods as in previous works¹⁻³. This part deals with the influence of time duration, pH, ionic strength and initial concentration of copper(II) ions in solution.

It was found that for the same duration of diffusion ε -value (ratio of ion concentration in the gel and in the solution in final equilibrium) is constant for different initial concentrations of the solution but it varies for different duration of experiment. This fact could be explained by the time-consuming formation of stable structural or chemical complexes between gel and ions. This affects the mobility of ions (retention of ions can lead up to their immobilization in gel) and their equilibrium in gel and solution. The knowledge of ε -value allows the calculation of theoretical concentration profiles of copper (II) ions in humic gel for individual experiment conditions. Very good agreement between computed and measured concentration profiles was obtained. Total diffusion flux increased not only with higher initial concentration of copper(II) ions or time duration but also with increasing pH-value. On the other hand it showed complex dependency on the ionic strength. For small NaCl additions, total flux decreased with the increase of ionic strength, on the contrary substantial increase appeared in higher NaCl concentration range. No copper(II) ions were determined in water, which confirmed high capacity of humic gel for metal ions immobilization.

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EFFECT OF PHYSICO-CHEMICAL CHARACTERISTICS OF AGRICULTURAL SOILS ON FUNGAL BIOMASS. IMPACT OF COPPER POLLUTION

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The agricultural management of soils has a great impact upon the functional process of soil microbial communities, particularly on fungal biomass. So, fungal biomass could be used as a biomarker to assess soil fertility and evaluate impact of environmental pollution.

This work consists in the determination of fungal biomass by several approaches: (1) genetic using real time PCR (18S rDNA) (2) chemicals, by extraction and quantification of total ergosterol, free ergosterol and specific PLFAs (C18:2 ω 6,9, C16:1 ω 5). Those results are compared to physicochemical characteristics of soils (microbial carbon, cation exchange capacity, carbon content, phosphorus, total nitrogen, pH, apparent density, moisture and granulometric data). Two experimental sites located in Normandy with contrasted agricultural practices (grassland, intensive management crop) have been chosen (i) to evaluate the consistence of the selected parameters (ii) to establish the relationships between physicochemical characteristics and fungal biomass. Four samplings (April, June, August, October) have been realised in order to observe seasonal impact on the measured parameters.

The results show significant rank correlations between total ergosterol (Legras 2004) and free ergosterol (Gong 2001), however free ergosterol is 30% of total ergosterol in intensive management and 50% in grassland. Both extraction methods give access to two types of fungal biomass (degraded or total biomass). The mean values of fungal biomass are higher in meadows than in crops and their spatial variations are less in crops than in meadows. As for the ergosterol contents, the mean values of the physico-chemical characteristics behave in the same way (higher contents in meadows, variations are less in crops)

Relationships between physicochemical characteristics and fungal biomass show that pH, carbon content and clay content are discriminant variables. But there is no direct correlation between the physicochemical characteristics of the soil and the fungal biomass (at the plot scale). Moreover, by taking into account all the data of the study, there is a good relation between the apparent density and the total ergosterol content ($r=0,88$). A multiparametric modeling is necessary to reach a better understanding of the effect of the various variables.

Moreover, whatever the approach (18S rDNA, ergosterol, PLFA), very significant correlations were found (Legras 2006) indicating that molecular and chemical protocols are efficient to access fungal biomass (Linear correlation: Free ergosterol vs 18S rDNA: 0.72 - Non-Linear Correlation (Spearman test): Total ergosterol vs 18S rDNA: 0.69).

Experiments of inoculation of various copper concentrations in 90 soil core microcosms do not show any significant effect on the fungic biomass.

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DIVERSITY OF ORGANIC SUBSTANCE MATURATION STAGE IN RECENT ALLUVIAL SEDIMENTS: THE CLUSTER ANALYSIS AS A TOOL

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The research area, the Makiš plain near Belgrade, is a part of the Sava river alluvion of Quaternary age. Makiš alluvion has a rather complex lithologic structure, showing frequent changes of lithologic members (sandy, silty and clay sediments) with depth. Sandy and clay sediments have many differing physical and chemical characteristics, and consequently represent widely different environments in a geo- and eco-chemical sense.

The aim was to investigate the differences of hydrocarbon maturation stage in clay and sandy sediments in which pollutants may have differing fates.

By cluster analysis, the objects are grouped in such manner that similar objects fall into the same class and closer to each other. The Statistical Package for Social Sciences (SPSS, Ward's clustering procedure with the squared Euclidean distance measure) has been used to carry out this analysis. Cluster analysis was applied on 9 sand and 9 clay samples of sediments for 6 steranes and terpanes maturation parameters: 1) Moretan/Hopane; 2) C_{31} 22S/(22S+22R); 3) Ts/(Ts+Tm); 4) C_{27} Diasterane/(Diasterane+Sterane); 5) C_{29} 20S/(20S+20R); 6) C_{29} $\beta\beta/(\beta\beta+\alpha\alpha)$. The results indicate that there are significant differences between the maturation of alkanes in clays and sandy sediments. The possibility of hydrocarbon pollution is discussed.

RARE EARTH ELEMENTS SPECIATION IN THE BACKGROUND FOREST SOILS OF CENTER OF EUROPEAN RUSSIA

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Rare earth elements speciation in the profiles of background podsoluvisol and histosol was studied by sequential extraction procedure of Tessier et al. (1979) using ICP-MS. The investigated soils are located on the territory of Prioksko-Terrasny biosphere reserve, South of Moscow region. In the studied soil's types the greater part of lanthanides is accumulated in the structure of primary and clay minerals of residual fraction. The highest concentrations of elements fractions in the podsoluvisol are in the bedded loamy moraine. In top layers of the soil concentrations of metals in mobile fractions are increased relatively due to low pH and soluble organic matter. Light and heavy lanthanides are characterized low mobility; elements with middle atomic mass have more high mobility. The fractional composition of metals in the different horizons is contrasted. Organic matter plays important role in the accumulation of elements in the upper horizons, oxides/hydroxides Fe and Mn – in the lower (illuvial and parent rocks) horizons. There are two maximums of concentrations of all fractions in the histosol – in the top peat horizon and in the bedded rocks. Concentrations of mobile fractions of rare earth elements in the peat horizons are decreased. In spite of absence of Fe/Mn minerals in the horizons there is high amount of elements in the fractions of oxides/hydroxides Fe and Mn. The similar profile distribution of all forms of lanthanides is testifies about equilibrium between forms of element in non polluted natural soils. The study was supported by Grant of President of Russian Federation.

CADMIUM AND ZINC UPTAKE BY ACCUMULATING PLANTS OF BRASSICACEAE FAMILY

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Phytoremediation uses higher plants to clean polluted environment. In our study previously discovered accumulating plants – three *Thlaspi* species (*Thlaspi caerulescens* J. et C. Presl, *Thlaspi goesingense* L., *Thlaspi rotundifolium* (L.) Gaudin) and *Arabidopsis halleri* L. were tested in the pot experiment on two soils of different soil type and level of contamination by toxic elements. The first soil Příbram (Cambisol, pH_{H₂O} 6.5, loamy soil) was taken from the field polluted by emissions from mining and smelting industry of lead. The concentration of Cd is 5 and Zn 266 mg kg⁻¹. Second soil Litavka (Fluvisol, pH_{H₂O} 5.7, sandy soil) was taken from the same polluted area near the polluted river. The concentration of Cd is 27 and Zn 3440 mg.kg⁻¹.

The concentration of cadmium and zinc was measured in the dry plant biomass using AAS and OES. On the Příbram soil *Thlaspi caerulescens* accumulated up to 286 mg Cd kg⁻¹, it is the highest concentration from three tested *Thlaspi* species. *Arabidopsis* accumulated lower levels of cadmium but up to 5000 mg Zn kg⁻¹. On the Litavka soil *Thlaspi caerulescens* contained 400 mg Cd kg⁻¹. The concentration of zinc in *Arabidopsis* reached also up to 5000 mg kg⁻¹. *Thlaspi goesingense* and *Thlaspi rotundifolium* accumulated low concentrations of Cd and Zn on both soils. *Thlaspi caerulescens* met the requirements of hyperaccumulating plants when planted on both tested soils.

Key words: cadmium, zinc, phytoextraction, pot experiment, *Thlaspi caerulescens* J. et C. Presl, *Thlaspi goesingense* L., *Thlaspi rotundifolium* (L.) Gaudin, *Arabidopsis halleri* L.

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THE APPLICATION OF R-MODE FACTOR ANALYSIS IN GEOCHEMICAL AND ECOCHEMICAL STUDY VALJEVO-MIONICA SEDIMENT BASIN (SERBIA)

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Bulk and specific organic geochemical parameters and content of major, minor and trace elements were examined in core lacustrine sediments, collected from the central part of the Valjevo-Mionica basin, western Serbia (neogene complex, 1000 m depth). Investigated samples were taken from 400 m depth.

R-mode Factor analysis was applied on obtained geochemical data. The purpose of this statistical analysis was determination of significant relationship between these geochemical parameters and reduction of data by extraction in small number of latent factors.

Four factors with 86.13% of total variance were defined. Factor 1 (30.59% of total variance) expressed content of SiO₂, Al₂O₃, Fe₂O₃, TiO₂, CaO, Sr and LOI (Loss Of Ignition) association, representing mineralogical composition of sediments, and showing that Sr is in form of carbonates. Factor 2 (27.48% of total variance) showed important relationship between organic matters content with Na₂O and boron. Common contamination source for organic matter and boron was discarded after biomarker analysis, which has shown that organic matter was immature. Also, enhanced concentrations of boron were noticed at about 200m depths in spite the fact that the boron is not so much mobile element. Factor 3 (18.13% of total variance) has contained only maturation parameters. Finally, factor 4 (9.93% of total variance) expressed the association between MgO, Li and K₂O indicating their lithological origin.

OXIDATIVE DEGRADATION OF DINITROPHENOLS BY FENTON REAGENT: EFFECT OF INORGANIC SALTS

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Phenol nitroderivatives are widely used as multi-purpose pesticides though they are toxic towards haematothermal animals. Detoxification of nitrophenols is of an importance; oxidation is considered as one of the most effective detoxification procedures. Although conventional oxidative agents are quite active, advanced oxidative processes with environmentally benign reagents are still being sought. Fenton reagent (hydrogen peroxide in the presence of ferrous ions) attracts much attention because of high redox potential and relative harmlessness. Numerous studies demonstrate advantages of Fenton reagent. However only few publications are devoted to Fenton oxidation in the presence of inorganic salts and the publications mainly describe low salt concentrations. Meanwhile wastewater is typically concentrated solution.

In the present study oxidation of 2,4- and 2,6-dinitrophenols by Fenton reagent was investigated in solutions containing 0,1 – 1 M salts: nitrates, sulfates, chlorides. Cation was also varied, sodium, ammonium and cesium salts were used. Chloride was the only ion to affect significantly rate and result of dinitrophenol destruction. Solution of 1 M sodium chloride is able to inhibit totally oxidation of dinitrophenols (fig.1). This is not the case for sulfate and nitrate. The fact can not be accounted for only complexation of iron ions. Possibility of concurrent chloride oxidation by Fenton reagent is discussed.

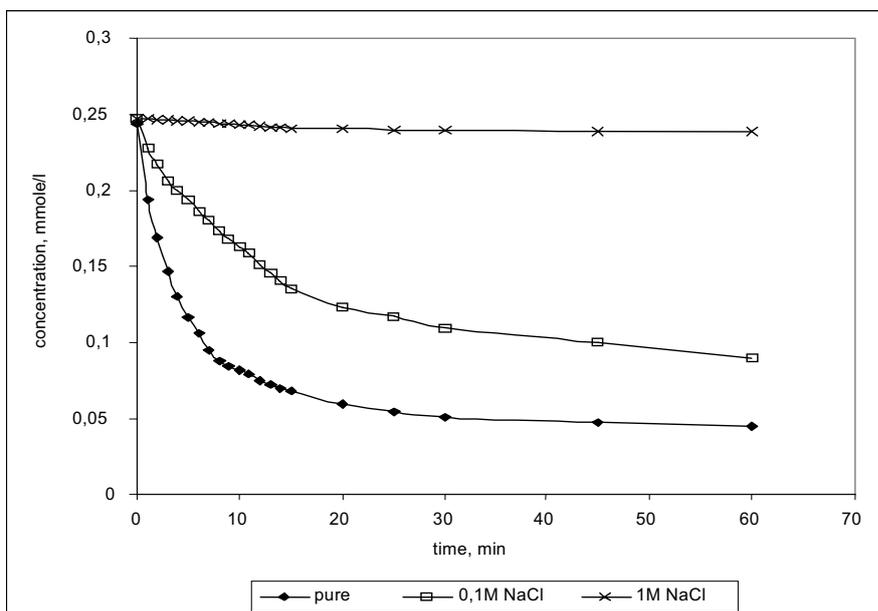


Fig.1. Effect of chloride ion at 2,6-dinitrophenol oxidation by Fenton reagent

Influence of Wheat Ash on the MCPA Immobilization in Agricultural Soils

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Anionic herbicides such as MCPA, widely used in agricultural practice, may pose threat to groundwater quality due to possible leaching. Their mobility in soil profile depends to great extent on their sorption-desorption behaviour. Previous studies have shown that soil organic carbon content is one of the main factors influencing the ability of soils to immobilize potential organic pollutants such as herbicides. Burning crop residues in the fields is a routine post-harvest practice and results in a direct accumulation of ashes in soils. Recent studies have shown that the ashes representing a specific form of organic matter may significantly contribute to the herbicide sorption in soils. This study was conducted to evaluate the potential role of ashes in immobilization of anionic herbicide MCPA in soils. Batch equilibration method was used to determine sorption-desorption behaviour of MCPA in two soil samples (Fluvi-Gleyic Phaeozem - soil I, and Eutric Regosol - soil II), using pure soils, pure ash and ash-amended soils. Sorption of MCPA by the pure soils displayed nonlinear isotherms. The sorption of MCPA by the soil I appeared to be slightly higher than by the soil II, which can be attributed to the higher organic carbon content of the former soil. Generally, MCPA sorption by the two soils was low, indicating that MCPA is a potentially mobile herbicide in soils. The results showed that ash arising from the burning of wheat residue is highly effective sorbent for dissociable herbicide MCPA. Sorption of MCPA by pure wheat ash displayed the characteristics of the Langmuir adsorption isotherm, suggesting the surface adsorption of MCPA by the ash. Wheat ash was 90-390 times and 230-1490 times more effective sorbent for MCPA than the soil I and II, respectively (Fig. 1a). Amendment of Fluvi-Gleyic Phaeozem and Eutric Regosol with 1% wheat ash caused a 8-fold and 16-fold increase in MCPA sorption, respectively (Fig. 1a). Assuming that the presence of wheat ash in soils did not change their sorption characteristics for MCPA, simple calculations show that 1% wheat ash contributed to the sorption in ash-amended soil I and II by 85% and 91%, respectively. The soils, which formed 99% of the sorbent mass, sorbed only 9-15% of MCPA. Desorption of MCPA was also influenced by the presence of wheat ash in soils. The desorption results showed that 23-55% of sorbed MCPA were resistant to desorption in both soil samples (Fig. 1b). However, the addition of wheat ash to both soils increased the resistant fraction to 80%, which was the same as that in wheat ash alone (Fig. 1b). The field burning of crop residues appears to increase the sorption of pesticides in agricultural soils and decrease their leaching. As the burning of crop residues is still a common practice in Slovakia, applied herbicides in agricultural soils may be significantly immobilized due to the presence of ashes, and hence it may reduce their potential to leach into groundwater.

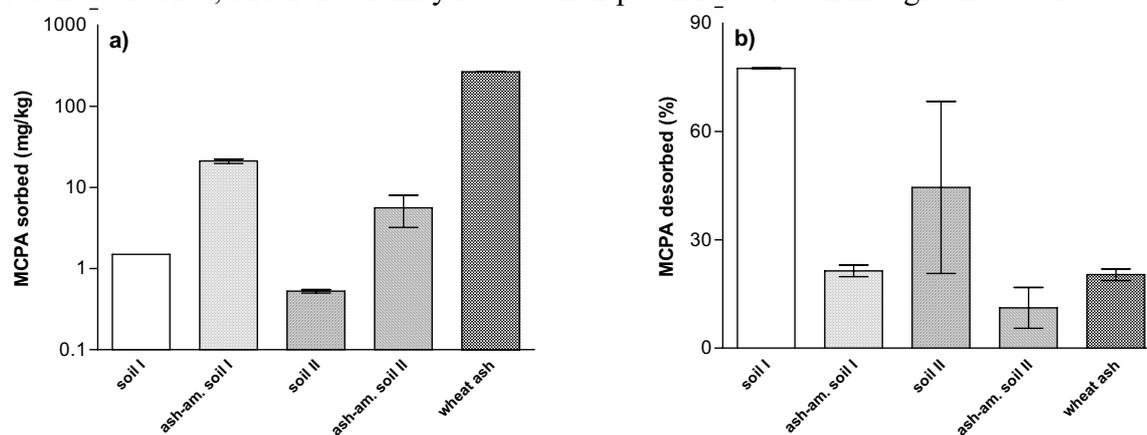


Fig. 1. a) Equilibrium sorbed amount of MCPA in pure soils, ash-amended soils (1% of ash) and pure wheat ash at MCPA initial concentration of 1.66 mg/l. b) Percentage of MCPA released from geosorbents investigated.

4. ECOTOXICOLOGY

POSTERS No. 34 – 44

AFFECTING OF SELENITE ON GROWTH OF STINGING NETTLE (*URTICA DIOICA*)

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Nettle is the common name for any of between 30-45 species of flowering plants of the genus *Urtica* in the family Urticaceae, with a cosmopolitan though mainly temperate distribution. They are mostly herbaceous perennial plants, but some are annual and few are shrubby. The most prominent member of the genus is the stinging nettle *Urtica dioica*, native to Europe, North Africa, Asia, and North America. Extracts from the nettles can be used to treat arthritis; it is also believed to be diuretic and uses treating hay fever are being investigated. The aim of this work was to describe selenium effect by one-shot and two repeated selenium additions to the soil (2.0 and 4.0 mg Se per kg of substrate) on the growth and the Se accumulation in the certain plant parts (roots, leaves, stem and apex) and possible mechanisms of Se transport in nettle (*Urtica dioica*). We used graphite furnace atomic absorption spectrometry to determine selenium accumulated in the plant tissues. Selenium amount in roots increases linearly with dose of this element. Growth of above-ground part of plant and root stagnated in connection with increasing selenium concentration. Selenium concentrations in roots of all treated plants markedly exceed its amounts in other plant tissues. Moreover, marked differences in selenium concentration were founded between older and younger leaf tissues. In the conclusion, Se treated plants could be use for preparation of new pharmaceutical drugs with higher selenium content.

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Pentachlorophenol bioavailability and ecotoxicity in *Eisenia andrei* Bouché: influences of aging and compost amendments in contaminated soils

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The threat of a contaminant in soil is related to its bioavailable fraction that, in a fairly long period of time, could potentially constitute an ecotoxicological risk. The bioavailability and toxicity of organic xenobiotics in soils are related to “aging” processes and organic matter content. Pentachlorophenol (PCP), an organochlorinated pesticide, has been listed as a priority pollutant by the environmental protection law and banned in several countries for its high toxicity and persistence.

The present research aims to assess potential and actual bioavailability, and ecotoxicity in an agricultural soil spiked with 15 and 150 ppm of PCP, amended with compost (10 and 30 t/ha) and aged up to 240 days under sterile conditions.

The potential bioavailability was measured by desorption kinetics with Porapak P resin. The amount of PCP desorbed from the soils spiked with 15 ppm, decreased after 240 days of aging (Fig. 1a). Compost added at 30 t/ha influenced the desorption since 20 days of aging (Fig. 1a). No decrease in potential bioavailability was appreciated at 150 ppm of PCP.

The actual bioavailability was detected by PCP uptake in the earthworm *Eisenia andrei*. At 15 ppm of PCP and 240 days of aging, the amount of xenobiotic detected in earthworm body decrease to 0.20 ± 0.01 ppm (Fig.1b).

The toxicity of PCP was evaluated on coelomocytes extruded from exposed worms by means of lysosomal membrane stability test (Neutral Red Retention Time); genotoxic effects by comet assay; cell viability using Trypan blue; variability in coelomocyte subpopulations using flow cytometry. Neutral red and comet assay showed a PCP dose-dependent effect on lysosomal membrane and DNA (Fig. 2a-c).

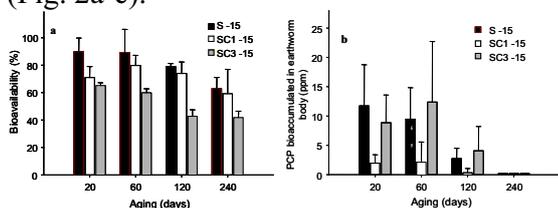


Fig. 1a, Potential bioavailability; b, Actual bioavailability. Soils spiked with 15 ppm of PCP: S-15: soil not amended; SC1-15: soil amended with 10 t/ha of compost; SC3-15: soil amended with 30 t/ha of compost.

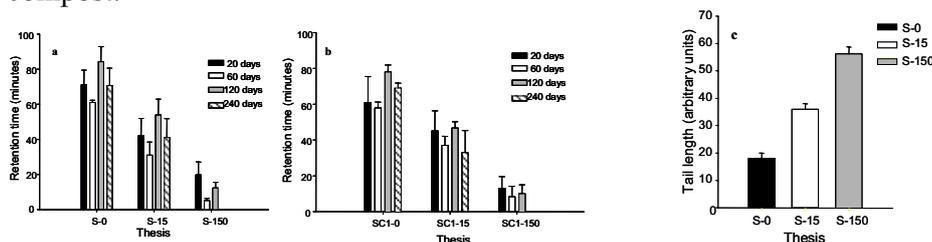


Fig. 2a: Retention time after 20, 60, 120 and 240 days of aging in not amended soils; Fig. 2b: Retention time after 20, 60, 120 and 240 days of aging in soils amended with 10 t/ha of compost; Fig. 2c: Comet tail length after exposure to soil variously treated. S-0: control soil not amended; S-15: soil not amended and contaminated with 15 ppm of PCP; S-150: soil not amended and contaminated with 150 ppm of PCP; SC1-0: control soil amended with 10 t/ha of compost; SC1-15: soil amended with 10 t/ha of compost and contaminated with 15 ppm of PCP; SC1-150: soil amended with 10 t/ha of compost and contaminated with 150 ppm of PCP.

ECOTOXICITY AND BIOAVAILABILITY OF PHENANTHRENE IN POLLUTED SOILS: COMPARISON ON *Eisenia andrei* BOUCHÉ (OLIGOCHAETA LUMBRICIDAE) AND *Galleria mellonella* (LINNAEUS) (INSECTA PYRALIDAE)

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The bioavailability evaluation of pollutants in soil has recently increased the interest of the international scientific community. Total chemical analysis of contaminants in samples collected from polluted soils are usually carried out. However, the environmental risk assessed by means of these procedures may be overestimated. The aim of present contribution is to compare the acute and the chronic ecotoxicity and the bioavailability of phenanthrene (PHE) in two different test species: an earthworm, *Eisenia andrei*, and an insect, larvae of *Galleria mellonella*. A specific organic substrate and an artificial soil (OPPTS-1996 protocol) were both contaminated with 15, 30, 60, 105, 150 ppm of PHE and aged for 20 days before animal exposure. The test species were placed in contact with contaminated substrate or soil in order to compare their responses to different doses of PHE. For both species LC₅₀ and the PHE (bio)accumulation in the animal body were assessed at the end of two exposure periods (7 and 14 days). Furthermore, the influence of the pollutant on the immunological system of these two invertebrates was studied using Trypan blue dye exclusion, NRRT (Neutral Red Retention Time) lysozyme and acrylamide electrophoresis assays.

The exposing procedures to contaminated artificial soils and the biological assays appear to be more suitable for the earthworm than the moth larvae.

Key words Index: applied zoology, bioavailability, ecotoxicity, persistent organic compounds, aging, biomarkers.

USE OF SCREENING TOXKITS AND OTHER METHODS FOR CHARACTERIZATION OF NEW SYNTHESIZED FLEXIBLE POLYURETHANE FOAMS

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New flexible biodegradable polyurethane (BIO-PU) foams, synthesized according to a usual industry formula using polyol, diisocyanate, water and catalysts, were modified with various biodegradable fillers in order to avoid environmental pollution by non-degradable polymer waste dump. The used biodegradable fillers like starch and cellulose derivatives and wheat protein (gluten) are expected to provide better biodegradability and lower ecotoxicity of the new filled flexible BIO-PU foams.

The main goal of this work was to substitute as much bio-filler as possible for non-degradable polyol polyether without significant changes in physical properties of the original (control) flexible PU foam. It was found that it is possible to substitute polyol polyether by up to 5 wt%, 10 wt%, 10 wt%, 20 wt% and 30 wt% of wheat protein (WP), acetyl cellulose (AC), 2-hydroxyethyl cellulose (HEC), acetylated starch (AS) and carboxymethyl cellulose sodium salt (CMC-Na), respectively. The prepared BIO-PU foam samples were characterized by means of Fourier Transform Infra Red Spectroscopy (FT-IR) and Thermogravimetric Analysis (TGA) methods and subsequently hydrolyzed under reflux in freshwater. The ecotoxicological aspects (IC_{50}) of the BIO-PU foam leaches were determined by microbiotest screening toolkit „Thamnotoxkit FTM“. Values of toxicity were expressed as percentage mortality of the II-III larvae instars hatched from the cysts of freshwater fairy shrimps *Thamnocephalus platyurus* dependence on the effect criterion of the respective assay. The leach of BIO-PUR foam modified with 10 wt% of CMC-Na showed the lowest toxicity among the non-diluted (100%) leaches, whereas the leach of BIO-PUR filled with 5wt% of WP indicated the highest toxicity resulting from the side reactions of gluten with other raw materials during the BIO-PU foam preparation.

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MODULATIONS OF SEX DETERMINATION AND REPRODUCTION IN DAPHNIA MAGNA EXPOSED TO ENDOCRINE DISRUPTIVE CONTAMINANTS

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Daphnia has recently being evaluated as a model for endocrine disruption. However, little is known regarding endocrine system of these invertebrates. Our hypothesis was that various endocrine disruptors could interfere with different endpoints regulated by hormones in *Daphnia magna*. We studied short term and chronic effects of four endocrine disrupting chemicals (vinclozolin, flutamide, ketoconazole and dicofol) on survival, sex determination and reproduction in *D. magna*. Our results from the short term assays have shown that Daphnia sex ratio was modulated by vinclozolin and dicofol at 1 and 0.1mg/L respectively (there were no effects on viability, maturation or fecundity). Flutamide (1 mg/L) stopped embryonic development at certain stage, resulting in abortion of incompletely developed embryos or reduction in size of the daphnids. Consequently, smaller daphnids were unable to accommodate brood as big as brood in control groups. Ketoconazole has no significant effect on endocrine processes in *D. magna* within tested concentrations. Our results support the hypothesis that sex ratio is the most sensitive endpoint and that several contaminants affect sensitive endocrine-regulated processes in *D. magna* that might lead to populational changes and significant impact on quality of ecosystem.

STUDY OF INFLUENCE QUERCETIN ON BIOCHEMICAL PARAMETERS AT SEWER RATS

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Flavonoids are a group of polyphenolic compounds widely distributed throughout the plant kingdom. More than 4,000 flavonoids discovered to date can be classified into several classes. Flavonoids have received considerable attention because of their beneficial effects as antioxidants in the prevention of human diseases such as cancer, and some pathological disorder. Several mechanisms by which flavonoids play an important role in cytotoxicity have been identified. Anti-tumour activity of several flavonoids (e.g. quercetin) is attributed to their efficiencies to inhibit topoisomerase I and II. On the other hand, certain flavonoids like some other xenobiotics can induce activity of cytochrome P450s, which are responsible for activation of several carcinogens. Quercetin (3,5,7,3',4' - pentahydroxyflavon) belongs to mostly abundant flavonoids. Facts mentioned above and increasing content of flavonoids in the environment demonstrate the necessity of taking into account study of their influence on organisms. Here, we fed sewer rats by quercetin (0, 0.1, 0.25 and 0.5 g per kg of feed) for five days. The intake of the food and amount of excrements was observed daily. Moreover, the samples of urine and excrements were collecting daily also. At the very end of the experiment, the blood was collected, whereas the sewer rats was killed and dissected. The fundamental biochemical parameters (AST, ALT, GMT), level of metallothionein and quercetin concentration were determined in blood.

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EFFECTS OF SELECTED PRIORITY PERSISTENT ORGANIC POLLUTANTS (POPS) ON SOIL ORGANISMS

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The aim of the presentation is to inform about activities of finishing project which has been focused on following objectives: (1) to establish and validate a test battery using model soil organisms, (2) to use these tests for assessment the effects of selected new priority POPs on soil ecosystem. The reason for starting this project was that newly recognized priority POPs have not been ecotoxicologically characterized so far (particularly with respect to soil organisms) despite they are in environmentalistic focus and can be found in soils in significant concentrations. The new laboratory of soil ecotoxicology - SOILETOX was established and the test battery was introduced there which is unique for soil ecotoxicology in the framework of the Czech Republic. The tests protocols and cultures of organisms were introduced and optimalized to enable research of POPs effects on soil microorganisms, earthworms, enchytraeids, nematodes, collembola, and plants. Selected POPs (chlorinated paraffins, toxaphene, PANHs) were completely tested. In addition, research was started concerning (1) biochemical markers (markers of oxidative stress) of soil invertebrates, (2) bioavailability of POPs to soil organisms, (3) relationships between structure of POPs and their bioavailability and toxicity in soil, and (4) toxicity of complex environmental mixtures (sludge, contaminated soils …) to soil organisms.

GENOTOXIC/ANTIMUTAGENIC PROPERTIES OF HUMATES PROCESSED BY DIFFERENT WAYS: A COMPARATIVE STUDY

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Humic acids belong to wide group of organic compounds formed during decomposition of organic matter of vegetable origin. Humic acids are operationally defined as fraction of humic substances which is not soluble under acidic conditions. Isolation of humic acids from natural sources as soil, coal or peat is based on acidifying alkaline extract to pH 1-2, which results in precipitation of humic acids. Structure of humic substances is composed from alkyl/aromatic formations linked by groups of oxygen and nitrogen. Carboxylic acid, hydroxyls of alcohols and phenols are the main functional groups. The adsorption, dispersion or emulsification property and other attributes of humic matter attract the interest of medical science and the pharmaceutical industry. The potential of use of humic acids as antiviral, anti-inflammatory, estrogenic, profibrinolytic and anti-coagulatory agents has been under serious investigations.

The aim of this work was study of the potential antimutagenic effects of some preparatives of regenerated and processed humic acids using i) specific yeast strain *Saccharomyces cerevisiae* D7 and ii) protozoon *Euglena gracilis* as biological test systems. In *S. cerevisiae* test biological effects were observed as ability to inhibit the formation of mutant colonies (Trp-conversions, Ile-reversions) caused by affect of standard mutagen 4-N-nitroquinoline-N-oxide (4-NQNO). The extent of biological effect of humates in the cells of *E. gracilis* test was determined by measuring of absorbance of chlorophylls *a* and *b* at 663 nm and 645 nm, respectively. Six different partially purified samples of sodium and/or potassium humate were tested and compared: two regenerated humates (Na, K), three processed humates (Na, K, Na-250°C) and Humin-s 775.

Testing of antimutagenicity of humic acids processed by various techniques using the *S. cerevisiae* D7 test exhibited better reproducible results than in *E. gracilis* test. The highest antimutagenic effect was found in regenerated humate samples. This effect gradually increased with higher humate concentration. The *S. cerevisiae* D7 test showed genotoxic effect of sodium humate (250°C) at all tested concentrations, mild mutagenic effect was observed also in potassium humate at 0.03% and 0.06% and Humin-s 775 at 0.03% concentration. In conclusion, humic substances can act as antimutagens, antimutagenic effect of tested humates depended on the type. Except sodium humate (250°C) all samples exhibited better antimutagenic effect at higher concentrations. Promutagenic (= genotoxic) effect is probably caused by other biologically active substances present in humate preparatives; similar effects were observed in other complex biological matrixes.

The results obtained can be used for possible applicability of processed humates in medicine and pharmacy.

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EFFECTS OF HEAVY METAL IONS ON NTPDase ACTIVITY IN PLASMA MEMBRANES ISOLATED FROM RAT UTERUS

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The literature data classify cadmium and mercury as reproductive tissue toxicants. The aim of this work was to investigate the possibility of cadmium and mercury to modulate myometrial function by affecting purinergic cell signalization. Since the myometrium is widely innervated, ATP is co-released with neurotransmitters into extracellular space and activates specific membrane purinergic receptors inducing various signaling processes. Ecto-enzyme, NTPDase is responsible for hydrolysis of extracellular ATP and ADP and for termination of purinergic signalization. We investigated the effects of cadmium and mercury on myometrial plasma membrane (MPM) NTPDase ATP and ADP hydrolyzing activity under in vitro conditions.

The effects of Cd^{2+} and Hg^{2+} ions on hydrolysis of ATP and ADP were followed in the concentration range from 1×10^{-6} - 5×10^{-2} mol/l (Figure 1. and 2.). The half-maximum inhibitory ATPase activities (IC_{50}) determined by Hill analysis of experimental curves were 7.10×10^{-4} mol/l for Cd^{2+} and 1.05×10^{-3} mol/l for Hg^{2+} . IC_{50} values for ADPase activities in the presence of Cd^{2+} were 5.45×10^{-4} mol/l and Hg^{2+} , 8.67×10^{-4} mol/l.

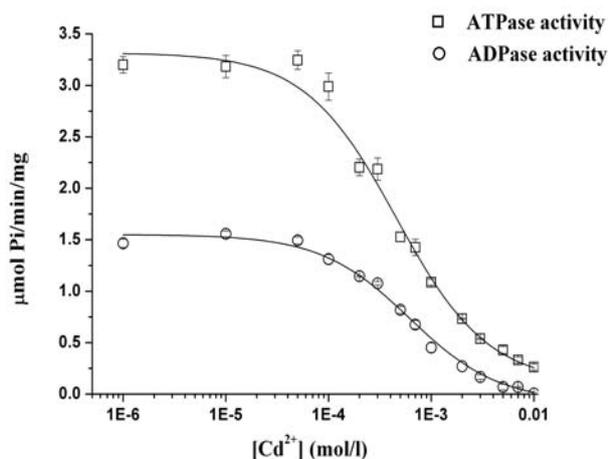


Figure 1. Inhibition of NTPDase activity by Cd^{2+} ions. Incubation medium contains 50 mmol/l Tris-HCl (pH 7.40), 1 mmol/l MgCl_2 , 1 mmol/l substrate, 7mg MPM protein and increasing concentrations of CdCl_2

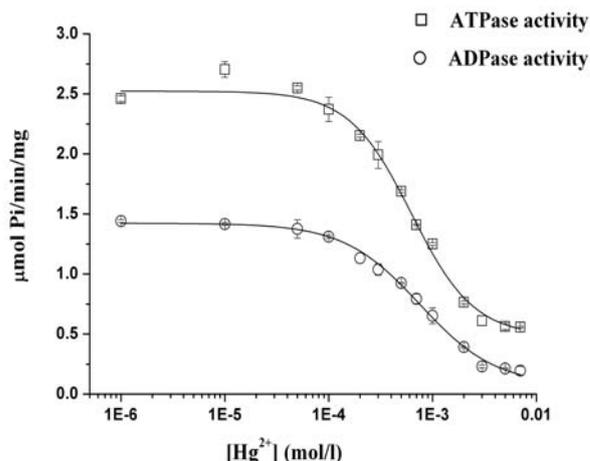


Figure 2. Inhibition of NTPDase activity by Hg^{2+} ions. Incubation medium contains 50 mmol/l Tris-HCl (pH 7.40), 1 mmol/l MgCl_2 , 1 mmol/l substrate, 7mg MPM protein and increasing concentrations of HgCl_2

Inhibition of enzyme activity was also investigated as a function of metal-enzyme contact time. Both metal ions produced about 40% inhibition during the first 5 minutes. The prolonged contact time did not influence the change of enzyme inhibition. Kinetic parameters (V_{max} and K_m) were derived using Edie Hofstee transformation of experimental data. The type of inhibition for ATPase and ADPase activity of enzyme in the presence of Cd^{2+} and Hg^{2+} was determined. Results indicated that cadmium ions were acompetitive inhibitors of ATP and ADP hydrolyzing activity, and mercury ions were noncompetitive inhibitors of ATP and ADP activity.

According to the obtained results, we may conclude that both Cd^{2+} and Hg^{2+} affect reproductive function by inhibiting NTPDase activity inducing an accumulation of extracellular ATP and prolonged purinergic activation.

ANTIMICROBIAL ACTIVITY OF COMPLEXES WITH SOME 2-AMINOBENZIMIDAZOLE DERIVATIVES

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Benzimidazole derivatives with substituent such as amino in different positions have been found to possess inhibitory effect on the development of several yeasts and bacteria. It has been described antibacterial activity of some nitro- and halogeno-substituted benzimidazole derivatives, as well as antifungal activity. The antimicrobial activity of these class of compounds were investigated against *Helicobacter pylori* and against oral streptococci. Also, benzimidazole and its derivatives are of considerable importance because of their antihistaminic, cytostatic, local analgesic, hypotensive, antiinflammatory activity and antiviral activity. It was confirmed to have a moderate *in vitro* anti-HIV activity. However, in the last time possible therapeutical properties of the metal complexes have been examined. It was found that the complexes of transition metal salts with benzimidazole derivatives showed a larger antimicrobial activity than only ligands.

Following our studies about the reactivity of benzimidazole derivatives with metallic halides, in present study we evaluated the antimicrobial activity of this type of complexes. Chlorides of copper(II) and nickel(II) react with 1-benzyl-2-aminobenzimidazole (L^1) or 1-(4-chlorobenzyl)-2-aminobenzimidazole (L^2) to give complexes of the type $[ML_2Cl_2] \cdot nH_2O$ ($M=Cu$ or Ni ; $L=L^1$ or L^2 ; $n=0.5$ or 1). We report *in vitro* antimicrobial activities of ligands and their copper(II) and nickel(II) complexes with 1-benzyl-2-aminobenzimidazole (L^1) or 1-(4-chlorobenzyl)-2-aminobenzimidazole (L^2) against *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Bacillus* sp. and *Saccharomyces cerevisiae*.

The antimicrobial activity of the 2-aminobenzimidazole derivatives and their complexes was first tested by the agar disc-diffusion method against gram-positive and gram-negative bacteria and fungi. The majority of the investigated compounds displayed *in vitro* antimicrobial activity against very persistent microorganisms. The ligand, 1-benzyl-2-aminobenzimidazole (L^1), as well as its nickel(II) complex showed no antimicrobial activity against fungi and gram-positive strains of bacteria. These compounds were found to be only active against gram-negative *Pseudomonas aeruginosa*. It may be concluded that the antimicrobial activity of these compounds is related to cell wall structure of the bacteria.

None of the compounds were found significantly effective against fungi *Saccharomyces cerevisiae*, except ligand L^2 and its copper(II) complex which very slightly or slightly inhibited the growth of fungi. Of the tested ligands and their complexes, the most active compound was the complex of 1-(4-chlorobenzyl)-2-aminobenzimidazole (L^2), which exhibited high inhibitory activity against all the tested bacteria isolates.

The minimum inhibitory concentration (MIC) was determined for all ligands and their complexes. The complex containing copper(II) was more active than starting ligand L^2 against *Pseudomonas aeruginosa* and *Bacillus* sp. with a MIC value of 250 µg/ml, as well as same active as ligand L^2 with a MIC value of 125 µg/ml against *Staphylococcus aureus*.

In view of the structural formula of the complexes that exhibited antimicrobial activity, it can be thought that metal may play a significant role. This can be explained in terms of chelation theory, which states that a decrease in the polarizability of the metal can enhance the lipophilicity of the complexes.

ACKNOWLEDGMENT

These results are the part of the project "*Physico-chemical, structural and biological investigations of complex compounds*", supported by Ministry of Science and Environment Protection - Republic of Serbia.

ECOTOXICOLOGICAL EVALUATION OF THE ACRYLIC MONOMERS AND POLYACRYLIC POLYMERS

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New polymeric compounds are finding their way to all areas of human activities, replacing traditional, currently used materials. As a result, research in this area concentrates particularly on the production of novel, multifunctional, homogeneous as well as heterogeneous polymeric materials. Various advanced syntheses of polyfunctional macromonomers, polymers and thin nanostructural polymer layers are particularly employed. From the environmental point of view, it is therefore essential to monitor the toxicological and ecotoxicological impact of synthetic polymeric materials.

The study is focused on ecotoxicological evaluation of selected esters of acrylic, methacrylic and dimethylacrylic acids. Two basic types of ecotoxicological biotests can be distinguished: the acute toxicity tests and chronic toxicity tests. Tests can be also classified into the following categories: standard and alternative tests, standard tests comprise the categories of aquatic tests and tests implemented on terrestrial organisms. Standard tests are approved by OECD. Alternative tests were implemented later on, they conform requirements on laboratories better. Until now they have not been validated. Their correlation with standard tests has been proved.

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5. WATER QUALITY, TREATMENT, REUSE

POSTERS No. 45 – 61

REGENERATION OF GRANULAR ACTIVATED CARBON SATURATED BY ORGANIC MATTER WITH IRRADIATION GAMMA ($^{60}\text{Co}^*$) AND THERMICAL REGENERATION

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The aim of the work described in the present paper is the study of thermal regeneration and gamma irradiation (^{60}Co) impacts on the efficient reuse of granular activated charcoal (GAC) in further water treatment processes.

The experimental work consisted in two steps:

The first consisted of studying the kinetic adsorption of GAC making use of BET analyses and relying upon the FREUNDLICH laws of adsorption.

The second part the saturated granular activated charcoal obtained from the first step experiments was submitted to many regeneration cycles both by thermal treatments and by gamma irradiations (^{60}Co source, 21 kCi). It was aimed at investigating and searching for the optimal operating conditions both for thermal treatment temperature and irradiation doses that would allow the treated Granular Activated Charcoal to be efficiently reused (table No. 1)

Table No. 1: Different Iodine Number for each treatment mode

Treatment Mode	Batch	Continuous
Optimum of Temperature (°C):	600	700
Iodine Number ($\text{mg}\cdot\text{g}^{-1}$)	734.7	739.7
Radiation dose (kGy)	8	10
Iodine Number ($\text{mg}\cdot\text{g}^{-1}$)	738.5	742.3

N.B: Iodine number of GACNEW = $810 \text{ mg}\cdot\text{g}^{-1}$.

It allows reaching about 90% regeneration efficiencies for the saturated GAC as compared to a new one. The optimal irradiation dose for each kind of treatments is respectively 8 kGy for the batch treatment and 10 kGy for the continuous treatment.

DEGRADATION OF TRIHALOMETHANES BY MICROALLOYED ALUMINIUM COMPOSITE IN AQUEOUS SOLUTIONS

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Degradation of trihalomethanes by a microalloyed aluminium composite (MAIC) in aqueous solutions was studied in this paper. Microalloyed elements in the MAIC significantly accelerated corrosion rate and increased reduction activity of metal by destabilizing oxide film. The degradation rates of THMs by the MAIC were described by a pseudo-first-order reaction. The results show that complete degradation of CHCl_3 , CHBrCl_2 and CHBr_3 could be achieved for 5-10 times shorter periods than those of zero-valent iron and bimetallic complexes. Capability of CH_2Cl_2 degradation and working under high pH conditions are additional advantages of the MAIC, related to other zero-valent metals. Results also show that the degradation process could be accelerated by using a semi-flow system and by increasing of the composite surface area, which indicate mass transport limited kinetics. Presence of Cl^- ion in solution in range from 0.3 to 3.0 g additionally increases degradation rate and reduction activity, because of aggressive influence on oxide. The MAIC could be an effective reagent for remediation of the THMs contaminated natural waters.

KINETICS STUDIES FOR TRIHALOMETHANE FORMATION BY CHLORINATION OF RAW WATER

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The formation kinetics of trihalomethanes (THMs) by chlorination of raw water was studied. The chlorination efficiency, THM speciation, and THM formation potential was determined in the river water of Cluj-Napoca, Romania. With regard to THM formation, raw water resources under typical treatment conditions (total chlorine residual 0.5–0.9 mg/L) were measured. The total THM formation was always below EU and USEPA drinking water standards. Based on chlorine exposure estimations, it was concluded that the current chlorination practice for waters is sufficient for inactivation of bacterial contaminants. Optimization studies are needed for proper chlorine addition in drinking for healthy reason.

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ANALYTICAL METHODS FOR THMS DETERMINATION IN DRINKING WATER

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Different analytical methods for trihalomethanes determination in drinking water are described. Trihalomethanes, chlorinated by-products in drinking water, were determined by some different techniques: liquid-liquid extraction-gas chromatography-mass spectrometry (LLE-GC-MS), headspace-gas chromatography-mass spectrometry (headspace-GC-MS), purge and trap-gas chromatography-mass spectrometry (purge and trap-GC-MS); and headspace extraction-gas chromatography-electron capture detection(headspace-GC-ECD). The compounds studied were chloroform, bromodichloromethane, dibromochloromethane and bromoform. The MS was operated in the SIM mode. The quantitative methods were validated and demonstrate the ability to identify and to measure reliably the yields of these toxic compounds.

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FLUORIDE CONTENT IN SPRING WATERS OF MOUNTAIN RTANJ

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In many regions of the world endemic diseases which seriously impair people's health are linked to excessive or insufficient levels of fluoride in the water. The presence of fluoride in drinking water at optimal concentrations (1 mg/L or 52.6 $\mu\text{mol/L}$ is recommended) prevents dental caries, but long-term consumption of water containing more than 1.5 mg/L could be detrimental to health. The teeth of consumers become mottled with a permanent black or grey discoloration, and the enamel becomes so severely pitted that they eventually lose their teeth. Bone changes and crippling fluorosis may also result consumption of water rich in fluoride.

The aim of this study was to measure fluoride content in certain spring waters in the region of mountain Rtanj, since water is one of the principal sources of fluoride intake into the organism. Water samples were taken from 6 springs of mountain Rtanj during summer 2005 year. Six water samples were collected from each spring. Fluoride levels were determined electrochemically, using fluoride-selective electrode, after mixing water samples with TISAB buffer in ratio 1:1.

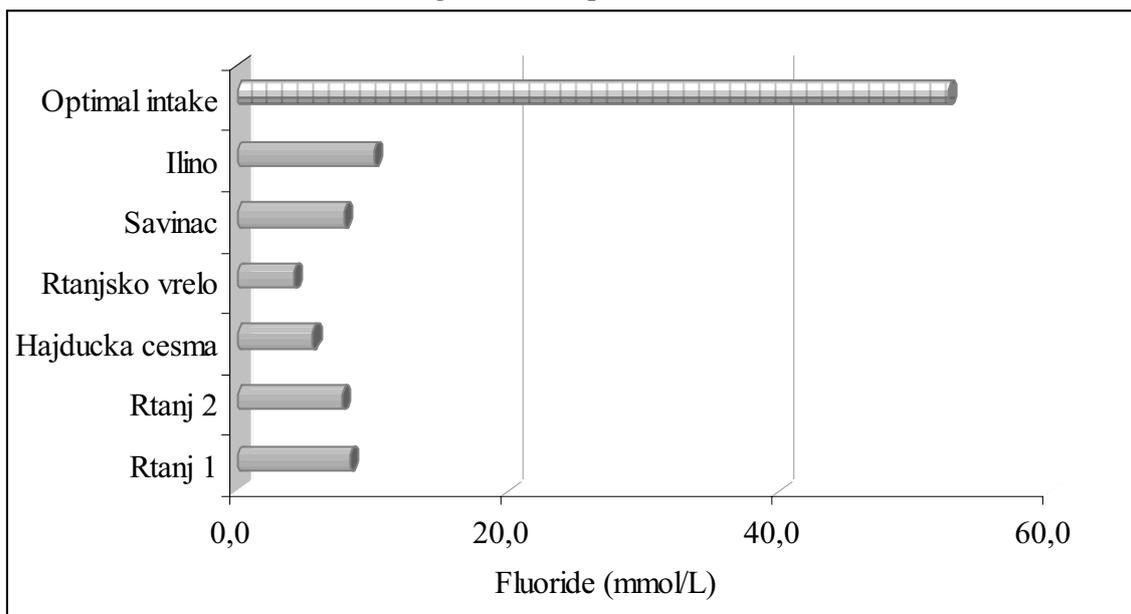


Figure 1. Fluoride content in spring waters of Rtanj mountain

The obtained results (Figure 1.) evidenced that water from all Rtanj springs contained low fluoride mean-values (2.1-12.6 $\mu\text{g/L}$). These waters belong to the category of fluoride-deficient waters. Dental caries is critical effect of fluoride deficient. These data contribute to the environmental monitoring and evaluation of mountain Rtanj as well as risk assessment related to fluoride deficient in investigated area.

TEMPORAL VARIATION OF TRACE ELEMENT CONTENTS IN WATERS POLLUTED BY LANDFILL LEACHATE

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The chemical composition of landfill leachate-polluted stream waters from an uncontrolled municipal landfill in Prague (Czech Republic) was monitored for over 4 years (2002-2006) through several long-term sampling campaigns. The studied landfill served as a principal disposal site of municipal solid waste (MSW) for the city of Prague between 1984 and 1993. However, the landfill was constructed in the source area without any engineering barriers preventing the leakage and the leachate was collected by concrete pipes and directly channeled into the small stream [1]. The emphasis of this study was to determine the temporal variability in concentrations and release of trace elements from the landfill body. The contents of trace element (20 elements including heavy metals and metalloids) in leachate-polluted stream waters were determined by quadrupole-based ICP-MS (VG Elemental PQ3). Bulk chemical and physico-chemical parameters were combined with the speciation-solubility thermodynamic modelling (MINTEQA2, PHREEQC-2) and treated using the NCSS statistical software. The trace element contents show a significant correlation with the precipitation: during rain events, the strongly polluted interstitial water is drained from the landfill body followed by a drop of trace elements concentrations due to dilution. The thermodynamic modelling indicated that metals are present in leachate-polluted waters mainly as carbonate complexes. The polluted waters were oversaturated with respect to Fe(III) oxyhydroxides, calcite (CaCO₃) and other carbonates. Three attenuation mechanisms were identified for trace elements in these waters: (i) co-precipitation with calcite and adsorption on calcite surfaces – a significant role of calcite in trace element removal was experimentally documented at this site [2] (ii) binding on newly formed Fe(III) oxyhydroxides and (iii) binding to sediment organic matter. The sequential extraction analysis (SEA) performed on stream sediments showed that under near-neutral conditions governing the sediment/water interface in the landfill environment, metals are relatively strongly bound to sediment constituents and remain relatively immobile.

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WASTE WATER GENERATION AND TREATMENT METHOD USED IN OIL REFINERY PANCEVO

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Waste water from the oil industry usually contains hazardous chemicals which originate from crude oil. High concentrations of : petroleum hydrocarbons, sulfides, mercaptanes, phenolic compounds, cyanides, suspended matter etc. may affect the environment of the receiving waters by directly harming the organisms, changing behaviours of some species and tainting or accumulating within the food chain.

This paper presents a summary of the waste water flows from refinery to the primary treatment unit – API separator, which function is to remove gross quantities of oil and suspended solids and further to secondary - biological treatment which consists of: flotation, activated sludge, stabilization and aeration. Special attention is given to waste water generation and treatment method used in Oil Refinery Pancevo. Treatment of oily waters, sour waters, alkali waters, drainage waters, streams washing waters and cooling waters in process is done in desalter, sour water treatment unit and spent caustic neutralisation unit, in order to remove oil matter, hydrogen sulphide and mercaptanes.

Technical description of API separator system functioning is also presented. The mechanical-gravity treatment unit reconstruction has been commented, and a detailed first phase description of the storm contaminated water treatment modernization has been proposed.

APPLICATION OF POLY(ACRYLIC ACID) AND POLY(ACRYLIC –CO-ITACONIC ACID) HYDROGELS FOR Cu²⁺ BINDING

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In recent time environmental protection has been confronted with increased contamination of waste water by heavy metals ions. For removal of heavy metals ions as pollutant different polymeric materials have been applied. Polymer materials are widely used type of materials and the most popular in present time are so called "hydrogels". Because one of the very important heavy metal pollutants is copper, the absorption of copper has become an object of many investigations.

The aim of this work was to investigate the possibility of Cu²⁺ binding to the poly(acrylic acid) hydrogels (PAA) and poly(acrylic-co-itaconic acid) hydrogels (PAA-co-IA) and its kinetics of binding under the isothermal conditions. The hydrogels samples were of our own laboratory production.

Binding of Cu²⁺: dry hydrogel samples (xerogels) was immersed in CuSO₄ solution (0.0005M-0.01M) at different temperature and the amount of residual Cu²⁺ in solution was determined by atomic absorption spectrometry.

It was found that capacity of Cu²⁺ binding to PAA-co-IA hydrogels was increased compared to PAA hydrogels. Mechanism of Cu²⁺ binding to these hydrogels was proposed. The new model of kinetics for investigated process was established and kinetic parameters are determined. It was found that process might be controlled by diffusion or kinetically controlled.

OPTIMIZATION OF OXIDATIVE DEGRADATION OF ALKYLPHENOL ETHOXYLATES WITH DIFFERENT POLYOXYETHYLENE CHAIN LENGTH

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In the last decade widespread nonionic surfactants such as alkylphenol ethoxylates are criticized because they are characterized by slow rate of their biodegradation. A development of effective procedures of water clean-up from bioresistant surfactants is of great ecological interest. The procedures could precede biodegradation or even substitute it.

In this study oxidative degradation is proposed for destruction of alkylphenol ethoxylates. Systems containing ferrous or ferric cations and hydrogen peroxide are applied as oxidative agents. Alkylphenol ethoxylates with trade mark "Neonols" produced in Russia were used in the experiments. Tensiometry and HPLC techniques were shown to be useful for study of kinetics of the nonionic surfactant oxidative decomposition. Colorimetry is less informative and reliable.

Systems with ferric ions have been studied in detail. Optimum conditions of oxidative destruction of the iso-nonylphenol ethoxylates with different polyoxyethylene chain length were determined and the extent of their conversion was estimated. Conversion depends on chain length: the longer the chain the poorer is conversion under the same conditions.

It was established that the effectiveness of oxidation is influenced by a variety of factors, namely the relation of component concentrations in the oxidative mixture, pH, temperature. Anion of iron salt also affects both the rate of degradation and the result. Nitrate as a counterion is preferential.

It was demonstrated that Neonols were decomposed to biodegradable compounds as a result of oxidation. No toxic intermediates were detected.

Thus chemical degradation of alkylphenol ethoxylates can become an alternative way to their biodegradation. The process rate and conversion can be regulated by varying of oxidation conditions.

MICROBIAL EVALUATION OF ACTIVATED SLUDGE PROCESS AT WWTP BRNO MODŘICE

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At present one of the most used methods of biological wastewater treatment is activated sludge process. The principal role in this process belongs to functional microbial culture. Two types of microbial cultures could be recognized, suspended culture (activated sludge process) and attached culture (biofilm process). Presence or absence of the specific microorganisms can indicate effluent wastewater quality. There are a lot of factors (pH, temperature, biochemical oxygen demand, etc.) and technological parameters (solid retention time, sludge load, sludge volume index, etc.), which can influence on the activated process and presence of microbial biocoenosis in activated sludge. By monitoring the microorganisms abundance, the behaviour of activated process and related eventual problems can be evaluated. For identification of microorganisms present in activated sludge a lot of methods can be used. The common method used is microscopic analysis of basic morphological characteristics of presented microorganisms.

The paper presents the results of microbiological analysis of the samples of activated sludge collected at the wastewater treatment plant Brno Modřice. One of the main goals of the work is the evaluation of influence of technological parameters on structure of activated sludge biocoenosis and evaluation of their effect on the process performance. The samples of activated sludge at WWTP Brno Modřice from March to November 2006 have been investigated. The different volumes (biochemical oxygen demand (BOD₅), dichromate value, temperature, flow volume) during 27.3.-5.4. were observed. This fact can be connected with floods. The volumes of total nitrogen and suspended solids changed as well.

According the results of technological and microbiological analysis the activated sludge corresponds to "low loaded" activated sludge (sludge load < 0.1 kg.kg⁻¹ BOD₅/suspended solids). The biocoenosis of the activated sludge is not very varied; there are a few dominant types of microorganisms (*Aspidisca cicala*, *Vorticella convallaria*, *Carchesium polypodium*, *Arcella hemisphaerica*, *Acineta*, *Opercularia*, *Philodina roseola*, etc.). On the basis of the obtained results of sludge volume index and microbiological analysis can be concluded that the activated sludge shows very good sedimentation characteristics. During November there was observed the slight increasing of concentration of filamentous microorganisms. In spite of this fact there are no problems with sludge bulking, deteriorated sludge separation or production of scumming which are usually typical for high presence of filamentous microorganisms.

The monitoring of abundance of selected microorganisms during the wastewater treatment process (from May to November) and correlation with technological parameters and process variables was investigated as well. Rapid decreasing of abundance of selected microorganisms was observed during June; this fact can be connected with the repairs in aeration tank performed in this period.

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WATER TREATMENT BY DC DIAPHRAGM DISCHARGE

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Nowadays removal of organic pollutants from water environment is highly required. Besides physical, chemical and expensive biological methods, so-called advanced oxidation processes (AOP's) are developed and applied for propose of water treatment. One possible method suitable for degradation of organic compounds is generation of electrical discharge in the treated medium. Processes initiated by the discharge in water leads to the formation of various reactive species (mainly radicals) that subsequently react with present molecules and cause their decomposition [1]. Also UV radiation and shock waves (in the case of pulsed voltage) are responsible for the molecule destruction. Our work focuses on the diaphragm discharge generated by the DC non-pulsed high voltage in water solutions containing model organic compounds (dyes) and some additives (electrolytes).

A batch discharge reactor with volume of approximately 3 liters is used for the degradation of organic dyes [2]. DC high voltage source giving the non-pulsed voltage of about 2 kV is used to create the discharge in a pin-hole of the dielectric diaphragm installed between two stainless steel electrodes. Properties of plasma formed in the reactor are observed by the optical emission spectroscopy, determination of the dye concentration in the solution is carried out by UV-VIS spectroscopy. Degradation process is investigated in water solutions of the dye Saturn Red (C.I. Direct Red 79), commonly used in the textile industry, with addition of various electrolytes adjusting the optimal solution conductivity.

Obtained results show that the dye concentration decreases more or less exponentially during the discharge treatment and the degradation is highly dependent on the applied voltage polarity. The typical absorption spectra of treated solution are given in Fig. 1 left. The dye concentration drops to approximately 20 % of the initial value already after 10 minutes of the experiment [3]. Besides high voltage magnitude, on which the dye decomposition is directly proportional, electrolyte kind and its concentration in the solution (conductivity) significantly influences the dye degradation, too (see Fig. 1 right).

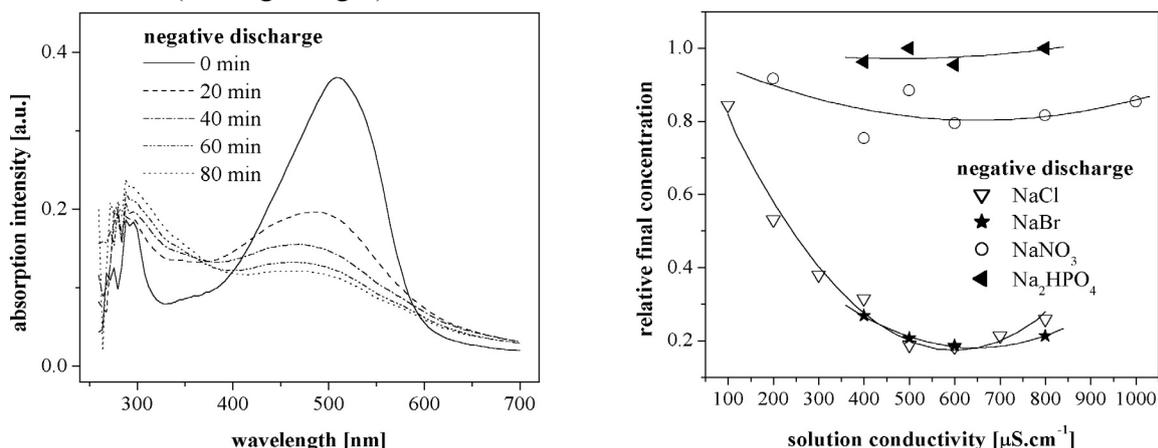


Fig. 1: Left: Absorption spectra of the dye Direct Red 79 obtained during the diaphragm discharge treatment in the 5 mM NaCl electrolyte solution (input power of 120 W, initial solution conductivity of 500 $\mu\text{S}\cdot\text{cm}^{-1}$). Right: Influence of solution conductivity and electrolyte kind on the dye Direct Red 79 decomposition by the discharge (initial concentration of 12 $\text{mg}\cdot\text{l}^{-1}$, input power of 160 W, treatment by the discharge for 40 minutes).

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EVALUATION OF THE LEVEL OF CONTAMINATION BY PCBS IN WATER RESERVOIRS

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This study investigated the level of contamination in surface water in reservoirs in Moravia. Samples of water collected from a total of six Moravian reservoirs were analysed for major pollutants such as indicator PCB congeners, which still represent the typical pollutants present in surface water. Selected analytes were identified and determined using separation procedures such as extraction (isolation of analytes), column chromatography (purification of extracts), and two-dimensional gas chromatography with two μ ECDs (identification and quantification). Only the Smrad'avka reservoir showed to contain increased levels of pollutants, namely PCBs. The limit concentration of indicator PCB congeners for surface water (Czech Government Regulation No. 82/1999 Coll.) – 10 ng/l (now recommend 12 ng/l) was exceeded in 11 of 19 samples.

This was the reservoir located in a massively contaminated region where old loads consisting of dyes with a high portion of PCBs were washed out during floods in 1997. These findings were comparable with the data published for the Labe region in 2004 that was affected by floods in 2002. Water in other reservoirs did not show massive contamination. However, it is alarming that indicator PCB congeners were detected in all examined samples of water. PCBs were observed in elevated concentrations both in abiotic samples and particularly in biotic samples from the localities which were suspected of secondary contamination. The highest level of contamination showed the areas notorious for occurrence of illegal dumping sites or in the vicinity of chemical plants which had used these compounds in the past.

Concentrations of indicator and minority PCB congeners in water samples - Smrad'avka (ng.l⁻¹)

Congener	mean	mediane	range	RSD
PCB 28	14.22	8.35	0.90-56.40	1.20
PCB 52	4.82	3.15	0.80-21.20	1.15
PCB 101	3.10	1.48	0.60-15.83	1.29
PCB 118	1.65	0.85	<0.60-5.80	1.24
PCB 138	3.62	1.40	0.60-29.33	2.01
PCB 153	6.21	2.20	0.90-52.93	2.07
PCB 180	4.92	1.20	<0.60-34.57	1.97
PCB 8	2.72	2.3	1.30-4.80	0.55
PCB 18	6.82	4.3	2.40-18.70	0.82
PCB 47	4.28	2.5	<0.60-17.10	1.22
PCB 49	3.86	1.95	<0.60-18.30	1.54
PCB 187	0.7	0.7	<0.60-0.80	0.20

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CHANGES OF QUALITY OF POTABLE WATER BY TRANSPORT TO THE FINAL USER

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There is no life without water. Average daily consumption of water is 118,6 litres per person. Potable water supplied to final user must fulfil specific qualitative and quantitative requirements. At present acquiring potable water from nature surface resources without adjustment in waterworks is not acceptable. Water quality is controlled in outflow of waterworks and reservoirs.

Potable water is transported to the final user by distribution system in several days. During transport water quality is changed. Distribution system consists of pipes, armatures, fixtures and other components. Various construction materials are used. Physical-chemical processes which have impact on water quality supplied to the final user come up in distribution system. Water also flows at different speed in distribution system. During stagnation there are ideal conditions for development of corrosion process. Incrustation or sediments can occur and also repeated expansion of micro-organisms can be promoted.

Unsuitable materials support expansion of biofilm and growth of micro-organisms which colonize components of distribution system, slime in them vegetate many microbes is created. Materials of pipes can release organic matters, hard metals and other compounds, this is signified by increased value of TOC, turbidity and by change of water quality and sensoric properties.

We studied both potable water quality in Brno and influence of construction materials on water quality. Corrosive stability of pipes used in water distribution systems under static and dynamic conditions was investigated. The effect of pH, retention period, structure and quality of surface and age of used construction materials and water composition on content of selected metals – iron, copper, manganese and zinc is discussed. Tubes used for contact with potable water were examined during 24 and 72 hours by pH of test water 6, 7, 8 and 9 under static conditions. Tubes under dynamic conditions will be tested on equipment with circulation of water. The content of metals in the water is determined by atomic absorption spectrometer SpektrAA 30. It was approved that in dependence on chemical composition of water, constitution of construction materials as well as on pH of water and retention period in distribution system there is a change of water quality. Considerable impact on water quality is possible to adjudicate to unsuitable construction materials.

Average daily consumption of water per person in the Czech Republic is approximately 120 litres. In distribution systems different construction materials are used and potable water is transported to final user by distribution system during several days. Moreover it is necessary to consult the age of current water distribution system and the life span of used materials.

It is possible to conclude that the impact of constructional materials of distribution system on transported water quality is evident and materials used for construction of potable water distribution systems should be chosen carefully. I think it's necessary to pay attention to these problems.

**DETERMINATION AND SIGNIFICANCE OF ADSORPTION CAPACITY
OF ION-EXCHANGE RESINS IN POTABLE WATER TREATMENT
PROCESSES**

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As much as the difference between the ion-exchange and adsorption processes is apparently well-defined, in actual practice making a distinction is not always a straightforward task. Determination of ion-exchange resin adsorption capacity is one of the essential technological parameters required when designing the drinking (potable) water treatment plants. Results of testing conducted with several resin types, based on type and manner of recovery, point the way for determining specific adsorption by application Freundlich linearized equation and adsorption capacity in compliance with the linear form of Lengmuir equation.

Key words: organic substances, ion-exchange resin, adsorption capacity, adsorption isotherms

QUALITY OF BOTTLED NATURAL WATER IN SERBIA

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Bottled water intended for human consumption and available on the market, is classified in the Serbian legislation into three categories: natural mineral water, natural spring water and table water. The present paper submits an analysis of bottled water on the basis of chemical composition, classification and geotectonic origin. Geological, tectonic and hydro-geological conditions in this region are very complex which consequently resulted in numerous springs of natural mineral water. Content of minerals, ionic composition and carbon-dioxide content (shown in the paper by means of diagrams and charts) are used in classifying said water into specific groups, based on which their geotectonic origin is determined, indicating specifically to which of the geotectonic bodies found across the Serbian territory particular water is associated with.

Key words: bottled water, mineral substances, water chemical analysis, geological environment.

CHROMIUM ADSORPTION ON CRAB CARAPACE

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Crab carapace, an abundant by-product of the shell-fishing industry has been proposed as a potential biosorbent for metal removal from aqueous solutions. Crab carapace consists principally of CaCO₃ and chitin, usually cross-linked with protein and a proportion of lipids. Recently, this sorbent has been used for copper removal from aqueous solution [1]. In this work, crab carapace has been used for chromium removal from aqueous solutions. Most treatment processes to remove chromium from wastewater require the removal of both Cr(VI) and Cr(III), therefore, the objective of this paper is to examine the use of crab carapace for the removal of chromium in both oxidation states. Batch experiments were performed to study the influence of initial pH, agitation time and metal concentration on chromium removal. In all the experiments, pH and calcium concentration in solution was measured in the residual solution to obtain information about sorption mechanisms. Solid-phase FT-IR was performed to ascertain the main functional groups involved in metal uptake.

Results show that highest Cr(VI) and Cr(III) sorption yields were registered at pH > 3. Chromium uptake begins with a rapid phase and after 60 minutes contact, chromium sorption of both oxidation states was practically complete. Equilibrium data for Cr(VI) and Cr(III) sorption on crab carapace were modelled by means of Langmuir and Freundlich sorption models.

After five minutes contact between the sorbent and solutions (blank, Cr(VI) Cr(III)), the solution pH increases from an initial value of 3 to within the range 7-9. Under initial acidic conditions dissolution of carapace CaCO₃ occurs and the subsequent increase in pH induces microprecipitation of some chromium compounds. FT-IR analysis confirms that CaCO₃ is involved in both Cr(VI) and Cr(III) sorption on crab carapace.

Acknowledgements

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BIOSORPTION OF Cr(VI) ON *Vibrio fischeri* MEMBRANES

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Conventional methods for removing metals from aqueous solutions may be ineffective or extremely expensive. For this reason, biosorption is currently gaining considerable importance as an alternative technology for the elimination of heavy metal from contaminated aqueous solutions. Last years, several authors have been investigating the use of different kind of bacteria as a replacement for currently costly methods. In this study, the adsorption capacity of Cr(VI) on the surface of the Gram negative *Vibrio fischeri* bacteria was investigated. Batch experiments were designed in order to study the effect of different adsorption medium, contact time, initial Cr(VI) concentrations and sorbent doses on metal sorption by bacteria.

From the results, NaCl medium was found to be a suitable media for sorption experiments. The adsorption equilibrium was reached after 6 days of agitation and the experimental data were well described by Langmuir isotherm model. Maximum capacity (q_{max}) of *Vibrio fischeri* was 200 $\mu\text{mol Cr(VI)/g}$ dried bacteria. Scanning Electron Microscopy and X-ray energy dispersion analysis were also used to determine the morphology of bacteria and presence of Cr(VI) on the bacterial membranes after the sorption experiments.

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6. BIODEGRADATION OF TOXIC COMPOUNDS

POSTERS No. 62 – 66

OPTIMIZATION OF DEGRADATION METHODS OF TRANSFORMER OIL ON THE BASIS OF POLYCHLORINATED BIPHENYLES (PCB)

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The degradation experiment results of polychlorinated biphenyles (PCB) based transformer oil have been shown.

The transformer oil has been chemically degraded using two different procedures: a) in the first series of experiments, using oleum; b) in the second series of experiments, by alkaline metal, in paraffine oil as a medium.

In the experiments the reaction parameters were selectively changed, aimed at obtaining a high percentage of degradation and ecologically harmless degradation products. All the experiments were completely carried out according to EPA regulations.

The transformer oil was sampled from the stored transformer in Refinery Pancevo (Republic of Serbia). According to the results of GC-MS analyses the transformer oil, declared as Arochlor 1260, contained 52.65 % PCB and 47.35 % solution (isomers of trichlorobenzene). During evaluation of the analyses results of degradation products and calculation of degradation efficiency the transformer oil had a role of reference sample.

The degradation products obtained from all the experiments and each procedure were analyzed by GC-MS and GC-ECD.

Efficiency of degradation procedure by oleum with Fe(II)-sulphate and using calcium-hydroxide and of alkaline metal procedure was 99.99 %, and 99.995 %, respectively.

Degradation experiments are carried out in a simple way, and the degradation products are ecologically harmless, so they can be safely stored in the environment.

BIOREMEDIATION OF CRUDE OIL BY BACTERIA AND FUNGI

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The petrochemical industry generates a series of liquid effluents during the petroleum-refining process. These effluents represent risk for ecosystem and human health. Applying bioremediation is one way of improving these soils and waters.

In Oil Refinery of Pančevo (Serbia) oil wastewaters are being collected in API separator, after which they are being sent to further biological processing. These waters have high content of oil matter and mercaptans, which complicates the biological processing of wastewaters. This is a reason for putting special sorbent into API separator in order to achieve absorption of oil matter. In order to achieve sorbent saturation with oils, the absorption process had 30 days duration. After 30 days there has been found 2.84 mg/g of total mineral oils.

The possibility of different microbial populations ((*Pseudomonas* sp., *Bacillus* sp., *Micrococcus* sp., *Mucor hiemalis*, *Alternaria alternata* i *Penicillium glabrum*)) for biodegrading oil matter derivating from oil industry has been analyzed in laboratory conditions. These microbial populations have been isolated from soils and waters contaminated with organic pollutants coming from oil refinery.

After three weeks saturation of sorbent with microorganisms, 65-85 % of oil matter concentration decrease was noticeable. These results indicate the possibility for using autochthonous microbial populations for bioremediation processes of crude oil, as well as reusage of sorbent for oil absorption.

Biodegradation by natural populations of microorganisms represents one of the primary mechanisms by which petroleum and other hydrocarbon pollutants can be removed from the environment.

ACIDOPHILIC BACTERIA IN SULFURIC ACID FORMATION: VARIABILITY OF METABOLIC PARAMETERS

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Biooxidation of elemental sulfur to sulfuric acid plays an important role in spontaneous biogeochemical processes in sulfide deposits (sulfide wastes, abandoned ore mines). Environmental acidification and metal migration are the results of those processes. The purpose of this study was to investigate a correlation among growth conditions, physiological factors and selected kinetic constants of elemental sulfur oxidation by *Acidithiobacillus ferrooxidans*. The values of maximum sulfur oxidation rate (v) and growth yield on sulfur (Y) were determined from data obtained in 69 batch cultures. The changes of the apparent Michaelis constant for sulfur (K_m) were investigated in resting cells.

Both the v and Y demonstrated very different values which exceeded one order. However, no trend changes of the v and Y within the same culture occurred. The changes in the Y values are related to the varying metabolic utilization of elemental sulfur for growth or energy formation. Although the results showed a high Y variability, the reason for the significant Y changes among different cultures of the same strain remains unclear. No significant correlation between the v and Y values was observed for most of data. Changes in the K_m were demonstrated in relation to different physiological conditions. The results show that the bacterial cultures produced sulfuric acid under very different metabolic conditions to increase either sulfur oxidation or cell growth rates. Factors of the metabolic control are unknown.

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MICROBIAL DEGRADATION OF MODIFIED POLYURETHANE FOAMS

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Microorganisms can be involved in the degradation of both synthetic and natural polymers. In this work, several types of polyurethane foams (PUR) modified by polysaccharide or protein component (10 % of acetyl-, hydroxyethyl- and carboxymethyl cellulose, activated starch, gluten) were prepared. Single cultures of *Aureobasidium pullulans*, *Arthrobacter globiformis* and mixed culture of *Thermophilus* sp. were used to biodegradation of modified materials. First, all materials were tested as potential carbon source. Further, all microorganisms were cultivated for 4 weeks in presence of PUR. In regular intervals growth characteristics were determined and surface microscopy of polyurethane was tested. Degradation degree of modified foams corresponded with growth of both bacterial cultures. The highest degree of degradation by bacteria was found in PUR modified by activated starch, high biodegradation exhibited also polyurethanes modified by HEC and gluten. As the most stable structure in all microbial systems was found PUR modified by acetyl cellulose. Yeasts were less active in biodegradation than bacteria, however, substantial adsorption of cells on PUR surface was observed. In conclusion, microbial cultures can be used to biodegradation of modified polyurethanes; degree of degradation is strongly dependent on type of modification agents and microorganisms.

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BIOREMEDIATION OF CRUDE OIL IN SITU

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In last decade ecological friendly and cheap methods of bioremediation have been used worldwide. In oil refinery Pancevo (Serbia) there are many soil patches originated from accidentally leak crude oil. These patches are sources of both soil and air contamination. To remedy these patches we use microorganisms and plants in situ without transferring soil to another place. Primarily, the patches were deep plough mixed (to get uniform polluted soil) and then in this soil consortium of cultivated microorganisms was added. Previously autochthonous microorganisms were isolated, selected and multiplied. Due to the autochthonous microorganisms from the oil polluted soil, which is adapted in that condition, they were prepared for introduction in oily soil. In the experiment the pH, activity and number of microorganisms and oily content in soil were measured. In the beginning of the experiments, the highest concentration found in the soil was 59000 ppm. After 24 days the concentration decreased to 3200 ppm. To improve activity and number of microorganisms on this oily patches a few species of grass were sown. Most of the incorporated seeds are germinated (90%). After successful germination, the rate of growth of grass was recorded parallel with measurements of microbiological activity.

The results showed that it is possible to use autochthonous microorganisms and plants at oily soil to improve bioremediation in situ.

7. INDUSTRIAL CLEAN TECHNOLOGIES

POSTERS No. 67 – 71

REMOVAL OF VOLATILE ORGANIC COMPOUNDS BY ATMOSPHERIC DISCHARGE COMBINED WITH CATALYST UNIT

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Conventional techniques for the abatement of volatile organic compounds, such as thermal and catalytic oxidation of industrial waste gas are widely spread techniques because of their ability of total VOC destruction, although both suffer from low energy efficiency given the high operating temperatures. Technologies based on non-thermal plasmas could offer a good alternative. Yet, none of those techniques is capable of total VOC destruction. Therefore, efforts are made to further increase the removal efficiency by non-thermal plasma linked with a catalytic unit. It is supposed that by combining plasma and catalysis, the high efficiency of plasma activation and the high selectivity of catalyst could result in measurable synergy effect. A new type of DC atmospheric pressure glow discharge combined with a Cu-Mn/Al₂O₃ thermal catalyst was applied to the removal of VOC. Catalyst (operated temperatures up to 300 °C) is placed in series with a discharge chamber. In this study, inlet concentration range of VOC was stable at 45 ppm. The energy efficiency of the toluene removal process and the existence of a synergetic effect of the combined application of plasma and catalysis were investigated, with the aim to operate the catalyst at a lower temperature, i.e. at a lower energy cost.

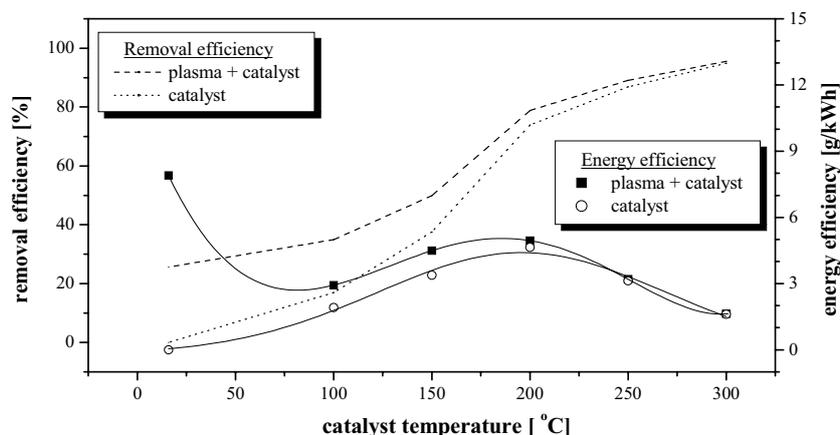


Fig. 1. Removal and energy efficiencies, toluene inlet concentration 45 ppm.

On the fig. 1 some important final results are demonstrated: removal efficiencies and energy efficiencies obtained in the discharge at room temperature, only for catalyst and for the plasma-catalyst combination at different temperatures in the concrete. To the results analysis obtained from the presented experiments we can say that the highest efficiency of decomposition – 96 % was reached at simultaneous operation of catalyst and plasma (catalyst temperature 300 °C, voltage 17,9 kV, discharge current 2,5 mA, energy efficiency 1,6 g/kWh). Fig. 1 shows particular conception of the energy consumption in experiment with heating of the catalytic bed. Seeing that the energy consumption for the heat activation of the catalyst is relatively high in comparison with the plasma generation, the energy efficiency does not reach such values at elevated temperatures as in the case of tests at room temperature. The removal process is the most energetically effective at 200 °C, there is the local maximum of the curves. The process is energy demanding at higher temperatures, we can obviously see a strong decrease of energy efficiency. At the same time there was very high efficiency of the whole decomposing process. Finally, the catalyst shows high decomposition ability of toluene, synergetic effect is visible especially at lower operation temperatures.

SOME POSSIBILITIES OF THE APPLICATION OF SOLID WASTES FROM FLUIDIZED BED COAL COMBUSTION

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This paper presents the preparation of composites of unusual composition based on solid residues after fluidized bed coal combustion, either fine fly ash from the separators or coarse bed ash. The main aim is focused on the determination and utilization of hydraulic properties of these untraditional materials. Submitted thesis is also devoted to the influence of superplasticizers of various type on physico – mechanical properties of prepared composites. The hardening of samples is dependent on the curing conditions (air, moist or water curing, influence of increased temperature, ect.). This work also considers the possibilities of preparation of lightweight composites based on the hydration of fine fly ash and on the decomposition of ettringite formed during the hydration process. The ratio bulk density to compressive strengths is very favourable, e.g. 1200 kg/m³ to 11 MPa (28 days). Further some possible correction of mixture composition in order to increase the quality of prepared composites are mentioned.

REDUCING EMISSION OF VOLATILE FLUIDS VAPOR

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Resolving the problem of various volatile fluids emission from storage tanks in Oil refinery Pančevo and Petrohemija Pančevo is not only of the environmental origin, but also the improvement of the process. This is very simple and cost-effective method which can be applied for reducing vapor emission of various oil derivatives. Causes of vapor emission from storage tanks are numerous: high temperature of the process, which leads to high partial pressure of volatiles, non – adequate thermic insulation, which implies on fluid evaporation at high environmental temperature, as well as when refilling tanks. Solving of these complex problems must include following steps: protective coating and thermal insulation coating system, which results in lowering volatile fluid temperature in tanks, mounting of heat exchanger (condenser) on the roof of tank, and condensate return to tank, which eliminate high loss of volatile fluids and improves process profitability.

Earlier researches regarding causes and level of air pollution, on Pančevo town territory confirmed high concentration of benzene, toluene and xylene in air of south industrial zone of Pančevo, which influence on air pollution in Pančevo. This air pollutants are produced by evaporation, insufficient combustion of oil derivatives in industrial and other furnaces, as well as in self combustion motor cars.

Poster No. 70:

CONSUMPTION SAVING AND EMISSION REDUCTION WITH CERTAIN FUEL ADDITIVES IN CASE OF GAS-TURBINE

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In the past years we have carried out numerous tests to reduce the emission and consumption of gas-turbines. The injection of the additive into the fuel gas, the exact load and consumption measuring of the turbine were always difficult. For this reason this year we have carried out a gas-turbine test on a 30kW large laboratory turbine. During the experiment, certain additives were mixed into the diesel fuel, while more than 100 parameters of the engine were continuously registered and analysed. The mechanism of the additive is double: on one hand it reduces the surface tension of the fuel that allows much better drop formation; on the other hand certain amine components of the additives help to reduce the NO_x emission of the turbine. Usually, in case of gas-turbines, the NO_x emission is the limiting parameter during the run of the engine

BONDING OF ENVIRONMENTALLY HAZARDOUS ELEMENTS IN INDUSTRIAL WASTES AND BUILDING MATERIALS MADE OF THEM

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The environmentally safe use of industrial waste materials (IWM) as components in building materials requires that the bonding of potentially hazardous elements in the inorganic components of these IWM is studied. The resulting knowledge is important for the assessment of the long-term stability of the bonding, and their possible tailoring aimed at minimization of hazardous elements leachability.

Within a large research project, a number of various IWM was collected. They involve above all fly ashes (from classical as well as fluidized-bed coal combustion), desulphurization products, different slags, waste rocks etc. The waste materials have been studied both as direct additives to cementitious building materials (concrete, mortars), and as components of raw meals for clinker burning. The individual mineral phases of clinkers resulting from burning of 3 – 23 % of IWM with suitable mix of ordinary raw meal components were analyzed using electron microprobe (EMPA) for major, minor, and trace (hazardous) elements. Simultaneously, bulk analyses of all components of the raw meal (including IWM) were obtained by wet silicate analysis (for major and minor elements) and ICP-AES (for trace elements). The third method used for assessing the apportionment of individual hazardous elements was phase analysis of clinkers by optical point-counting. The comparison of bulk contents with amounts of trace elements apportioned to alite, belite, and interstitial phases has shown that some hazardous elements are apportioned preferentially to the main clinker phase, alite (which makes 62 – 73 vol. % of prepared clinkers). This applies especially to Cr; while the major portion of elements like Ni, Co, V is incorporated in the interstitial phases. The apportionment of zinc varies from alite-prevalence to interstitial-phases prevalence. These findings are in accordance with observations of other authors – e.g. Shrisaka et al. (1996), Uchikawa and Hanehara (1997). The preferential bonding of some hazardous elements to the interstitial phases can be seen as beneficial - due to their lower solubility and leachability in settled concrete.

Another way of finding out the changes of original bonds and the correspondence of these changes to leachability is the comparison of direct EMPA observations with leaching tests - standard batch leaching tests (TCLP), batch leaching tests at differing solid / liquid ratios, sequential extractions, and column leaching tests. In the last method, IWM or the material containing processed IWM is leached in counter-flow by percolation at several different flow rates, analogous to different solid / liquid ratios used in batch leaching tests. Obtained results will be used for modeling the behavior of hazardous elements under various conditions and prediction of long-term evolution of their leachability.

Acknowledgements: The research was performed within The Scientific Research Project MSM 2623251101.

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8. WASTE VALORIZATION

POSTERS No. 72 – 33

DEACTIVATION OF V-NA-K-S₂O₇-SiO₂ CATALYSTS IN SO₂ INDUSTRIAL CONVERSION AND RECOVERING OF THE CATALYTIC PHASE IN AQUEOUS MEDIA

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The main part of the sulphuric acid is industrially produced from SO₂ oxidation in air. The catalyst is constituted of a ternary mixture of vanadium, sodium and potassium pyrosulfates molten at the reaction temperature (400-600 °C) upon silica support of low specific surface area. After using it for 3 years, the deactivated catalyst (several tons) is replaced and generally evacuated in open rubbish dump.

First, catalysts and their supports were characterized in their initial state and after deactivation, by N₂ adsorption, chemical analysis, electron microscopies (BEM, TEM), X-rays diffraction, IR, Raman and XPS spectroscopies. Deactivation is known as mainly resulting from V(IV) precipitation from the molten catalytic phase. We showed that deactivation additionally results from the decreasing of the specific surface area of the lamellar silica support, from metal ion diffusion into silica and possibly from the change of the crystalline form of part of silica. These catalyst transformations increase the deactivation rate.

Second, the kinetics of the dissolution of the catalytic phase in acido-basic aqueous solutions was studied. In all cases the vanadic phase was dissolved within two hours. This shows: i.) the danger for groundwater to leave the catalyst in open dump, ii.) the easiness of recovering the catalytic phase before throwing the catalyst out, iii.) the possibility of recycling the active phase.

BLACKCURRANT SEEDS (WASTE BY-PRODUCT) AS A SOURCE OF PHARMACOLOGICALLY IMPORTANT POLYUNSATURATED FATTY ACIDS

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Blackcurrant seeds are presently available in the Czech Republic as a waste by-product of blackcurrant juice production, which is available in relatively large quantities as a residue from the production of jams, jellies and juice liquors. Our results demonstrated feasibility of the effective extraction of blackcurrant seeds in SC-CO₂ recycling reactor. Both, the yield of the blackcurrant oil and their fatty acids profile were found to be similar to those achieved previously by our experiments using a conventional extraction of blackcurrant seeds by hexane.

The project was focused on obtaining α - and γ -linolenic acids from blackcurrant oil by enzymatic hydrolysis in SC-CO₂. The linolenic acids belong to two families of essential fatty acids, which are not inter-convertible in humans, display different physiological functions and act in concert with one another to regulate biological processes. Based on the significance of these acids new selective lipases from *Geotrichum candidum* displaying specificity to natural unsaturated compounds (such as polyunsaturated fatty acids and their derivatives from natural plant oils) have been prepared. The lipases were used as biocatalysts in the blackcurrant oil hydrolysis performed under SC-CO₂.

Acknowledgement: The authors thank Grant Agency of Czech Republic for financial support of this research through the GA CR 203/04/0120 project and Czech part of the project (D30.001) funded by Ministry of Education of the CR.

**9. ATMOSPHERIC CHEMISTRY, AIR POLLUTION,
MODELING OF POLLUTANTS DIFFUSION**

POSTERS No. 74 – 81

ACTIVE BIOMONITORING WITH WET AND DRY MOSS: BELGRADE URBAN AREA CASE STUDY

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Active biomonitoring with the moss species *Sphagnum girgensohnii* was tested in an urban area of the city of Belgrade (Serbia) to examine the role of different humidity conditions on the efficiency of element accumulation and retention during the exposure time. Bags with moss from a pristine wetland area (Dubna, Russia) were exposed in parallel with and without irrigation, using specially constructed holders placed about 5–10 m above the street level. The moss bags were exposed for 3 and 6 months respectively. A total of 32 elements were determined by INAA (Na, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Sb, Cs, Ba, La, Ce, Sm, Tb, Yb, Th, U) and by AAS (Cd, Pb, Cu). Higher relative uptake in the irrigated moss bags was evident for Al, Cl, Cr, Fe, Cu, Zn, Rb, Sr, Cs, and Pb. For a majority of the investigated elements a positive accumulation trend with time was observed (6 *versus* 3 months of exposure). However, some elements (Cl, K, Mn, Rb, Cs) were released from moss during the exposure time as evident from a decrease relative to initial element concentrations. It was shown that the relative humidity of the exposed moss is an important factor in its accumulating capacity. The moss transplant technique applied enabled assessment of contamination levels of the elements studied through calculation of contamination factors in the sampled area and distinguishing the main pollution sources.

CONTENT OF HEAVY METALS IN FOOD SAMPLES IN THE SURROUNDING AREA OF ALUMINUM FACTORY PODGORICA DURING THE PERIOD 1993-2005

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Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. Heavy metals are dangerous because they tend to bioaccumulate. Still, food poisoning from heavy metals is very rare and in most cases only occurs after environmental pollution. The expansion and accelerated technological development, especially the area of chemical industry, cause serious problems at local as well as at global level of the environment contamination.

An immediate mental association with environment is “pollution”. Pollution of the environment is a major world wide issue. The contribution of heavy metals and their ions toward pollution problems is of very serious concern, largely because the physiological effects of some of them may be substantial even at concentrations that are extremely low. This is especially true for the heavy metals (any alkaline or nonalkaline earth element below the second period of the periodic table) 1.

The aim of this work was to show the content of some heavy metals such as Cu, Zn, Fe and Mn in a food samples (milk, cheese and green cabbage) in surrounding area of Aluminum Factory Podgorica during the period 1993-2005, as medium concentration for each metal in samples per year. The testing results show that there was no contamination of milk and cheese samples, but it is noticed slightly increase of content of metals in mentioned period in this samples which is still below the recommended values (RV-Table 1) for chemical content of food 2.

In a green cabbage concentration of heavy metals is higher than recommended values and constantly increase. Minimum concentration for Zn was 2.25 mg/kg and maximum 6.25 mg/kg, for Fe min. 14.3 mg/kg, max. 30.1 mg/kg, Cu min. 0.55 mg/kg, max. 1.87 mg/kg and for Mn min. 3.52 mg/kg, max. 5.72 mg/kg. The explanation for these results is probably the consequence of the influence of Aluminium Factory.

Table 1. Recommended values for chemical content of food

Food samples	Cu	Zn	Fe	Mn
Cheese mg/kg	-	-	4	-
Milk mg/l	0.4	4	1	-
Green cabbage mg/kg	1	4	6	-

References: 1. Bailey, Clark, Ferris, Krause, Strong, Chemistry of the Environment 2. Tables of chemical content of food

TEMPORAL AND SPATIAL VARIATIONS OF GENOTOXICITY AND POPS CONCENTRATIONS IN URBAN AIR

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Zlín town with about 80 000 inhabitants lies along the river Dřevnice in a mild climatic area of southeastern Moravia – Czech Republic. The extent of the town is 118 km². Most significant in this town are energetics, rubber, plastic industry and shoemaking trade. The aim of this study was to demonstrate temporal variations of quality of the air samples collected in 10 urban sites in Zlín. Air samples were collected with passive air sampling method. The passive samplers were situated at 10 selected sites in Zlín in eight campaigns (from February to October 2006), 28 days each. Short-term bacterial genotoxicity test (SOS chromotest) was used for the genotoxicity detection of collected samples and results from this test were compared with chemical analyses of air samples. Biological and chemical results were compared in dependence on temporal variations. Passive air sampling technique coupled with a biological system and chemical analyses proved to be a sensitive tool capable of monitoring the air quality. Integration of these techniques came right to localization of “hot spots”, identification of most significant sources of pollution including seasonal variations and this all with very low costs.

Keywords: genotoxicity, ambient air, POPs, passive air samplers

PASSIVE AIR SAMPLING TECHNIQUE AS A TOOL FOR THE LONG-TERM AIR QUALITY MONITORING

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The potential of passive air sampling (PAS) devices to assess the influence of local sources on the quality of surrounding environment was recently investigated as well as their sensitivity to the seasonal variations in the ambient air concentrations of POPs. The fact that PAS showed a very good capability to reflect temporal and spatial fluctuation in POPs concentrations makes them applicable for monitoring on the local and regional scale.

Following the results of those pilot studies, PAS have been employed in the long-term monitoring of the various local sources in the Czech Republic starting 2004, with a number of rural and mountain sites estimating the role of the long-distance transport added to the network in 2005. The steps for extending the program to cover most of the Central and Eastern Europe were taken in 2006. Results of the long-term employment of PAS in the regional monitoring program as well as the unique study employing PAS as a tool for monitoring of decontamination processes and assessment of risks connected with the old burden sanation will be presented here.

POLYCHLORINATED NAPHTHALENES IN THE AIR AND SOIL SAMPLES FROM THE CZECH REPUBLIC

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Polychlorinated naphthalenes contain one to eight chlorine atoms per naphthalene molecule, and they form complex mixtures of 75 congeners. They were used as preservatives, intermediates for paints, additives to machine oils or rubber products, and flame retardants. The production of PCNs decreased in the late 1970s. PCNs are persistent, more or less planar, and several investigated congeners exhibited a high dioxin-like toxicity.

Air and soil samples were taken in 2005. Passive air samplers based on the PUF as a sampling medium were used. Samples were collected from 33 sampling sites representing industrial, urban, rural, and background locations.

Air samples: PCN levels were determined in the most of samples. In general, the PCN concentrations in the air samples are low (2, respectively 4 orders of magnitude lower when compared to PCBs and PAHs). The average amount of PCNs (18 congeners, mono- to octachlorinated) sequestered in the passive filter exposed for 28 days ranged from 114 to 519 pg/filter. Homologue profile was dominated by mono- and dichloronaphthalenes at rural and background sites. At urban and industrial sites, tri- to pentachloronaphthalenes were also detected. No hexa- to octachloronaphthalenes were detected in any of the air samples.

Soil samples: PCN concentration in the soil samples ranged from 37 to 1120 pg g⁻¹. Mono- to octachlorinated congeners were found in the soil samples, the homologue profiles significantly varied among individual locations. PCN concentration in the soils was 2-3 orders of magnitude lower when compared to PCBs.

EFFECTS OF THE VICINITY OF INDUSTRIAL POLLUTERS ON THE ACCUMULATION OF HEAVY METALS IN GRAINS

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Heavy metals are environmental pollutants that play an important role in the induction of many diseases due to their ubiquity, large affinity to biological tissues and long half-life in living organisms. Their biomagnification within the food web leads to significant contamination of food used in human nutrition. Grains (especially wheat) comprise the large part of human diet. The aim of this research was to investigate the impact of the vicinity of industrial polluters on the accumulation of heavy metals in grains. Sampling of wheat was conducted in 2003 in the city of Pancevo in southern Vojvodina (Serbia) from the cultivated land at three distances from the industrial polluters (500, 1000, 1500 m). Samples were prepared for AAS by digestion with mineral acids. Statistical processing of experimental data indicates that distance between polluters and plants has no significant effect on the concentration of iron and zinc. The statistically significant difference exists for manganese, copper, nickel and cadmium, but no regularity could be established between detected amounts of metals and dista

ASSESSMENT OF THE LEVELS AND SOURCES OF TRACE ELEMENTS IN PM₁₀ AND PM_{2.5} IN BELGRADE

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An assessment of air quality of Belgrade, Serbia, was performed by determining the trace element content in airborne PM₁₀ and PM_{2.5} in 2-years period of June 2003 through July 2005. In order to provide information about the annual average and daily maximum concentrations and to compare them to the corresponding EU standards. The results may be used in the future to assess the effectiveness of the implemented emission control strategy.

24 h samples were collected at two locations in a heavy polluted area with low volume air samplers provided with PM₁₀ and PM_{2.5} cutoff inlets.

The annual mean PM₁₀ and PM_{2.5} mass concentrations exceeded the European Union air quality annual standard. Chemical analysis of the metal content showed that Zn (1998 ng m⁻³) was the most abundant element in PM_{2.5} and PM₁₀ (besides Fe), and higher than the reported values for other urban areas in Europe. The mean Ni concentration of 28.4 ng m⁻³ in the PM_{2.5} fraction was above the critical value of 20 ng m⁻³ for PM₁₀ according EC, 2003 regulations.

The concentrations of 10 elements (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) were determined with graphite furnace atomic absorption spectrometry (GFAAS). Results indicated that among trace metals, the ambient concentrations of Zn, both in PM₁₀ and PM_{2.5}, were the highest (1389.18 and 1998.00 ng m⁻³), while Cd concentrations were the lowest (1.39 and 0.85 ng m⁻³). The limit values of toxic trace elements from WHO and EC Air quality guidelines were not exceeded except for Ni.

Enrichment factors for elements in aerosols were determined to evaluate anthropogenic versus natural sources. Elements with a toxic character (Zn, Cd, Pb and Cu) were highly enriched, confirming that they originate mainly from anthropogenic sources.

The meteorological study revealed some differences in concentrations, stratified by prevailing wind directions. The classification of concentration levels by defined wind subgroups can provide important information on the potential impact of various sources and particle transport between zones of a wider geographical area. Data evaluation showed that higher trace element concentrations were associated with calm conditions suggesting a great influence of local sources. The appearance of stronger W, SE and NE flows is responsible for the transport of particles originating from the thermoelectric plant complex and industrial zones surrounding Belgrade.

A multivariate receptor modeling (Principal Component Analysis, Cluster Analysis) has been applied to a set of data in order to determine the contribution of different sources of specific metallic components in PM₁₀ and PM_{2.5}. The obtained results showed that vehicle traffic and anthropogenic emissions related to fossil fuel combustion in stationary objects were the main sources of trace metals in Belgrade urban aerosols.

CONTINUOUS DETERMINATION OF PAHS IN URBAN ATMOSPHERE

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Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion of carbonaceous material at high temperatures [1]. PAHs are ubiquitous in the lower atmosphere and generated from both natural and anthropogenic sources. Human exposure to PAHs can occur through several environmental pathways due to their numerous sources. However the occurrence of PAHs in urban air has caused particular concern because of the continuous nature of the exposure and the size of population at risk. Polycyclic aromatic hydrocarbons in the atmosphere are known to be predominantly associated with particulate matter [2].

In this work, airborne particulate matter from the atmosphere of the city of Arak was collected on ultra-pure quartz fiber filter (Whatman QM-A) using a high volume air sampler. Sampling flow rate was $1 \text{ m}^3 \text{ min}^{-1}$ and performed in days and at nights. $1 \text{ m}^3 \text{ min}^{-1}$ respectively. The exposed filters were extracted by soxhlet procedure with dichloromethane. The determinations were carried out on a Varian gas chromatograph, Model CP-3800. The system was equipped with a FID detector and a temperature programming was used for successive separation. The day to day and also day and night variation in concentrations of PAHs in the atmosphere were investigated.

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10. MARINE CHEMISTRY AND MARINE POLLUTION

POSTERS No. 82 – 84

**EVALUATION METALS AND ALIPHATIC HYDROCARBONS
DISTRIBUTION IN BIVALVES FROM HUELVA ESTUARINE AREAS
(SOUTHWEST SPAIN) AFTER OIL SPILL**

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Huelva coast in the southwest Spain is an important production area for bivalve and shellfish used for consumption. In the past few decades, the high industrialization and the increase of shipping traffic in Huelva have led to special attention being given to the monitoring programs about the occurrence of petroleum hydrocarbons in the marine environment. A recent oil spillage caused by a refinery located in the area has been the focus of different studies related with the assessment of hydrocarbons in the most characteristic marine organisms. The study is similar to other previously performed in the northwest coast of Spain after the Prestige oil spill (1).

The present work considers the presence of toxic metals and aliphatic compounds in six sampling sites selected in connection to their position with the oil spill: “Enebrales, Espigón, Río Piedras, Rompido I, and Rompido II”.

Aliphatic hydrocarbons were analyzed by GC-FID. The metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Cd, and Pb) were evaluated by using ICP-MS after sample digestion with in acid medium. Organic compounds were Soxhlet extracted with hexane followed by clean-up in Florisil column. Results obtained are discussed in relation to the potential pollution of the area.

(1). N. Carro, J.Cobas and J.Maneiro, Environ. Res. 100 (2006) 339

SPECIATION OF INORGANIC ANTIMONY IN TRAFFIC-RELATED AIRBORNE PARTICULATE MATTER

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(1). N. Carro, J.Cobas and J.Maneiro, Environ. Res. 100 (2006) 339

MERCURY PARTITIONING IN WATERS EXCHANGING BETWEEN A CONTAMINATED LAGOON AND THE ATLANTIC OCEAN

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Ria de Aveiro, a coastal lagoon on the north-west coast of Portugal received during four decades a mercury (Hg) contaminated effluent from a chlor-alkali industry, which resulted in the accumulation of more than 30 ton of mercury in its sediments. Sediments are recognized as major repositories of mercury in estuaries and could be a significant source of metal to the overlying water column via release from the solid phase during resuspension. The subsequent distribution between the suspended particles and the water (dissolved fraction) determines its reactivity, bioavailability, transport and fate. Being the main forcing of water circulation in Ria de Aveiro, tides can play a major role in the dispersion of mercury within the lagoon and in the transport to the Atlantic Ocean through the single outlet connection.

To understand the effects of hydrographical and geochemical factors on the distribution of mercury in waters exchanging in the interface of this contaminated lagoon and the Atlantic Ocean, mercury partition in the water column was investigated during four tidal cycles, in contrasting season and tidal regimes (summer/winter and neap/spring tides). Total and reactive dissolved Hg and particulate Hg were measured and their concentrations were related with parameters such as salinity, chlorophyll a, dissolved organic carbon, suspended particulate matter as well as particulate organic carbon content.

Seasonal variability was more evident for particulate Hg, with concentrations in the four campaigns ranging between 0.28 and 1.05 $\mu\text{g}\cdot\text{g}^{-1}$. No pattern was observed for dissolved mercury concentrations during the tidal cycles, with levels ranging between 1.5 and 17.5 $\text{ng}\cdot\text{L}^{-1}$. Furthermore, all mercury fractions present higher concentrations during winter regardless the tidal amplitude. Moreover, spring tides conditions showed higher mercury levels than cycles with lower tidal amplitude. During winter and especially in spring tides, the higher river discharge and the higher tidal currents (double intensity of neap tide currents) enhances resuspension of particles in the shallow and more contaminated areas. Besides, addition to dissolved fraction is also enhanced by salt intrusion that moves upstream in spring tides, with an increase in ionic strength and competing ions (ion exchange and chloro-complexes formation). In fact, although mercury is mainly associated with particles in the four campaigns, the highest additions to dissolved phase were observed in spring tides.

The nature of particulate organic carbon and dissolved organic carbon present in water column during the year and for different tidal amplitudes is probably contributing to differences in metal partition. An organic enrichment of suspended particles was observed for lower concentrations of suspended particulate matter, but no evidence of particle concentration effect was observed. Fluxes measured during the tidal cycles showed a contrasting behavior of dissolved and particulate fractions, evidencing the importance of understanding factors controlling the particle-water reactivity and partitioning of mercury in estuaries.

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11. ANALYTICAL METHODS FOR ENVIRONMENTAL SCIENCE

POSTERS No. 85 – 128

A SUGGESTING OF BIOSENSOR FOR DETERMINATION PALLADIUM

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The literature survey shows that the concentration of platinum group metals in diverse environmental matrices has increased significantly over the last two decades. Therefore, the amount of Pt and Pd released into the environment, their impact on human health, and routes for bioaccumulation and transformation in urban environment have to be monitored. Despite recent advances in instrumental techniques the analysis of Pt and Pd in geological, industrial, biological and environmental samples is still difficult task. Recently, we suggested a biosensor for determination of cadmium and zinc. Due to convincing results obtained, we focused on utilizing of the suggested biosensor to determine palladium. The suggested biosensor is consisted from hanging mercury drop electrode and metallothionein (MT), which belongs to group of intracellular, cysteine-rich proteins with high affinity to heavy metals. To suggest biosensor, we utilized adsorptive transfer stripping technique (AdTS) coupled with differential pulse voltammetry (DPV). We were interested in the issue of how the DPV record of MT modified electrode surface looks like in the presence of palladium. We observed three signals: CdT at -0.66 V, ZnT⁻ at -0.87 V and peak at -1.11 V called PdMT that could correspond to reduction of platinum bounded to MT. For analytical purposes we studied the dependence of the PdMT peak and/or CdT signal heights on palladium concentration. We were able to determine tens of pmoles of palladium in 5 μ l.

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INVESTIGATION OF SILVER IONS INFLUENCE ON PLANT EMBRYOS BY MEANS ELECTROCHEMICAL TECHNIQUES

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Pollutants containing heavy metals and toxic organic substances enter the ecosystem especially from applications of fertilizers, pesticides and other industrial products. Studies of plant responses to heavy metal stress are especially important for the understanding of a number of biological processes. On the other hand, study of influence of heavy metals on a tree is rather difficult, sometimes, almost impossible. Thus, possibilities how to simplify this kind of study is need. A using of cell cultures for the above mentioned purposes is one of these possibilities. Thus, we investigated influence of silver ions on early somatic embryos of Blue Spruce clone PE 14 by means of different electrochemical techniques. We were interested in the issue how much silver ions can embryos uptake during four days long treatment. For this purpose, we used optimized high performance liquid chromatography with electrochemical detection technique. The content increased with increasing treatment time and applied concentration. We also studied how silver ions can influence thiols content in the treated embryos. We used adsorptive transfer stripping voltammetry in connection with differential pulse voltammetry – Brdicka reaction to reach this aim. It clearly follows from the obtained results that content of thiols increased with increasing treatment time and applied concentration.

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A DETECTION OF METALLOTHIONEIN CONTENT IN TISSUES OF VARIOUS ANIMALS

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Metallothioneins (MT) belongs to group of intracellular, high molecular and cysteine-rich proteins with molecular weight from 6 to 10 kDa. Thanks to their high affinity to heavy metals e.g. zinc, copper and/or cadmium, homeostatic control and detoxification of the metals are their main physiological function at evolutionary different animal organisms. The MT was discovered in 1957, when Margoshes and Valee isolated it from horse kidney. MTs consist of two binding domains (α , β) that are assembled from cysteine clusters. A crystal structure of metallothionein binding cadmium and zinc was described in 1986. In addition, it seems that MT could have crucial biological properties than regulation of content of toxic metals in an organism. Particularly, very interesting links between MT concentration and cell proliferation or foetus development have been described. Here, we focused on determination of MT in tissues of different species of birds (pheasant, quail, partridge, guinea fowl and turkey) due to characterization of these species with respect to content of MT. The adsorptive transfer stripping technique in connection with differential pulse voltammetry – Brdicka reaction has been utilized for this purpose. We found out that the content the protein of interest differed among the species markedly.

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EXTRACTION EFFICACY AND ANALYSES OF MULTIPLE CYANOBACTERIAL TOXINS IN ENVIRONMENTAL SAMPLES AND DRINKING WATERS

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Massive developments of cyanobacteria in recreational reservoirs or drinking water supplies have become a worldwide problem due to eutrophication of surface waters. The dominance of cyanobacteria has negative effects on environmental water quality (decreased biodiversity, low transparency, pH changes, odours release, production of toxins). Cyanobacteria produce various types of toxins differing in chemical structure such as hepatotoxins (microcystins, nodularin, cylindrospermopsin), neurotoxins (anatoxin-a, anatoxin-a(s), saxitoxin) and lipopolysaccharides. In spite of a variety of cyanotoxins, the WHO guideline value of 1.0 microgram per litre of drinking water was recommended only for a single type of cyanotoxins - microcystins. Chemical monitoring of cyanotoxins is complicated as cyanobacteria produce complex mixtures of toxins that might be bound to biomass or released into the water column. In this report we summarize our studies of microcystins as well as other toxins (anatoxin-a, cylindrospermopsin) in the water bodies of the Czech Republic. We demonstrate development and applications of various extraction and analytical methods using HPLC-PDA or ELISA for analyses of different matrices. The results are discussed in relation to human health risks associated with cyanotoxins. Supported by the Ministry of Education CR project IM6798593909 "Research Centre for Bioindication and Revitalization" and the GAAV Grant No. KJB6005411.

OXIDATION OF ORGANOPHOSPHORUS PESTICIDES WITH CHLOROPEROXIDASE ENZYME IN THE PRESENCE OF AN IONIC LIQUID AS CO-SOLVENT

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Organophosphorus (OP) insecticides can be detected in various media using the acetylcholinesterase (AChE) enzyme inhibition assay coupled with the thermal lens spectrometric (TLS) technique. Thio-OP pesticides (with the P=S moiety), which are mostly used in agriculture do not inhibit acetylcholinesterase *in vitro*, therefore the detection limit for their determination is relatively high. To achieve satisfactory limit of detection for these compounds oxidation of thio- to oxo-OP (P=O moiety) compounds is required. In our previous work we already showed almost complete (stoichiometric) conversion of some thio-OP to oxo-OP insecticides using chloroperoxidase (CPO) enzyme from marine fungus *Caldariomyces fumago*, both in batch and in flow system with immobilized CPO enzyme. Using TLS detection technique 20-30 times higher sensitivity can be achieved with ionic liquid (IL) as a medium instead of water. ILs have better thermo-optical properties than water, comparable to organic solvents, but the latter have high vapor pressure, and are problematic from environmental standpoint. And what is even more important, enzyme activity in organic solvents is greatly reduced. Consequently their use in AChE inhibition assay is limited.

As our goal is development of a rapid detection of OP insecticides using AChE inhibition assay coupled with on-line CPO oxidation step, we tested several ILs as co-solvents in the CPO oxidation reaction. Oxidation reaction yield obtained was compared to yield obtained in citrate buffer. Some ILs like those based on EtPyTFA (EtPy⁺Cf₃COO⁻) and BMIM⁺ Methylsulphate⁻ gave good reaction yield comparable to those obtained in citrate buffer, while others completely inhibit the CPO oxidation reaction (EtPy⁺PF₆⁻ and BMIM⁺ Br⁻). Generally, increasing the concentration of the IL from 2% to 30% decreased the CPO activity and oxidation yield. This could be partially explained by reaction mixture pH change as oxidation reaction has pH optimum around 2,9 and pH values above 4 give no oxidation products. In some cases reaction mixture pH could not have been measured and was not corrected. When choosing IL convenient for AChE inhibition assay one have to take into account also the inhibition potency of IL for AChE enzyme as some ILs are strong AChE inhibitors. However, it has been shown before that pesticide inhibition effect in IL presence can be enhanced thus further improving the sensitivity of the assay.

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MONITORING OF TRACE METALS CONCENTRATIONS IN THE SVITAVA RIVER BY DIFFERENT ANALYTICAL TECHNIQUES

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During the April 2005 and October 2005 an experiment was carried out in Svitava River (Czech Republic, South Moravia). The concentrations of Cd, Cu, Cr, Pb, Ni and Zn were monitored using different sampling techniques. The diffusive gradient in thin films technique (DGT) [1] was used for sampling of kinetically labile metal species, which plays the main role in the toxicity toward the biota. The phytoavailable concentrations of trace metals were monitored by application of moss bags with *Fontinalis Antipyretica* aquatic moss species. Total dissolved and total metal concentrations were also monitored in the river water using the conventional sampling techniques. The deployment time of *Fontinalis Antipyretica* moss bags [2] and DGT sampling units was the same (28 days). This allowed better comparison of the two techniques.

The study demonstrates, that concentrations of Cd, Cr, Pb and Zn measured by DGT are comparable with phytoavailable concentrations measured by deployment of aquatic moss *Fontinalis Antipyretica*. On the other hand significant differences between DGT_{Cu} and DGT_{Ni} concentrations and phytoavailable concentrations were found. The phytoavailable concentration of Cu correlated better with the total dissolved concentration of Cu, while phytoavailable concentration of Ni does not correlate with any of measured concentration. Different incorporation mechanism and uptake of Ni and Cu to the *Fontinalis Antipyretica* may give rise to these findings. DGT technique measures only kinetically labile metal species which are able to diffuse through the diffusive gel and which are able to be captured in the sorption gel. If we assumed that the thickness of diffusive gel used during the experiment was 0,8mm, only free metal ions and metals bonded in complexes able to dissociate within 2 min. were measured by DGT. On the contrary, diffusion through the biological membrane is more difficult process and the time for dissociation of metals bonded in complexes with natural ligands should be higher. From this case *Fontinalis Antipyretica* is able to accumulate also the fraction of metals which can be not measured by the DGT.

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A RAPID APPROACH TO EVALUATE THE PRESENCE OF POLYCYCLIC AROMATIC HYDROCARBON (PAH) IN URBAN SOIL

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An increasing interest was focused in the last decades to monitoring the fate of polycyclic aromatic hydrocarbon (PAH) in urban areas, due to their persistence in soils and their potential carcinogenic effects in mammals. A study was conducted to investigate the distribution of PAH in a sub-urban soil in Falconara city (Marche region, Middle Italy). The soil was sampled in a traffic island (grass field) very close to an oil refinery, stored in a glass bottle at 4°C in the dark prior to analysis. An sample of 5 g was put into a glass tube, added with 20 ml of dichlorometane/acetone (1:1) extractant solution, shaken by hand for 2 min, and finally sonicated with a total energy of 1312 J for 6 min. Then, the sample was centrifuged and filtered through 0.2 µm regenerated cellulose filters. An aliquot of 2 ml was concentrated under a gentle steam of pure N₂ and recovered with 1 ml of acetonitrile. The PAH were analyzed by a Dionex HPLC system equipped with a UV detector, a C-18 reverse-phase column (150 l x 4.6 mm i.d.), and by using a gradient separation acetonitrile/water. A standard solution of naphthalene, phenanthrene and pyrene, used to evaluate the instrumental response, showed a good correlation coefficient (> 97%) (tested range 0.01-1 mg L⁻¹). Preliminary data seems to support the effectiveness of this approach, indicating the occurrence of all the PAH, respectively, at 0.23 mg Kg⁻¹ for naphthalene, 0.15 mg Kg⁻¹ for phenanthrene, and 0.28 mg Kg⁻¹ for pyrene.

THE ROLE OF SPECIFIC MOLECULAR FRACTIONS IN SYNCHRONOUS FLUORESCENCE SPECTRUM OF LIGNITE HUMIC ACIDS

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Humic acids represent unique and ubiquitous natural substrate with profound properties and important role in many natural processes. Their genesis is associated with microbial decomposition of dead plant tissues and animal bodies. From the chemical point of view humic acids were traditionally assessed like a polydispersive macromolecular system. This aspect was and still is the basic premise in the conventional interpretation of their fluorescence spectrum. In contrast, recent experiments show humic acids as the complex associations of relatively small molecules (up to 1000 Da) randomly bonded together by weak hydrophobic interactions and hydrogen bonds.¹ High molecular dimension which was frequently reported could thus be attributed to the humic molecules self-aggregation properties that are a logical consequence of their mostly amphiphilic nature.

The aim of this work was to investigate the role of specific sequentially extracted molecular fractions (water-soluble components, free and bonded lipids) in the secondary structure of humic acids (domains) and to assess consequent changes of optical properties using synchronous fluorescence spectroscopy (SFS). The advantage of applied extraction technique relies in the selective removal of humic constituents and identification of labile diagnostic molecules without the profound structural alteration of more drastic degradation methods. In principle, the sequential extraction included three steps: hot water extraction in which mostly hydrophilic molecules were removed (alcohols, acids); second step included the extraction by dichloromethane and methanol (fatty acids, alkanes, steroids, and tricyclic diterpenic acids, mid-chain and ω hydroxyl-substituted carboxylic acids) and third step the transesterification by boron trifluoride and methanol solution (removing of di- and tri-hydroxyalkanoic acids, α , β and ω -hydroxy fatty acids, alkanolic acids, α,ω -alkanedioic acids, *n*-alkanols, phenolic acids and sterols).² After each extraction step a part of the solid rest of humic acids was removed, titrated by NaOH to pH 13 and freeze-dried. Further, each fraction was then dissolved in water and measured on synchronous fluorescence spectroscopy ($\Delta\lambda=20$ nm).

As demonstrated recently,³ the main problem of fluorescence measurement of humic substances can be seen in the inner filter effect (quenching) caused by interactions among self assembled humic molecules. Hydrophobic effect is the driving force causing pressing of individual amphiphilic molecules together which results in creation of highly conjugated system of unsaturated bonds. As a result typical fluorescence spectrum seems to indicate a system of specific fluorophores which supported the conventional approach to interpret individual peaks as a superposition of particular fluorophores; in line with our results traditional view can be swapped by the finding that the character of fluorescence spectrum is a function of conformation arrangement of humic molecules.

SFS spectra of humic acids shows main peak at 488 nm and minor peaks at 360, 380, 418, 471, 488, 501 and 512 nm. Removing of water-soluble components caused an increase of fluorescence intensities by all peaks except one at 360 nm. Removing of free lipids showed decrease of fluorescence intensities by all peaks from 360 nm (the most intensive decrease) to the main peak at 488 nm (slight) while at 501 and 512 nm increase of fluorescence intensity. Removing of bond lipids resulted in a decrease of fluorescence intensities by all peaks in comparison with original humic acids, however it showed a relative increase of intensities at lower wavelengths.

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QUALITY CONTROL OF MINERAL INSULATING LIQUIDS – ENVIRONMENTAL AND SAFETY ASPECTS

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Aromatic compounds are naturally present or added in insulating oils for improving their properties - gas absorbing properties, oxidation stability, dielectric strength and low flammability. It is well known that presence of natural polycyclic aromatics (PCA) in mineral insulating oils and synthetic insulating aromatics - polychlorinated biphenyls (PCB) above limited amounts, produces negative influence on environment and represent health and safety risk. Using of aromatic compounds in mineral insulating oils in certain concentration is regulated by International Electrotechnical Committee Standard (IEC) –Standard for unused transformer oils 60296, which includes PCA and PCB as obligatory measurements. Transformers in electrical power network system are mainly filled with mineral insulating oils. Mineral insulating oils naturally contain significant amount of aromatic compounds. Particular group of polycyclic aromatic compounds PCA which has significant amount of carcinogenic and mutagenic influence on humans are presented in this work. Synthetic insulating liquids based on polychlorinated biphenyls PCB's, where used in significant number of transformers and capacitors in industry because of their well known properties - excellent dielectric properties and also because of their very low flammability. Their properties are linked to the toxic nature of PCBs and their negative biological effects. PCBs are not compounds naturally present in base oils, but can be introduced by contamination. PCB contaminated oils presents actual risk in spreading contamination in testing laboratories and in equipments for oil treatment. An example of transformer oil contamination in hydro power plant is presented in this work. Transformer contamination with PCB's encounters great economical losses, due to lack of maintenance which involve high risk in electrical power production and transmission. According to EPA regulations and Basel Convention Serbia started to retreat PCB electrical equipment from use. In Serbia Laboratory for Testing and Standardization, department for insulating materials testing regularly control quality of new and used mineral oil, including PCA and PCBs testing. In particular, this paper deals with importance of preventive laboratory testing and ecological requirements to the use of new and used mineral insulating oils.

Key words: transformer oils, polychlorinated biphenyls (PCB), polycyclic aromatics (PCA)

EVALUATION OF EXTRACTION/DISSOLUTION TECHNIQUES USED FOR THE DETERMINATION OF THE LEAD ISOTOPIC COMPOSITION IN FOREST SOILS

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Lead isotopic studies in soils present an efficient tool for tracing the sources of lead pollution. However, there is no agreement between authors concerning the analytical procedure of lead isotopes analyses, especially the extraction or dissolution method chosen. Five different extraction/dissolution techniques (0.05 M EDTA, 0.5 M HNO₃, 2 M HNO₃, *aqua regia*, total dissolution) were used for lead isotopic composition (²⁰⁶Pb/²⁰⁷Pb) determination in three forest soil profiles with a different prevailing type of contamination (unpolluted area, smelting area and vicinity of a motorway). The obtained results show that all extraction/dissolution methods used for the determination of ²⁰⁶Pb/²⁰⁷Pb ratios in surface horizons containing high amounts of organic matter give statistically identical values (according to the Tukey test). In mineral soil horizons the differences between the individual extraction/dissolution methods can be observed (the lowest ²⁰⁶Pb/²⁰⁷Pb ratios obtained from EDTA-extracts, corresponding to weakly bound anthropogenic lead, and the highest ²⁰⁶Pb/²⁰⁷Pb ratios obtained from total dissolution). The extremely contaminated soil in the vicinity of the smelter can be regarded as an exception where results obtained from all methods in both organic and mineral horizons are statistically identical. The combination of total dissolution and EDTA extraction (bioavailable lead) seems to be the optimal combination for ²⁰⁶Pb/²⁰⁷Pb ratio determination and optimal result interpretation.

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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF NITRITE IN POLLUTED WATER AND SOIL SAMPLES USING DIAZO-COUPPLING REACTION

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A simple and sensitive spectrophotometric method was described for the determination of nitrite. The method is based on the reaction of nitrite with 3-amino-5-methyl isoxazole to form a diazonium ion, which is coupled with resorcinol in an alkaline medium to form the azo dye, with a maximum absorption at 354 nm. Beer's law is obeyed over the range of 0.02- 4.0 µg/ml, with a detection limit of 0.01µg/ml. The molar absorptivity, Sandell index are 2.195×10^4 L/mol Cm and 0.0026 µg/ml respectively. The effect of 35 cations and anions were studied. The method was applied for determination of nitrite in polluted water and soil samples, the results were compared with the standard method, NEDA. The prepared azo dye was extracted into 1:1 (v/v) mixture of isoamyl alcohol-isobutyl methyl ketone. Nitrate was determined over the range of 0.001-2.0 µg/ml with a detection limit of 0.0005 µg/ml and molar absorptivity 6.704×10^4 L/mol. cm.

FLUORESCENCE SPECTROSCOPY OF HUMIC SUBSTANCES ISOLATED FROM EUTRIC CAMBISOL

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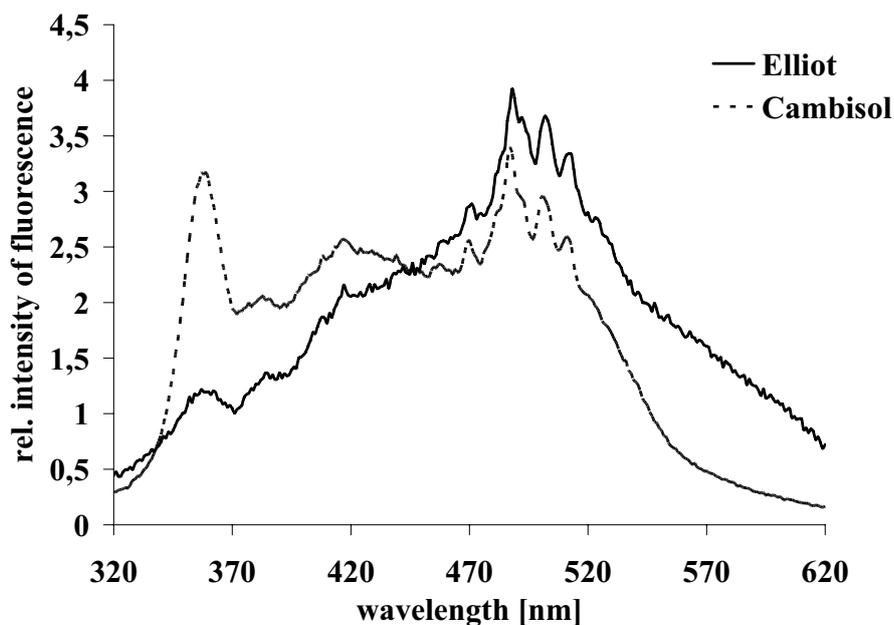
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Determination of humic acids (HAs) optical and chemical properties performed fast and convenient techniques for evaluation of soil quality and precision soil management. In our work we followed excitation, emission fluorescence spectra and fluorescence scan spectra (SFS) and elemental composition of HAs isolated from Eutric Cambisol. SFS spectral lines and indexes were measured in mixture of 0.1M pyrophosphate sodium solution and 0.1 M sodium hydroxide, after filtration and appropriate dilution (Fig.1). Our results were compared with 1S102H-Elliot Soil Humic Acids Standard (IHSS) and showed that isolated HAs reflected lower carbon content (52.65%) to compare with Elliot standard (58.1%). Nitrogen, hydrogen and oxygen content were higher to compare with Elliot standard. Excitation spectra of samples at emission 440 nm and emission fluorescence spectra at excitation 350 nm were obtained. Some changes in SFS spectra about 359 nm were found. Presence of higher content fluorophore groups in Eutric Cambisol sample at lower wavelength was determined. We used spectrofluorimeter Aminco Bowman Series 2 (Thermospectronics, Xe-lamp, scan sensitivity 60%, autorange 845 V, bandpass of both monochromators 4 nm, 2D scan mode, temperature 20 °C and the constant difference was $(\Delta\lambda_{em.} - \lambda_{ex.})=20$ nm between both excitation and emission monochromators). Spectra were corrected at 845 V. Elemental composition of HAs was determined by micro analyser Carlo Erba (Italy).

Key words: humic acids, elemental composition, SFS spectra

Fig 1. SFS spectra at constant difference $\Delta\lambda=20$ nm.



PARTICLE REACTIVITY WITH DISSOLVED ORGANIC NITROGEN IN ESTUARIES

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Globally, nitrogen (N) loadings to estuaries will continue to increase due to changes in climate, urbanisation etc. Organic N (ON) constitutes >50% of the total N input to estuaries. However, the speciation and reactivity of ON in estuaries are poorly quantified, thereby invoking uncertainties regarding the factors controlling the estuarine behaviour of N. A key uncertainty is the particle-water interactions of ON and the role of estuarine variables in modifying ON partitioning and reactivity.

Suspended particles (SPM) within turbid estuaries can be broadly separated into those that are permanently (P-SPM) and temporarily (T-SPM) suspended. The residence time of P-SPM approximates to that of the surrounding water, and is much shorter than T-SPM. Furthermore, the physicochemical and biological properties of the two fractions are reported to be significantly different. On this basis we aimed to test the hypothesis that the reactivity and flux of ON in turbid estuarine systems is significantly controlled by specific fractions within the SPM population.

We determined the reactivity of the particle fractions to ON, using ¹⁴C – labelled amino acids (basic, acidic and neutral) as proxies for ON, in relation to particle characteristics and the potential master variables of salinity, dissolved organic carbon and bacterial activity. The results indicate that the SPM-associated bacteria are a conduit in the sorption behaviour of dissolved ON and the implications are discussed.

MULTI-ELEMENT PROFILING IN MICE (MU SPRETUS) BY SEC-ICP-MS AND IDENTIFICATION OF METALLOBIOMOLECULES BY ESI-QQ-TOF AS BIOMARKERS OF ENVIRONMENTAL POLLUTION

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During the last two decades a great interest has been focused on metals bound to small molecules from anthropogenic activity. The analytical characterization of these chemical species (speciation) provided information about their toxicity or bioavailability.

However, in living organisms and in particular in cells, the situation is much more complex, because a lot of unknown metallobiomolecules are present. In this context the identification of metalloproteins gets especial importance: Metallomics (1,2). The new metallomics analytical approach requires the use of multidimensional instrumental techniques in which at least three components have to be considered (2): chromatography-elemental detector - mass spectrometry.

In this work the metallomics approach was applied to different tissues (liver, brain, lungs, spleen) of the sequenced mouse *Mus spretus*, for further identification of metalloproteins expressed under pollution conditions (biomarkers). Preliminary evaluation of metals was performed by ICP-MS. Latterly, cytosolic extracts were fractionated using size exclusion chromatography coupled to ICP-MS. After further purification with RP- or SAX-HPLC-ICP-MS, proteins were tryptic digested for analysis by MALDI-TOF and ESI-Qq-TOF-MS to identify the peptide sequence that contains these elements.

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POLYCYCLIC AROMATIC HYDROCARBONS AND PESTICIDES ASSESSMENT IN DOÑANA NATURAL PARK (SOUTHWEST SPAIN)

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Doñana Natural Park is located in the delta of Guadalquivir River (SW Spain) and represents an area of great environmental interest (1). The mine activities in the surrounding region and the contaminated mud spillage occurred in 1998, perhaps one of the most severe pollution episodes in Spain, have attracted the de interest of environmental experts on this zone, specially to consider its temporal evolution.

The present study considers the analysis of the 16 PAHs listed in the US Environmental Protection Agency (US EPA). Moreover, 38 pesticides of different group such as, organochlorine, organophosphate, pyrimidines, carbamates, thiophosphate, triazoles, piretroides and phtalamides as well as PCBs were studied. The analyses were performed in sediments and water samples.

PAHs were analysed by liquid chromatography with fluorescence and UV detectors (EPA method 3810), after liquid-liquid extraction from water (EPA method 3510C) and soxhlet extraction of sediments (EPA 3540C). Sample clean-up was carried out in sediments as it is described in the EPA method 3630C.

Pesticides were analysed by GC ion-trap MS using MS/MS mode in order to compound confirmation.

Results obtained are discussed in relation to the pollution control of this area.

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CHANGES OF THIOLS CONTENT AT PLANTS TREATED WITH HEAVY METALS

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Sulfur exists in multiple stable oxidation states; hence it is a versatile component in biological systems. The most active and reduced form of sulfur in biomolecules is the thiol group (-SH), present in number of biologically active compounds. Thiol compounds have a huge number of biological activities, e.g. control of gene expression, signal transduction and heavy metal detoxification. Thiols responsible for heavy metal detoxifying in plants are called phytochelatins. These small peptides consists of 4-23 amino acids, participate in the detoxification of heavy metals, because they have an ability to transport heavy metal ions to vacuole, where an immediate toxicity do not menace yet. PCs have a basic formula $(\gamma\text{-Glu-Cys})_n\text{-Gly}$ ($n = 2$ to 11). PCs are synthesized from glutathione. Reduced glutathione (GSH) itself plays the important role in cell protection against heavy metals, and reactive oxygen species that are able to oxidize GSH to GSSG (oxidized glutathione; disulfide glutathione). The aim of this work was to suggest, optimized and different analytical techniques and approaches to determine thiols (cysteine, reduced and oxidized glutathiones, phytochelatins) in various plant species. Particularly, we treated maize with cadmium and duckweed and peas with cisplatin with respect to changes in the mentioned thiols with increasing time of treatment and dose of heavy metal. We determined and identified PC2 in all tissues of the plants as consequence of the treatment.

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MOVEMENT OF POLYETHYLENGLYCOLE (PEG) THROUGH ARTIFICIAL SOIL COLUMNS AS OBSERVED BY ALL-LIQUID-LASER-DESORPTION-IONISATION (ALLDI) MASS SPECTROMETRY

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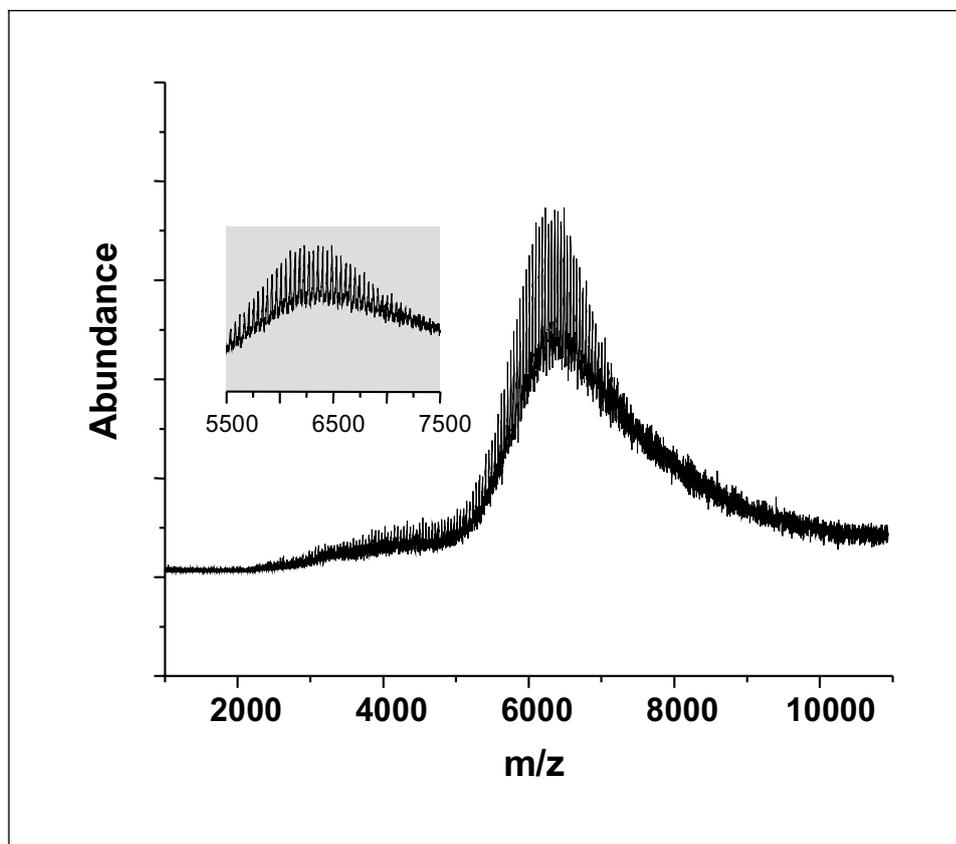
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The movement in soils and sediments of macromolecules, synthetic or natural, is determined by many factors. We choose polyethyleneglycol (PEG), in order to obtain a more detailed description of the movement process governing the movement of these large molecules. This synthetic technical polymer is used in many industrial and household chemicals. On the other hand the chemical functionality is rather limited.

We used All-Liquid-Laser-Desorption Ionisation mass-spectrometry as analytical tool. This new mass-spectroscopic method allows the direct quantitative determination of macromolecules in their aqueous solution. The mass-spectroscopic signal is linearly correlated with the concentration of the analyte over at least three orders of magnitude.

The soil sample was taken from a Cambisol, passed through a 2 mm sieve and filled into a stainless steel column with 1.5 cm inner diameter. The height of the percolated bed was ca. 25 cm. The flow of the percolated solution was adjusted to 2 mL/h by using a syringe pump. The concentration of the PEG was 1000 ppm in potassium-chloride solution (1000 ppm chloride), with chloride being a conservative tracer.

We found, that the breakthrough curve of the conservative tracer was not followed by the breakthrough of the PEG. Even small amounts of eluted PEG could not be determined by this very sensitive mass-spectrometric technique.



Mass spectrum of aqueous solution of polyethylene glycol 6000 (10^{-4} M) ($\text{HO}-[\text{C}_2\text{H}_4\text{O}]_n\text{-H}$, $70 < n < 160$)

THE PHTHALIC ACID ESTERS (PAE) CONCENTRATIONS IN ANIMAL FEEDS AND THEIR COMPONENTS

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Samples of animal feed, premixes and feed additives (n = 68) were collected by a competent personnel of the Central Institute for Supervising and Testing in Agriculture (CISTA) Division of Feedstuff, National Reference Laboratory, Regional Department Opava in accordance with the valid Code No.124/2001 Coll.

The samples were analysed in the laboratory of the Department of Food Technology of MUAF in Brno. The samples were packed in plastic bags or in glass jars (liquid) and send off for analysis to the laboratory of the Department of Food Technology of MUAF in Brno. The samples were collected within the official regular checks at animal feed producers and other registered plants (in accordance with the valid Act No. 91/1996 Coll.) from the input and output stores and from the mixture in the multi-component weighing machine. PAE concentrations were determined using reliable methods for PAE determination in food (JAROŠOVÁ, 2004).

The concentration of PAE was detectable in all samples except for L-lysine (produced by Brenntag). The highest values were found in samples with fat matrix. Soybean oil samples contained 110.96 and 19.89 mg DBP and 20.46 and 8.60 mg DEHP in 1 kg of raw material. Feed components of animal origin (animal fats) contained 26.22 and 47. 29 mg DBP and 15. 33 mg and 11.58 mg DEHP in 1 kg of fat.

Fishmeal contained 9.55 and 5.95 mg DBP and 1.48 and 2.01 mg DEHP in 1 kg of raw material. Dairy products were represented by dried whey which contained 1.68 mg PAE in 1 kg of raw matter. The soybean meal samples contained 2.41 mg and 3.15 mg PAE, rapeseed meal 1.21 mg PAE. PAE content in cereals (wheat, maize, barley) and their by-products (feed meal) ranged between 0.08 – 2.94 mg DBP and 0.31 – 3.15 mg DEHP in 1 kg of raw material. Water-soluble vitamins (B vitamins, biotin and niacin amid) contained from 0.06 to 2.04 mg of PAE and fat-soluble vitamins (A, D, E, K3) contained 0.52 to 9.71 mg of PAE in 1 kg. PAE content in minerals (declared as feed components) was below 1 mg.kg⁻¹. The sums of both phthalates content in the observed premixes ranged between 0.42 and 3.71 mg. PAE content in feed mixtures for piglets and breeding hens and in minerals for finishing pigs ranged from 0.42 to 1.89 mg PAE in 1 kg of mixture.

In amino acids the PAE values varied considerably. DBP content in both samples of L-lysine was below the detectable threshold (<0.03 mg.kg⁻¹); in contrast, a relatively high content of DBP was found in Alimet-methionine (38.36 mg.kg⁻¹). The highest value of DEHP (1.04 mg in 1 kg of raw material) was found in L- lysine.

The study was supported by the National Agency for Agricultural Research of the Czech Republic (NAZV ČR), project QG 60066/2005.

Key words: phthalates, feed, feed components, farm animals

USING A THIN-LAYER CHROMATOGRAPHY AS A TOOL FOR THE IDENTIFICATION OF RIOT CONTROL AGENTS

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Riot control agents belong to the important organic compounds which are mentioned in "Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction". They can be utilized during disturbances by the police or other defence units of particular countries because of their fast effect on the disorderly crowd of people due to their capability to make the eyes to hurt and cry. Their effects disappear within a short time following termination of exposure. Further, these chemicals can be used for chemical warfare defence training and for personal self-defence.

In this work, our efforts has been lead to determine and quantify trace amounts of chloroacetophenone, o-chlorobenzylidene malononitrile, dibenz[b,f]-1,4-oxazepine and capsaicin by the thin-layer chromatography. In contrast to modern analytical methods, it is a simple, rapid, relatively cheap technique that has given us an answer within a short time. Amount of μL and lower of one of these agents was applied to the silica gel thin layer. Mobile phase ingredients were optimised to obtain the best R_f resolution. More than twenty spray reagents have been studied for their sensitivity and selectivity.

We developed the method able to distinguish chloroacetophenone, o-chlorobenzylidene malononitrile, dibenz[b,f]-1,4-oxazepine and capsaicin in amount lower than μg in a spot. For the simplicity, this technique is suitable for the field analysis.

SUGGESTION FOR SELECTIVE DIFFERENTIATING OF NERVE AGENT G AND V TYPE WITH UTILIZATION OF MODIFIED ELLMAN'S METHOD

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Organophosphorus warfare agents G and V type belong to the group of irreversible inhibitors of acetylcholinesterase interfering in the cleavage of substrate acetylcholine in the neurotransmission process. The inhibition of the enzyme results in accumulation of acetylcholine in the synaptic cleft and thus in excessive stimulation of the nerve receptors.

We studied issues of analysis of organophosphorus agents. Immobilized enzyme-inhibitors complexes, e.g. acetylcholinesterase-organophosphorus nerve agent were studied with modified Ellman's biochemical method utilised for assignment of acetylcholinesterase activity. Biochemical reactions are widespread and the most frequent used analytical method for determination of nerve agents. This modified method is based on the nucleophilic reactions of mono- and bispyridinium aldoximes of a type 2-PAM, MMB-4, HI-6 and obidoxim, their homologues and isomers with enzyme-inhibitor complexes.

The procedure for a gradual analysis of G and V type, sarin (GB), cyclosarin (GF), soman (GD), tabun (GA), agent VX and R-33 (Vx) was suggested on the basis of the results of quantification of studied nucleophilic substitution reactions. This method enables selective determination of these chemical warfare agents. A gradual analyse was evaluated by statistic method probabilistic calculus. This way of analysis can be used for assessment of acetyl cholinesterase inhibitors in very low concentrations close to hygienic limits.

NEW DESIGNED AND FULLY AUTOMATED GERDIEN AIR-ION COUNTER

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Concentration of small air-ion is one of the crucial parameters in the ionizing radiation measurements and atmospheric electricity research. Also, beneficial influence of negative small air-ions on mood and behaving of people and animals is well-known.¹ Small air-ions consist typically of 4-12 molecules of water clustered around central ion. Their typical mobility is $1.3 - 3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ depending on their polarity.²

Aspirated Gerdien condenser is the most prevailing instrument used for measurements of air-ion concentration and mobility. Our new designed detector³ which is based on Gerdien's principle and named CDI-06 (Cylindrical Detector of Ions), is fully automated and portable instrument which measures and performs acquisition of not only positive and negative small air-ions, but also temperature, relative humidity and pressure. Power supply of the instrument is managed with 12 V lead accumulator, so autonomy of the instrument can be extended up to a few months, depending on frequency of programmed measurements. Data are represented on internal 2-row display or on PC in the form of tables and graphs and stored in 1.2 MB internal memory.

CDI-06 consists of cylindrical electrostatic condenser with outer and central coaxial electrodes made of stainless steel, fan (Micronel D604Q) that enables air flowing axially through the condenser, and femtoampermeter which is current amplifier (Low Power CMOS Dual Operational Amplifier: LPC662IM). Central measuring electrode is hanging on sapphire bulbs due to stopping of surface current leakage. Typical measuring current is about 100 fA. To avoid cable capacity, triboelectric, piezoelectric and similar effects which generates small currents that could disturb our measurements, amplifier is positioned on the outer electrode, as near as possible to central measuring electrode. Amplifier is directly connected to 24-bit A/D converter, which sends digital signal in acquisition and controlling system. Converter ADS1224 manufactured by Texas Instruments is used. It works on sigma-delta prinipal with 24-bit resulting resolution. Control of the system is done with 8-bit RISC microcontoller ATmega 128 manufactured by ATMEL.

CDJ-06 is an instrument of high accuracy and sensitivity with large capabilities for measuring and monitoring of the ion and meteorological parameters of the atmosphere.

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DGT MEASUREMENT IN SOILS AND SOIL MOISTURE EFFECTS

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In the past years one of main concerns in environmental sciences is fate of toxic heavy metals in soils, their accumulation and significant increase of their concentrations particularly in agricultural soils due to various anthropogenic processes such as industrial activities, utilization of fertilizers and sewage sludge etc. Heavy metals may be transfer into plants and enter the food chains and thus affect the plant growth, microbial communities, soil fauna, animals, humans and soil fertility. Therefore the prediction of biological importance of heavy metals is necessary.

In 1990s the new method, in short DGT (Diffusion Gradients in Thin Films), for in situ measurement of labile metal concentrations in waters was developed. Recently, its application in soils has been investigated. It has proved to be a very good tool to predict the bioavailability of metals to plants. Like plant roots, DGT locally decreases the metal concentration in the soil solution and triggers resupply by diffusion from the soil solution and solid phase. The plant uptake depends also on the field conditions well on the soil moisture. This technique uses two polyacrylamide gel layers placed in a plastic unit. Metal cations diffuse across the membrane filter and diffusive layer and they are immobilized and concentrated by sorption in the specific ion-exchange resin. Trapped metal ions are eluted from the resin by nitric acid and trace metals are determined in eluate by ET AAS, ICP AES or ICP MS. The accumulated mass of metal is calculate and used for calculation of the metal flux or DGT concentration from Fick's laws of diffusion.

Two types of polyacrylamide diffusive gels with different pore size were used in this study. APA gels (polyacrylamide gel crossed by agarose cross-linker) with pore size > 5 nm were used for assessment of the sum of labile inorganic and organic forms of metals. RG gels (polyacrylamide gel crossed by Bis acrylamide) with pore size < 1 nm (DGT Research Ltd., UK) were used for assessment of labile inorganic forms of metals, it means metal ions and hydrated ions. In soil samples selected metals were determined by ET AAS (SpectrAA-40, Varian, Australia) in the soil solution after centrifugation and filtration and in the resin gel after elution in 1 ml of 1 mol.dm⁻³ nitric acid. These gels were used for assessment of moisture effects on DGT measurement of cadmium, copper, nickel and lead in selected South Moravia arable soils fertilized by sewage sludge in 1980s.

Results were represented as dependence of the metal ion flux on the moisture of the soil mixture in individual soil samples. The metal flux changed with the water content in the soil mixture and curves varied for individual metals and soil samples. However, flux values were scattered and curves correlated with published results (Hooda P.S., Zhang H., Davison W., Edwards A.C.: *Europ. J. Soil Sci.* 50, 1999, 285) only in some cases. There the flux increased with the moisture at first and then it decreased after overrun of the specific moisture value (MWHC - maximum water holding capacity). In these experiments the homogeneity of the soil mixture under low water content conditions and the constant moisture during the DGT units deployment were very problematical to ensure and next experiments will be necessary to carry out. The soil solution concentration varied for individual metals and soil samples as the metal flux. It related to the water content, metal species and their mobility in soils and the ability of the soil to resupply the metal ions from the solid phase to the soil solution.

Acknowledgement

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Poster No. 107:

ANALYSIS OF ELECTRONIC PARTS WITHIN THE SCOPE OF THE ROHS AND WEEE REGULATION

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The Restriction of Hazardous Substances Directive (RoHS) 2002/95/EC was adopted in February 2003 by the European Union and took effect on July 1, 2006. The RoHS restricts the use of six hazardous materials in the manufacture of various types of electronic and electrical equipment. It is closely linked with the Waste Electrical and Electronic Equipment Directive 2002/96/EC which sets collection, recycling and recovery targets for electrical goods and is part of a legislative initiative to solve the problem of huge amounts of toxic waste. The directive applies to equipment as defined by a section of the WEEE directive.

The cryogenic grinding was used as the method for the sample preparation of electronic parts. Optimisation of cooling time, impactor frequency and number of grinding cycles with the respect to final sample grain size distribution was performed. The total content of Cr, Pb, Hg, Cd and Br in ground samples was determined by using of X-ray fluorescence spectrometry (WD XRF or ED XRF). The XRF results were compared with results of ICP OES (Pb, Cd, total Cr) after microwave digestion and AMA 254 mercury analyser results (Hg).

Financial support from the projects GAČR203/06/0134 and MSM 0021627502 used in this work is greatly appreciated.

**METHODOLOGICAL INSIGHTS INTO ANALYSIS OF
POLYACRYLAMIDE BASED FLOCCULANTS BY
THERMOCHEMOLYSIS-GC-MS**

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Within the last few years efforts have been attempted for establishing suitable analytical procedures for analysing polyacrylamide based flocculants (PAF). These polymers show a high matrix affinity and corresponding solutions are characterised by high viscosities preventing the compounds' extraction and their analysis by liquid chromatography. Therefore, thermodegradation of the polymers by TMAH-thermochemolysis to low molecular weight compounds, which can be unambiguously related to the former molecular structure and identified by GC-MS has been considered as an appropriate procedure. Off-line open and closed system thermochemolysis, on-line approaches and pyrolysis experiments have been applied on pure flocculants, on spiked matrices as well as on environmental samples. The experiments revealed different distribution patterns of glutarimide-related degradation products depending on the applied method and associated matrices. Generally, thermodegradation of different derivatives of PAF revealed the same glutarimide based degradation products. Only the relative amounts of the products varied. Besides the successful qualitative detection of PAF in natural samples, calibration experiments for quantitative analyses have been performed and applied on sewage sludges. One problem of such approaches is the high detection limit of 250 mg/kg. Further research efforts will be made in order to establish the methods for routine applications.

DETERMINATION OF MANGANESE IN NATURAL MEDIA BY ANODIC STRIPPING VOLTAMMETRY USING ROTATING DENTAL AMALGAM ELECTRODE

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In aquatic systems, dissolved metals, even present at trace levels are generally accumulated all along the trophic chain and may result in a global contamination of the biota. For instance, manganese, an essential micronutrient for all organisms, can be very toxic at high concentrations and contribute for example to the development of Parkinson's symptoms. Generally detected at very low concentration level in the oxygenated freshwater, its concentrations can also increase temporarily but drastically when sediment porewaters are mixed with the overlaying water during intensive fluvial traffic.

At the present time, various techniques for the manganese analysis are used, mostly atomic emission and absorption spectrometry. However, these techniques necessitate sampling, pre-treatment (including filtration and acidification) and analyses in the laboratory.

The purpose of this work consists in the development of a new voltammetric method for the determination on-line and on-site of electrolabile manganese in river, using a rotating Hg-Ag amalgam electrode. For a deposition time of 1500 s, a detection limit of 5 ppb for manganese in freshwater has been obtained by differential pulse anodic stripping voltammetry. Well-defined peaks of manganese between 30 to 1000 ppb have also been observed without addition of any reagents for 500 s deposition time. Moreover, several potentially important metallic interactions (like Pb, Zn or Ni) with manganese have been tested in this study.

FLUORIMETRIC DETERMINATION OF URANIUM(VI) IN AQUEOUS SAMPLES WITH ITS PREVIOUS SEPARATION ON BARE SILICA

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The fluorescence of Uranium (VI) in phosphoric acid at 493, 515 and 539 nm excited by xenon high pressure lamp in continuous regime has been often recommended for the determination of Uranium [1, 2]. In our study, the medium of 0.5 – 2.5 M H₃PO₄ and the concentration interval of 0.5 – 4.0 mg l⁻¹ U(VI) has been found optimal for the determination. Detection limits are X_D^α = 0.044 mg l⁻¹ U and X_D^β = 0.015 mg l⁻¹ U. The usually used sulphuric acid in the mixture with phosphoric acid rather showed negative influence on the fluorescence intensity. Unfortunately, the fluorescence is negatively influenced by a number of ions and complexing agents. A considerable quenching was observed from transitory metal ions. Cationic, anionic and non-ionic surfactants either in subcritical or micellar concentrations also interfere. Thus, the previous separation of Uranium(VI) is indispensable, for which its separation and preconcentration on bare silica has been suitable under optimized conditions at pH 4.2. Final elution of UO₂²⁺ from the column was carried out with 2.5 M phosphoric acid. This procedure could be used for the determination of Uranium(VI) in various kinds of water samples.

MONITORING OF ACRYLAMIDE CONTENT IN THE COURSE OF MALTING AND BEER PRODUCTION

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Acrylamide in food is produced in the course of Maillard's reaction and its precursors are reducing saccharides and amino acid asparagin. The quantity of mechanisms of the acrylamide origin in food depends on food composition and processing conditions.

Acrylamide is created in a significant quantity by heat treatment of food above 120 °C, the highest quantity of acrylamide is created at 150 – 180 °C. At higher temperatures acrylamide creation is substantially lower as the elimination reaction is faster than that producing acrylamide.

Raw material for malt production is barley, a crop with content of nitrogen compounds and high content of starch. During malting enzymes increase the content of reducing saccharides in malt, during kilning biochemical changes are induced by temperature and melanoid substances originate. These conditions are favorable for acrylamide creation.

Changes of acrylamide levels were followed in malt and subsequently in the produced beer.

CHARACTERIZATION AND DEGRADATION BEHAVIOUR OF BIOCOMPATIBLE TRIBLOCK COPOLYMER

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Poly(lactic acid) and poly(glycolic acid) have been under extensive study since they were introduced as biodegradable polymers having hydrolytically unstable backbones. Therefore, these biopolymers can be used for a certain type of biomedical application such as injectable polymer drug delivery systems, tissue implants or resorbable bone adhesives. The prevailing mechanism for the biopolymer degradation is a simple random chemical hydrolysis. This work is focused on the studying of the thermoreversible behaviours of two copolymers, PLGA-PEG-PLGA and the same but modified with itaconic acid (ITA-PLGA-PEG-PLGA-ITA).

The critical gel concentrations (CGC) and the critical gel temperatures (CGT) were determined. As for PLGA-PEG-PLGA the CGC and CGT equal to 19.2 w % and 34.5 °C, respectively, was observed. Second polymer of ITA-PLGA-PEG-PLGA indicated the shift of the sol-gel transition curve down to the lower values of both CGC (15.3 w %) and CGT (25 °C). The degradation behaviours of PLGA-PEG-PLGA in a phosphate buffer (pH 7.4) at 37 °C were investigated. A significant decrease in the molecular weight and increase in the polydispersity within 10 days (until the samples have dissolved) was observed.

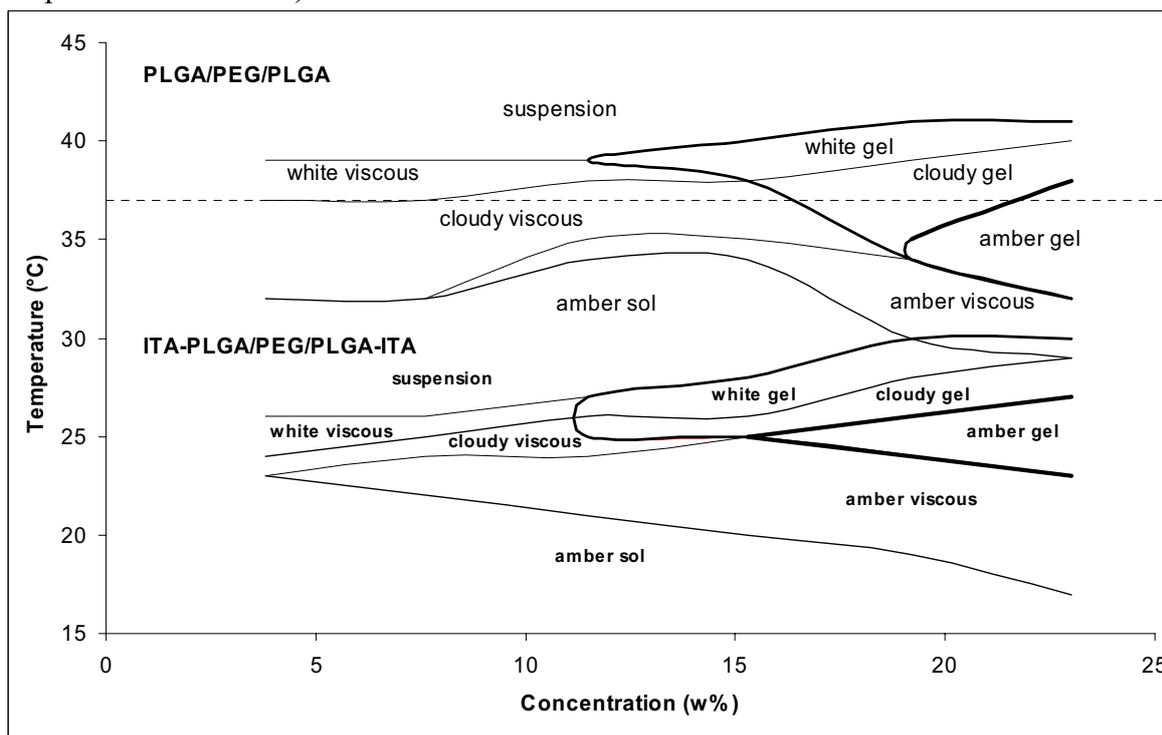


Fig. 2: The sol-gel transition phase diagram of the triblock copolymers PLGA-PEG-PLGA and ITA-PLGA-PEG-PLGA-ITA

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POLAROGRAPHIC DETERMINATION OF INORGANIC ARSENIC SPECIES AT TRACES LEVELS: EFFECT OF IRON SPECIES.

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According to many regulating agency, the maximum contaminant level of arsenic in drinking water was recently levelled to 10 µg/L. As a result, the development of innovative, efficient and sensitive analysis methods, which can allow the measurement of very low amount of arsenic, is required.

It is known that the use of Square Wave Cathodic Stripping Voltammetry coupled with a Static Dropping Mercury Electrode (SW-CSV-SMDE) allows such a determination. A set of parameters was then selected in order to combine the best sensitivity and reproducibility for either As(III) or As(V). However, other inorganic species can interfere with the dosage, and particular attention was paid to the behaviour of iron ions versus arsenic because of the use of iron (III) salts for the removal of arsenic by coagulation/flocculation during the potabilization process.

Thereby, the probable influence of Fe(II), Fe(III), Fe_T, As(V), As(III) and organic matter on the As(III) and As(V) determinations is investigated. The preliminary results allowed the following conclusions to be drawn: i) no interference of Fe(II) and/or Fe(III) on As(III) determination for various arsenic concentrations and for iron concentrations below 1 g/L; ii) no influence of the presence of As(V) up to 50 µg/L on As(III) determination. However, the presence of organic matter causes a decrease in the peak current, probably due to a competitive adsorption at the drop surface.

EVALUATION OF NANOMETER THICK MERCURY FILM ELECTRODES FOR SCANNED STRIPPING CHRONOPOTENTIOMETRY

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Stripping chronopotentiometry (SCP) has been proposed as an alternative to more conventional stripping techniques, in order to minimize the problems caused by adsorption of species onto the mercury electrode. SCP was recently applied to micrometer thick mercury film electrodes (MFE). The results pointed out some advantages of SCP at the MFE, compared with the hanging mercury drop electrode however, the preparation procedure of the MFE is complex and often presents low reproducibility¹.

The present work evaluates the potentialities of thin mercury film electrodes (TMFE) plated onto glassy carbon in thiocyanate medium for SCP. The present mercury films were very reproducible, stable and present a homogeneous distribution of small size mercury droplets².

SCP curves were easily obtained for Pb concentrations of 1.2×10^{-8} M. In the scanned deposition potential mode (SSCP) the experimental result is a transition time vs. deposition potential curve. SSCP yields information on the metal complexation via the potential shift (using an equation similar to the DeFord-Hume formulation). The ability of the TMFE to perform reproducible SSCP curves was evaluated being the metal speciation parameters for labile complexes determined³.

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CHANGES IN THE MYCOTOXIN CONTENT IN THE COURSE OF BARLEY TECHNOLOGICAL PROCESSING

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Today requirements for the production of high-quality and health suitable food have been increasing. For complex assessment of food quality and thus also of barley grain, it is necessary to follow not only nutritiously valuable substances but also risk components, such as industrial contaminants, heavy metals, pesticides and also natural toxins, including mycotoxins.

Deoxynivalenol (DON, belonging to type B trichothecenes) is generally used as a marker of fusarium mycotoxins.

Levels of the selected mycotoxins were determined both in the barley caryopses and in malt of the selected malting barley varieties Kompakt, Jersey and Prestige. The varieties were grown after two previous crop on locality Kroměříž. Contents of the selected mycotoxins (DON and HT-2 toxin) were determined in identical barley and malt samples.

The effect of previous crop, chemical treatment and variety on the content of deoxynivalenol in barley caryopses and malt was studied. In all samples of barley and malt, deoxynivalenol content exceeded the lowest detection limit.

POLYELECTROLYTE COATED THIN MERCURY FILM ELECTRODES FOR ION-EXCHANGE VOLTAMMETRY OF TRACE LEAD

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The direct determination of trace metals in environmental matrices by Anodic Stripping Voltammetry (ASV) with Mercury Film Electrodes (MFEs) is usually strongly disturbed by the presence of surfactants which adsorb onto the electrode [1,2]. The most promising procedure to minimize the electrode fouling is coating the electrode surface with a thin layer of a semi-permeable material, such as an ion-exchange polymer [2]. Ion-exchange voltammetry (IEV) at ion-exchange coated electrodes allows a fast and selective preconcentration of ionic species followed by their sensitive voltammetric detection [1-3].

In the present work, MFEs were modified with coatings of two polyelectrolytes: the cation-exchanger poly(sodium 4-styrenesulfonate) (PSS) and the anion-exchanger polyallylamine hydrochloride (PAH). Both approaches produced reproducible and stable electrodes, suitable for the fast and direct determination of lead(II) at trace levels ($[Pb] = 6.00 \times 10^{-8}$ M, for an accumulation time of 20 s) in solutions of high ionic strength (0.5 M NaCl). The performance and permselectivity of PSS- and PAH- coated MFEs towards several surface-active compounds were evaluated and compared.

The polyelectrolyte modified electrodes were successfully applied in the analytical determination of trace levels of lead(II) in untreated polluted estuarine water samples, where the un-modified MFE failed due to fouling.

Acknowledgement: Thanks are due to “Fundação para a Ciência e Tecnologia” (FCT) for financial support (project POCI/AMB/55939/2004).

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ELECTRON PARAMAGNETIC (SPIN) RESONANCE SPECTROSCOPY (EPR/ESR) OF FREE RADICALS AND ANTIOXIDANTS IN PLANTS

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EPR/ESR is a non destructive method allowing determination of free radicals, metal complexes, and excited states in gaseous, liquid, and solid samples. In environment, and engineering systems free radicals are generated, mainly reacting by oxidative mechanism. We used an up-to-date EPR Bruker Elexys E-540 spectrometer to study reactive oxygen and nitrogen species /RONS/ and interactions of free radicals of natural origin with antioxidants. We found the influence of duration and intensity of exposition to xenobiotics or sun irradiation.

- there are interactions of antioxidants in Moravian red wines, vegetable, and fruit juices
- humic, and fulvic acids contain complexes of Fe, Mn, Cu, and V, forming ROS when irradiated
- dry rot fungi noticeable spectra of stable organic radicals, Fe, and Mn complexes
- plants under chemical stress form protective free radicals
- needles of trees damaged by air pollutants contain ROS, and complexes of Mn/II/, and Fe/III/ ROS concentrations increase with the duration and intensity of exposition to pollutants.
- surface concentrations of hydroxyl radicals on the surface of *Heracleum Metaquarzium*, and of ROS on Cyanobacteria are generated, increasing with duration of exposition to sun irradiation
- some pollens are allergens, because ROS are generated on the surface of their particles

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DEGRADATION OF CHIRAL POLLUTANTS IN A SOIL SAMPLE ENVIRONMENT

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Chiral pollutants undergo enantioselective degradation in the environment by the reason of selective activity of specific microbial communities. Activity of microbial community and a course of degradation depend on specific properties of soil. One of substantial parameter in view is pH of soil; which can vary in relative wide range of values. The method of effective and precise soil sample pH adjustment for long time stabilization is presented. Long time pH soil sample stabilization is necessary for reproducible observation of enantioselective degradation of chiral pollutant, especially in the case of small changes of enantiomeric fraction EF of chiral pollutants under study. The method makes possible to stabilize and measure pH value in soil sample with high precision and reproducibility. Five chiral pollutants; mecoprop, mecoprop-methylester and PCBs 84, 135, 175; were chosen as an example of hydrophilic and hydrophobic compounds for testing of suitability of methodology and analytical procedure for observation of small changes of enantiomeric fraction during relative small period. Chiral HPLC on cyclodextrine stationary phase was used for enantiomeric fraction determination in treated dichloromethane Soxhlet extracts of pollutants from spiked soil samples. Influence of soil pH in the range of 4.0 – 7.0 on enantioselective degradation of selected pollutants in the course of 50-70 days was investigated. Different time behavior was observed depending on soil pH setting.

DETERMINATION OF TRINITROTOLUENES AND PRODUCTS OF THEIR BIOTRANSFORMATIONS BY SOLID PHASE MICROEXTRACTION-LIQUID CHROMATOGRAPHY

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Nitroderivatives of toluene such as 2,4,6-trinitrotoluene (TNT) belong to most used explosives. In the environment TNT is often stepwise biologically reduced to aminodinitrotoluenes (ADNT) and diammonitrotoluenes (DANT). These compounds belong to typical labile environmental pollutants which can be biotransformed by the soil indigenous microorganisms or photodegraded by sunlight and be distributed in the environment. They have mutagenic, carcinogenic and toxic effects. TNT, 2-ADNT, 4-ADNT, 2,4-DANT, 2,6-DANT have been found to be cytotoxic presumably due to induced oxidative stress. TNT, and the TNT-derived metabolites demonstrate mutagenic capability. To identify and quantify individual compounds in environmental samples the complete separation of selected TNTs, ADNTs and DANTs is necessary. The most commonly used method for the analysis of these structurally similar compounds is high performance liquid chromatography (HPLC) with UV detection due to its widespread availability. The using of coupling solid phase microextraction and HPLC for determination of nitrotoluenes was aim of this study. The effect of mobile phase composition and different gradient elutions in reversed phase liquid chromatography system was studied. The applicability of SPME-HPLC method under investigation for determination of nitroderivatives of toluene in environmental samples was discussed.

UNCERTAINTY SOURCES IN DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

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Assessment of measurement uncertainty is often used to assess the suitability of the method of analysis to be used by the laboratory. Because of that, the uncertainty is an unavoidable part of any measurement.

In this paper, we give an overview of the most important uncertainty sources encountered in determination of volatile organic compounds (VOC) in ambient air, using sampling onto sorbent tubes, solvent desorption and gas chromatography with flame ionisation detector (GC/FID). All results are based on data from the in-house development and validation studies.

Two major uncertainty sources were identified: sampling uncertainty (u_{sam}) and uncertainty of analytical measurement (u_a). For each of them all relevant uncertainty sources were identified and investigated in details.

These uncertainty components lead to a combined standard uncertainty (u): $u = \sqrt{[(u_{\text{sam}})^2 + (u_a)^2]}$.

The combined standard uncertainty is multiplied by a coverage factor $k = 2$, which defines an interval having a level of confidence of approximately 95 %, and gave an expanded uncertainty (U): $U = 2u$.

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UNCERTAINTY SOURCES IN DETERMINATION OF CONTENT OF HYDROCARBON IN THE RANGE C₁₀ TO C₄₀ IN SOIL BY GAS CHROMATOGRAPHY

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Uncertainty of measurement is a parameter, associated with the result of a measurement, which characterizes the dispersion of the values that could reasonably be attributed to the measurand¹. According to International Organization for Standardization (ISO), the term uncertainty is preferred over measurement error because the latter can never be known²

In this paper we give an overview of uncertainty contributions in determination of content of hydrocarbon in the range C₁₀ to C₄₀ in soil by gas chromatography according to ISO method 16703:2004³. Identification and evaluation of uncertainty sources were followed by calculations of combined and expanded uncertainty.

Based on in-house validation studies, the main sources of uncertainty of measurement were identified as the uncertainty due to the inhomogeneity of the sample, the uncertainty of the analytical measurement, recovery and repeatability, indicating that these parameters are the most significant for reducing the measurement uncertainty in determination of content of hydrocarbon in the range C₁₀ to C₄₀ in soil by gas chromatography.

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A NEW PURIFIED CHOLINESTERASE FOR SEPARATE DETECTION OF ORGANOPHOSPHATES AND CARBAMATES

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Some years ago for the first time we discovered that only the blood serum of freshwater fish from family of Cyprinidae (blue bream - *Abramis ballerus*, roach - *Rutilus rutilus*) contains nonordinary ChE with unusually high sensitivity to organophosphates - dipterex and DDVP and low sensitivity to carbamate neostigmine. The fish's blood plasma ChE of these species was purified for study of kinetic behaviour and sensitivity to antiChE compounds. The sensitivity of enzyme to 45 organophosphates (including sarin, soman and Vx) and carbamates has been determined. We investigated the activity of new fish's purified enzyme relatively to a choline and thiocholine esters hydrolysis as a function of substrate concentration. The results of this and the following experiments indicate that the new ChE from the blue bream and roach blood serum can be classified as BuChE. At the same time, this type of new enzyme differs from other typical BuChE, so the hydrolysis rate of butyrylcholine by fishes ChE is in 10 - 13 times more rapid as compared to hydrolysis of acetylcholine. The sensitivity of fish's ChE to organophosphates is in 100-2000 times higher than the sensitivity of all types of commercial ChE. On the other hand a new enzyme has an extremely low sensitivity to carbamates. It is very important that with the help of a new purified fishes ChE the separate identification of organophosphorus CW, pesticides and carbamates may be carried out.

MICRODETERMINATION OF THALLIUM WITH ET-AAS AND ICP-AES AFTER PREVIOUS PRECONCENTRATION ON MODIFIED SILICA

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The toxic Thallium is a relatively extended metal in the environment which fluently awoke attention to the analyst. Since the determination of Tl by ICP-AES is of limited sensitivity the $Tl^{III}Cl_4^-$ in the form of ion associate with various cationic surfactants is previously preconcentrated on modified hydrofobized silica sorbent SeparonTM SGX C18 of 60 μm particle size. The formation of ion associate with cationic surfactants (Carbathoxypentadecyltrimethylammonium bromide - Septonex[®], benzyl-dimethyldodecylammonium bromide - Ajatin[®] and benzyldimethyltetradecylammonium chloride - Zephyramine[®]) was tested and various ion interaction mechanisms were assumed during the sorption process. The sorption till 20 μg of Tl (III) was successful from 50 -1000 ml of aqueous solutions in presence of 0,1M HCl. The subsequent elution with 96% ethanol was quantitative. Ethanol was partly evaporated under an infra-red lamp in the presence of HCl. The remaining solution was filled up to 10 mL in a volumetric flask and finally analyzed by the ICP-AES at 190,86 nm. No interference by large amounts of Cl^- 500 excess of SO_4^{2-} , NO_3^- , Ca^{2+} , Mg^{2+} and K^+ , 100 excess of Fe^{3+} and Al^{3+} was observed. This procedure was used for the determination of Thallium in surface and mineral waters. The activation of the sorbent was provided with 0,005M Zephyramin in presence of 0,1M HCl. Samples were filtrated and degassed and a similar procedure used as before. The calibration plot was made from spikes of 1, 3 and 5 mg Tl/L and 0,5, 2 and 4 mg Tl/L spikes analysed after sorption in triplicate. The recovery of 97 – 99 % Tl was again observed. The presence of macrokomponents and microkomponents in waters was without influence on the sorption but considerable changed the calibration plots.

The ET-AAS at 276,8 nm was also suitable for the direct determination of 1 – 10 μg Tl. However, the volatility of Thallium at increased temperature especially in the presence of chloride is a considerable disadvantage when using ET-AAS. A number of modifiers have been tested under them $PdMg(NO_3)_4$, $PdNH_4(NO_3)_4$, $Pd(NO_3)_2$, ascorbic acid and ammonium vanadate with their influence on the slopes of calibration plots for Thallium at the resonance line at 276.8 nm. The largest plot of the calibration line observed for $PdMg(NO_3)_4$ for which the blank values reaches zero. Moreover, the best temperature program for the instrument corresponded for the drying at 90 - 110 °C (20 s), charring at 700 °C (10 s) and the atomisation at 1500 °C (3 s) in presence 100 excess Cl^- , SO_4^{2-} , NO_3^- , Ca^{2+} , Mg^{2+} , Na^+ and K^+ , as well as 100 excess of Fe^{3+} and Al^{3+} . The Zeeman correction was used for the elimination of the background. In this case Thallium has been determined in urine and spruce needles according to the standard addition method.

DETERMINATION OF SULPHONAMIDES IN WASTEWATER

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Antibiotics are widely used in human and veterinary medicine. They are biological, semisynthetic or synthetic compounds. They consist of two groups: bactericidal and bacteriostatic substances. They are used for bacterial infection treatment. These compounds have been shown to block biological processes in wastewater treatment plants. They harm natural ecosystems and they may concentrate in food chain. Furthermore, bacterial resistance against them has been proven to establish easily.

Sulphonamides are derivatives of p-aminobenzenesulphonamide and the first used antibacterial pharmaceuticals. They inhibit folic acid and other enzymes e.g. dehydrogenase and carboxylase resulting in decrease of bacterial respiration. When sulphonamides react with other compounds it can influence their toxicity and cytostatic properties. Sulphonamides are excreted by urine from body (60-90%) as basic sulphonamide, acetylated form and glucuronide. That is why they can enter wastewater. Amount of sulphonamides in wastewater is influenced by elimination biological half-life and various ways of reabsorption.

Sulphonamides especially sulphathiazole were determined in this work. Analysis of sulphonamides is influenced by their properties, namely insolubility in water, alcohol, ether and dichloromethane.

Samples were collected from wastewater treatment plant in University of Veterinary and Pharmaceutical Sciences Brno campus. Samples from effluent and influent were taken into 1L plastic bottles once a day.

Samples were processed immediately or stored in refrigerator until next day. First step of sample treatment was filtration through filter paper (pore size 0.07mm). Sulphathiazole was extracted by using ethyl acetate and concentrated by rotary vacuum evaporator (RVO Büchi, Switzerland). Residues of evaporation were dissolved in 1 ml of methanol and 1 ml of mobile phase (60:40, acetonitrile : 0,1%HCOOH). As mobile phase was used acetonitrile and 0.1% formic acid in purified water. Samples were filtered by membrane filters (0.2µm) into amber glass vials.

The HPLC with diode array detector (Agilent 1100 Series, USA) equipped with ZORBAX Eclipse XDB-C18 column (150 x 4.6mm) was used for determination. Elution was carried out using gradient mode (0min...5:95, 17min...27:73 - 0,1%HCOOH : acetonitrile). Other parameters were following: feeding 5µl, flow rate 0.5ml.min⁻¹, column temperature 20°C, wavelength 270 nm, total time of analysis 30 minutes.

Average recovery obtained for sulphathiazole was 84.1 ± 6.8 % Limit of quantification (LOQ) for sulphathiazole was 0.5 ng.ml⁻¹ and limit of detection (LOD) was 0.2 ng.ml⁻¹.

Concentration in samples of wastewater was fluctuated in range 2.3 – 99.3 µg.l⁻¹ (average value 40.6 µg.l⁻¹). The highest levels were reached short time after cleaning at the animal stabling and veterinary clinic.

**IDENTIFICATION OF DIFFERENTIAL EXPRESSION
METALLOPROTEINS IN THE BIVALVE CHAMAELEA GALLINA UNDER
ENVIRONMENTAL STRESS USING AN METALLOMICS ANALYTICAL
APPROACH (MMA)**

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The use of sessile organisms such as bivalves as indicators of pollution is a very established tool in environmental contamination assessment. In addition a number of proteins have been proposed as biomarkers, especially oxidative proteins and metallothioneins [1]. *Chamaelea gallina* is a bivalve extensively used in the southwest Spain to evaluate the chronic metal contamination caused by pyrite mining tips deposited in the last century in this area. In these studies protein characterization was based on the traditional proteomics approaches using 2D-electrophoresis and proteins identification by MS. However, more recent studies combining both metal detectors (ICP-MS) and molecule structure characterization devices (MALDI-TOF-MS and n-ESI-Qq-TOF-MS) provide a more easy and unequivocal metal-biomolecules (Metalloomics) identification [2, 3].

In the present study, *Chamaelea gallina* extracts from the whole mollusc body, containing cytosolic proteins, were fractionated according to metallo-biomolecules molecular weight using the coupling SEC-ICP-MS. Fractions were later purified by RP-HPLC-ICP-MS. Finally, metalloproteins present in these fractions were identified by MALDI-TOF, followed by protein sequence confirmation with n-ESI-Qq-TOF-MS analysis of peptides after tryptic digestion and matching in protein base data.

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DETERMINATION OF AIR POLLUTION AND VOC CONTAMINATION BY VOYAGER–MOBILE GC

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Volatile organic compounds (VOCs) are omnipresent and commonly found in the environment, work place and consumer products. Human are easily exposed to these chemicals through skin, breathing and eating and even at low concentration these present long term health risks. There is some evidence on animal studies indicated that some of these VOCs have carcinogenic and mutagenic effects on tissue development. Benzene, toluene and xylene, known as BTX, are the markers for human exposure to VOCs; therefore, the monitoring of these three compounds is necessary in order to evaluate the risk to human health. Over the past several decades, regulations for many VOCs have been significantly increased. More stringent regulations coupled with public awareness of the dangers of VOCs have caused a need for fast, reliable equipment to monitor air quality on-site. The paper describes the mobile gass chromatograph Voyager by Photovac with columns and two detectors PID and ECD, on – line detection of 40 VOC compounds and discusses about experimental and work parameters of Voyager mobile GC. Voyager was used for detection of BTX concentration levels in Oil Refinery Pancevo, province of Vojvodina, Serbia.

Key words: VOC, BTX. Mobile GC, on-site monitoring

SPECTROFLUORIMETRIC DETERMINATION OF MICROCONCENTRATIONS OF THALLIUM AS COMPLEX WITH RHODAMINE B

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Thallium is more toxic than lead and is relatively slowly removed from living organisms after intoxication. Recently increased Thallium levels have been observed in environment, especially in soils and waters.

It was found, that fluorescence of Rhodamine B is decreased in the presence of Tl(III) (Fig.1). This can be used for fluorimetric determination of Tl(III) as quenching agent for Rhodamine B.

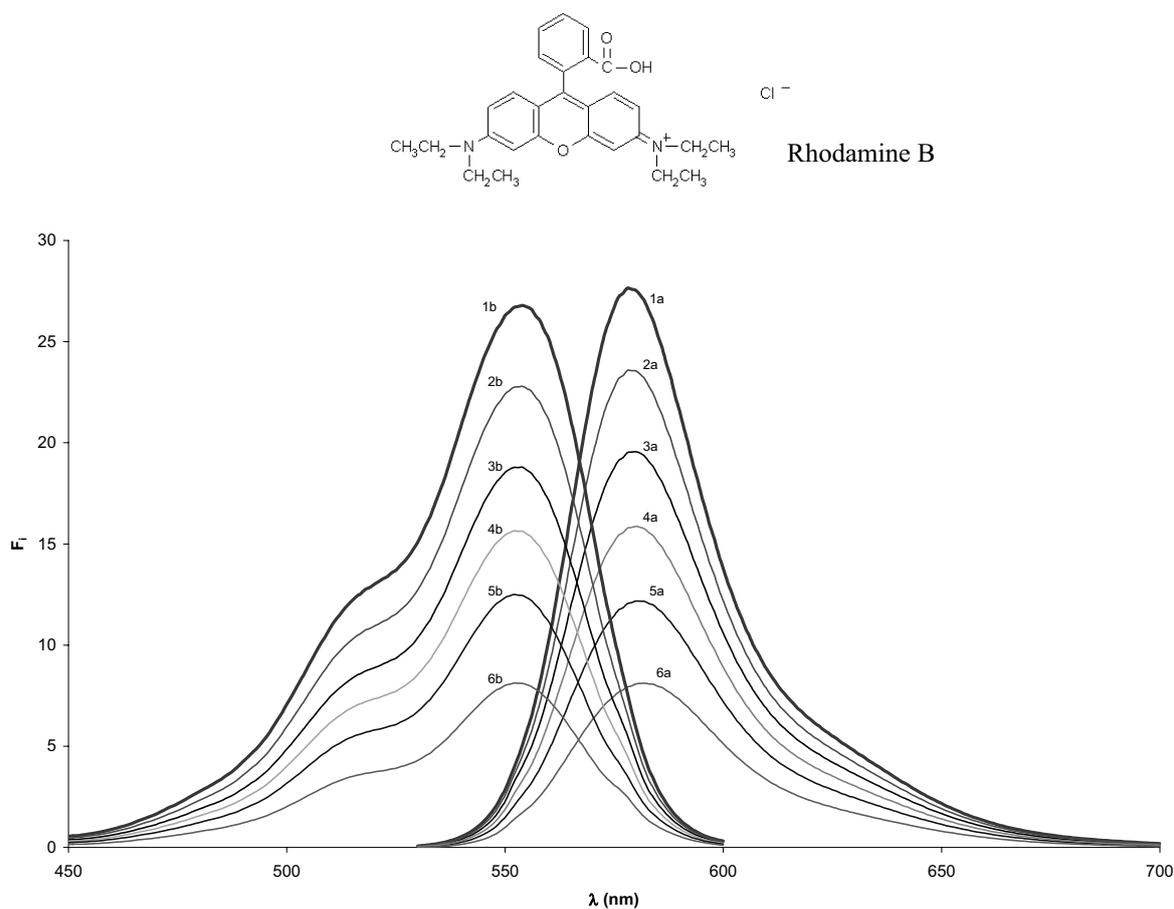


Fig.1.: Excitation(a) and Emission(b) spectra of $4,2 \cdot 10^{-6} M$ Rhodamine B in the presence of Thallium(III) in dependence on concentration of Tl(III).

1- $0 ng \cdot cm^{-3}$ (reaction blank), 2- $0,2 ng \cdot cm^{-3}$, 3- $0,4 ng \cdot cm^{-3}$, 4- $0,6 ng \cdot cm^{-3}$, 5- $0,8 ng \cdot cm^{-3}$, 6- $1 ng \cdot cm^{-3}$

In this paper the conditions for a method were studied in details, optimized and tested for the determination of Thallium in aqueous solutions.

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COMPARISON OF MOBILE ANALYTICS AND STANDARD SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF NITRATES IN SURFACE WATERS

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Human activities are reflected in all components of the environment including the hydrosphere. It is a well-known fact that there would be no life without water. This means that any change in the quality of water may put organisms living on Earth at risk. It is therefore crucial to address the issue of water pollution.

The high levels of nitrogen in water, which contributes to the eutrophization of surface waters, is one of the major problems to be addressed. In water, nitrogen may occur in several different types of compounds differing in effects on the living organisms.

The main object of this work was the determination of nitrates concentration in surface waters using arbitrary spectrophotometric method (following the Czech Norm ČSN ISO 7890-3) and mobile analytics. The first one was based on the formation of coloured nitroderivatives by nitration of salicylic acid with nitric acid released from water nitrates after acidification by H_2SO_4 . As mobile analytics the commercially available sets Nitrate Test 1.09713.0001 and Nitrate Test 1.14773.0001 by Merck and Viscolor ECO Nitrate 931041 by Macherey-Nagel were employed.

Real samples of surface waters were analysed within this study; the first set of samples was taken from localities at the Svratka River and from the artificial lake at Kníničky Dam, the second one came from the artificial lakes at Mariánské Valley (both in the close vicinity of the Brno town) and the last set comes from several ponds and artificial lakes at Bohemian-Moravian Highlands.

Results obtained by both methods were compared and statistically evaluated. The evaluation of the results was realized by the Snedecor – Cochran method (Analysis of Variance), by parametrical t-test and by graphical Youden method. No statistically important differences were found between results of tested methods at significance level 0,05. The mobile analytics was found to be very suitable method, as it gives not only the proper results in the comparison with the arbitrary method, but it represents also relatively cheap and very quick method usable in the field.

The nitrate levels determined in all analysed surface water samples by the arbitrary spectrophotometric method were within the range 2.34 – 26.83 $mg.l^{-1}$, i.e. in all cases they were below the limit of 50 $mg.l^{-1}$ set by the Government Regulation No. 61/2003 Coll.

12. SOIL – FRESHWATER – ATMOSPHERIC SYSTEMS

POSTERS No. 129 – 142

THE CONTENT OF POLYCHLORINATED BIPHENYLS IN TISA RIVER SEDIMENT

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This paper presents results of measuring concentration of seven PCB congeners (28, 52, 101, 138, 153, 180, 209) in sediment of the Tisa River. Sediment has been sampled during the Nautical-ecological research of Tisa in 2005 year, along the waterway of the river from 0 to 540th kilometre. The criteria used for assessment, comparison and interpretation of the obtained values of the results are Ambient Water Quality Criteria for Polychlorinated Biphenyls, Canada and Sediment Quality Guidelines, NOAA's U.S. Department of Commerce. The obtained results show that the residues of the detected polychlorinated biphenyls depend on the location of sampling. According to results it can be concluded that on the territory of Vojvodina the sediment of the Tisa River is not highly contaminated with PCBs, while at the Hungarian part of the navigable waterway of the Tisa the number of the polluted areas is much higher. The highest concentration of total determined PCBs is on 320 km of Tisa waterway, near Solnok. Concentration of PCBs is seven times higher than recommended maximum allowed concentrations. It's significant that high concentration of total PCBs is observed on every point of sampling between 400 and 525 km. One of the reasons of the high concentration of PCBs in Tisa River sediment, the part in the Republic of Hungary, is large number of tributaries, as it is well-known that the tributaries from Romania and Slovakia are heavily polluted with industrial waste water.

DISTRIBUTION OF Fe, Mn, Pb AND LEAD IN SEDIMENTS OF SKADAR LAKE

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Skadar Lake is most important aquatic catchment in Montenegro. The main inflows to the lake (from Montenegro) are the Moraca and Crnojevica Rivers. These rivers flow through industrial and urban settlements, which may ultimately result in pollution of the lake water.

The objective of this study was to provide more detailed information on the geochemical properties of the lake system through measurement of metal concentration and the role of sediment – water interaction in controlling their distribution. Sediments and water samples were taken from 15 sites and analyzed for iron (Fe), manganese (Mn), lead (Pb), and chrome (Cr).

The results indicate similarities in metal distribution mechanisms found with extraction sediment phases, and also suggest that the overall aquatic ecosystem of the lake is still in a relatively pristine state.

Distribution of examined metals in appropriate phases shows very low presence of anthropogenic fraction, while the fifth phase, which is geochemically of the least importance, is most abundant.

After comparison with US EPA (2002): „A guidance manual to support the assessment of contaminated sediments in freshwater ecosystems”, it was confirmed that concentrations of metals found do not endanger life in Skadar Lake.

DETERMINATION OF THE SOURCES OF CONTAMINATION IN SOME KARST SPRING OF BÜKK MOUNTAINS

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Karst water has an important role in the drinking water supply system all over the world. The Bükk Mountain, which is situated on the north part of the country, is one of the most important karst areas in Hungary. The present paper is a study of the potential and actual sources of contamination to the groundwater in the selected karst aquifers. In the context of groundwater contamination, a hazard is defined as an existing and potential source of contamination resulting from human activities taking place mainly at the land surface.

Samples of groundwater from selected springs were collected. The samples were analysed for different parameters as pH, EC (Electrical Conductivity), TDS (Total Dissolved Solid), Ca²⁺, Mg²⁺, TH (Total Hardness), Cl⁻, CO₃²⁻, HCO₃⁻, alkalinity, Na⁺, K⁺, NH₄⁺, NO₂⁻, NO₃⁻ and SO₄²⁻ by using standard techniques. Surface water and precipitation (rain, snow) samples were collected in the studied area. Samples was analysed for the anions and for the cations in addition to pH and conductivity measurements. The anions (Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻) from precipitation were determined by high-performance liquid chromatography.

The results showed that pH ranged from 7.06 to 7.38. We studied correlation among various parameters of water samples of karst springs. By comparing the water chemistry of spring and precipitation waters, an understanding may be gained of the interaction between surface water and ground water. The acid rain leached the soil carbonates and produced a nitrate- and sulphate-rich ground water. Ion ratios are used for comparison, since utilization of the ion ratio can negate concentration or dilution effects. Nitrate is an important pollutant in the environment, being generally derived from agricultural fertilizers, atmospheric input, and also from the nitrification of organic N. The karstic ground water system is sensitive to the influence of point and non-point nitrate pollution. The average Cl⁻/SO₄²⁻ molar ratio for rain water is within the range of the corresponding ratios for spring water studied here. Within the region studied, the aquifers are dominated by carbonate rocks (limestone and dolomite). Dissolution of carbonate minerals largely determines the chemical composition of spring water. Anthropogenic inputs into the surface and ground water mainly include Na⁺, K⁺, Cl⁻, NO₃⁻ and SO₄²⁻, according to chemical compositions of municipal sewage and rain water.

The variations in chemical composition of both precipitation and spring water during different seasons demonstrate an active interaction or mass exchange between surface and ground water in karst environments, and indicate that the karst ground water system is sensitive to impact by human activities. Groundwater composition also depends on the mineralogy of the rock.

The combined results of this study indicate that systematic studies on chemical characteristics of ground waters, their movement in aquifers, water/rock interactions, and the interaction of ground and surface water are of great importance for understanding the hydrogeochemical processes, and the protection and sustainable utilization of ground water resources.

TRACE METAL BEHAVIOUR IN AN ULTRA-OLIGOTROPHIC, GLACIAL FLOUR-RICH LAKE

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Unlike many of the synthetic organic compounds used in industry, medicine and agriculture, metals are part of natural biogeochemical cycles. Human activity influences their cycling in two interrelated ways: by altering the rate at which metals are transported among the different reservoirs and by altering the form of the metals from that in which they were originally deposited. Once mobilized from the Earth's crust, either by natural or by anthropogenic-enhanced mobilization, the availability of a metal depends on its potential to cycle among biogeochemical reservoirs. In principle, any observed metal distribution can be qualitatively explained on the basis of the metal's chemical properties but, in practice, the quantitative prediction of the actual metal species distribution can be rarely achieved.

In this communication, trace metal behaviour will be evaluated for a series of elements of contrasting chemical characteristics by performing mass balance calculations from flow and metal concentration ($< 1.2 \mu\text{m}$) data collected over 14 months in an ultra-oligotrophic, glacial flour-rich lake (Lake Brienz, Switzerland). Previously, organic carbon, refractory organic matter and inorganic colloid composition have been thoroughly characterised in the same size range and over the same period. The results obtained will be compared with cross-flow-filtration data and interpreted in the framework of chemical principles. The main pending issues that need to be addressed in order to achieve a rigorous prediction of trace metal speciation from the available data, as well as the plausibility of algae growth being limited by trace metal scarcity, will also be discussed.

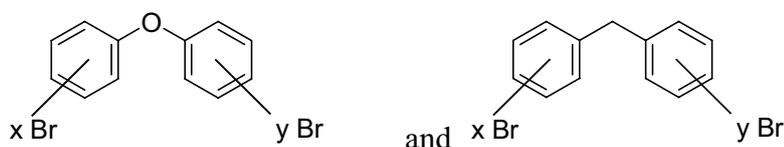
POLYHALOGENATED POLLUTANTS: A SERIOUS THREAT TO THE ENVIRONMENT

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In our work we have focused on two groups of polyhalogenated organic compounds – polybrominated flame retardants (BFRs) and polychlorinated biphenyls (PCBs). Excellent physical properties that made them suitable for lot of industrial applications. However, the same properties also made them persistent and remaining in most parts of the environment, and provably harmful to animals and humans.

PBDEs and PCBs



summary formula: $C_{12}OH_{10-(x+y)}Br_{(x+y)}$ summary formula: $C_{12}H_{10-(x+y)}Cl_{(x+y)}$
when $x + y = 1$ to 10

Brominated flame retardants BFRs are ubiquitous industrial chemicals, and are being found in significant levels in wildlife as well as humans. Among the BFRs, the best environmental and human risk assessment data are available for polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs). PBDEs are being found as contaminants of indoor and outdoor environments. The presence of PBDE was proved in all the components of the environment such as air, sediment and sewage sludge as well as biological samples including biota, human blood, adipose tissues and breast milk.

Polychlorinated biphenyls (PCBs) were also used in industry in many different applications. The main sources of PCBs in ecosystems after the ban of their industrial production are soils, in which over 90 % of these substances are deposited. The ratio of individual PCBs in different samples from the environment depends on both original composition of pollutants and their sources and physical and chemical properties of each congener. The purpose of this study was to evaluate concentrations of selected important PCB and BFR congeners in various kinds of samples from the environment as well as wildlife, and to compare our found concentrations with some previous corresponding studies and/or monitoring programs.

Chemical properties

Theoretically 209 congeners of PBDEs and PCBs exist with specific chemical and physical properties, which lead to various biological and toxicological effects. Alike other organohalogen compounds such as DDT and other organochlorine pesticides, PBDEs and PCBs are lipophilic and very stable and resistant to biodegradation.

ASSESSMENT OF THE ALIPHATIC AND AROMATIC HYDROCARBONS CONTAMINATION IN RIVER SEDIMENTS OF NORTHERN FRANCE

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Anthropogenic activities have contributed to a widespread contamination of aquatic ecosystems, especially of river sediments, where both metallic and organic contaminants can accumulate. In this study, we focused on two classes of organic contaminants : aliphatic hydrocarbons (n-alkanes) and polycyclic aromatic hydrocarbons (PAH), sixteen of which being listed as priority pollutants by the US Environmental Protection Agency. N-alkanes and PAH can originate both from natural and anthropogenic processes, including combustion of fossil fuels (pyrolytic source), spillage of petroleum (petrogenic source) and urban runoff. Each of these sources releases hydrocarbons having a typical fingerprint.

N-alkanes and PAH have been quantified in the various compartments (water column, suspended matters, sedimentary column and porewaters) of a frontier canal of France and Belgium. Contamination levels and partitioning between phases provided information on the quality and potential toxicity of the sediment. In addition, the contamination pattern has been examined thanks to well documented indices. A strong pyrolytic influence has been highlighted for PAH in the whole sedimentary core. In the aliphatic fraction, the high abundance of UCM (unresolved complex mixture) and the predominance of odd and long chain homologues revealed, respectively, biodegraded petroleum residues and terrestrial inputs. These results have been compared to others sediments collected in northern France and Belgium.

MOBILIZATION OF ARSENIC AND ZINC IN CONTAMINATED STREAM SEDIMENTS AND IMPOUNDMENT MATERIAL FROM CHEMICAL MANUFACTURING AND ENVIRONMENTAL IMPLICATIONS

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Arsenic and zinc at high concentrations are often toxic to living organisms. Toxicity and bioavailability of these two elements is related to their mobility in soils. One sample of an impoundment material and three samples of stream sediments from eastern Slovakia were studied for the leaching of As, and Zn and their mobility in relation to sediment properties. The source of As and Zn contamination in the studied region is an impoundment located near the village of Poša, in the upper part of the catchment of the Kyjov brook. Contamination with As and Zn was primarily found in surface waters of the Kyjov brook (mean As concentration 1780 µg/l) and related stream sediments (mean value of 630.6 mg/kg). The As concentration in the stream sediments was 20- to 401-times higher than the natural background level for this element (8 mg/kg). However, only one sample of stream sediment most proximal to the impoundment had Zn concentration above the natural background value (90 mg/kg). According to the results from the column leaching experiments, As displays higher mobility in all samples than Zn under the experimental conditions. The absolute amounts of As released were significantly correlated with its total content in samples ($r = 0.975^*$, $P < 0.05$), but no such correlation was observed for Zn. Only 5.30-7.83% and 0.27-6.53% of the total As and Zn, respectively, was released into the leaching solution. Although only about 8% of the total arsenic could be leached from the impoundment material, this amount represented high As concentrations in leachates reaching up to 8000 µg/l (Fig. 1a). The cumulative release of As from the impoundment material was estimated to be 132 mg/kg (Fig. 1b). As a consequence, the surface waters of the Kyjov brook and Ondava river and the stream sediments are highly contaminated with As with the mean values of 1780 µg/l, 26.6 µg/l and 630.6 mg/kg, respectively. Column leaching studies showed an influence of total and ammonium extractable Fe and Mn content and pH on both, As and Zn leaching. Enhanced release of As from the impoundment material was likely due to high sediment and leachate pH (8.55 and 9.00, respectively). The lowest relative mobility of both, As and Zn, in the sample most proximal to the impoundment could be attributed to the high Fe and Mn content in this sample, emphasizing a strong potential of Fe and Mn oxyhydroxides for metal immobilization.

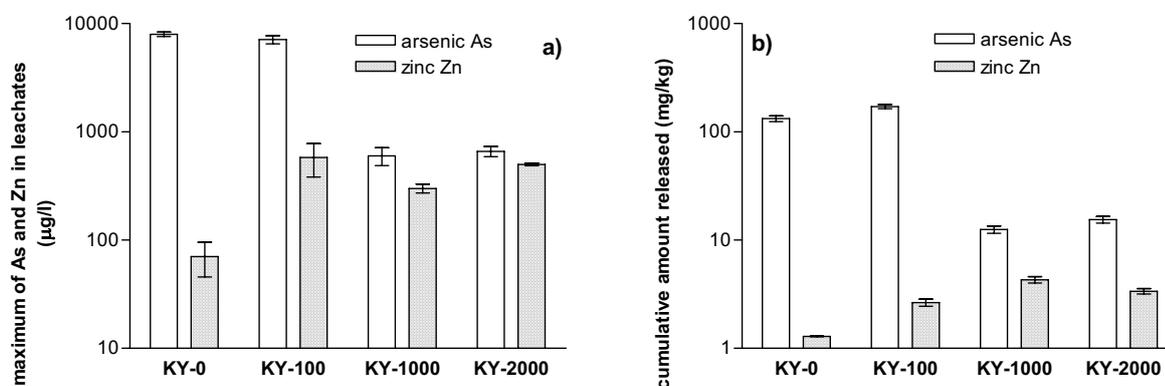


Fig. 1. a) Maximum concentrations of As and Zn observed in leaching solution outflowing from sediment columns. b) Cumulative amounts of As and Zn released from sediments investigated. The samples KY-100-2000 are stream sediments of the Kyjov brook located 100, 1000 and 2000 m from the impoundment, respectively. The sample KY-0 represents an impoundment material from chemical manufacturing.

INTERACTIONS BETWEEN SULPHIDES AND METALS DURING EARLY DIAGENETIC PROCESSES IN RIVER SEDIMENTS

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Several aquatic ecosystems from the northern France are subjected to significant anthropogenic contaminations. Most of the pollution is located in sediments but may diffuse back to the water column. In this context, it is paramount to well understand the biogeochemical processes, which take place at the water-sediment interface and in the first centimetres of the sedimentary column as well. These transformations, called also early diagenesis start generally with the oxidation of natural organic matter by bacterial activity and the joint reduction of electron acceptors like O₂, NO₃⁻, manganese and iron oxides and sulphates.

More particularly, sulphate reduction produced sulphides, which are either reoxidized or precipitated with metal compounds to form mainly 2 classes of minerals: the AVS (Acid Volatile Sulphides) and the CRS (Chromium Reducible Sulphur). Most of the metal sulphide compounds are rather stable (CdS, PbS...) and may thereby controlled the mobility and the toxicity of these metals trapped in the sediments.

This work deals mainly with the distribution of metals in the first centimetres of the sediment for three different sites (Escaut and Lys rivers) in relation to some inorganic sulphur compounds. Thus, after a presentation of analytical methods used, interactions between the profiles observed for some trace metals and dissolved and solid sulphides will be described and a discussion about the links between the mobility of metals and their toxicity will be detailed.

PERSISTENT ORGANIC POLLUTANTS (POPS) IN SOILS AND SEDIMENTS FROM JAMES ROSS ISLAND, ANTARCTICA

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Since many persistent organic compounds are a subject of the long-range atmospheric transport and deposition in cold ecosystems at high elevations and latitudes, the raising levels of persistent organic pollutants in cold regions are attracting the growing attention.

Twenty samples of soils and river, lake and marine sediments were collected from James Ross Island (south-east side of the Antarctic Peninsula) where the first Czech Antarctic research station of Johann Gregor Mendel has recently been built. The pilot study of the air contamination assessed using the passive air samplers were performed at the same time. Levels of PAHs (US EPA priority pollutants list), 7 indicator PCB congeners, β -, γ -, δ - and ϵ -hexachlorocyclohexane (HCH), p,p'-DDT, DDD and DDE, hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) were determined in all samples. Results confirmed the presence of POPs in the studied region and they will serve as a base for the future research in the region.

COADSORPTION OF IONS AND ORGANIC MOLECULES AT THE AIR/SOLUTION INTERFACES: THE ROLE OF WATER

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This paper reports on investigations about the adsorption at the air-water surface, and for the sake of comparison at the silica-solution interface, of two 1-2 electrolytes, $\text{Pb}(\text{NO}_3)_2$ and PbCl_2 , at first alone, and then from a mixture with carbofuran or with benzene. This study was aimed at trying to identify the part played in the surface by the different particles of the system components, and in particular the role of water. By combining experimental relative adsorptions and Gibbs excesses calculated from the Wagner-Onsager-Samaras theory, we will show that, in well-known solutions such as KCl ones, where the negative excess in salt can be very precisely modeled by the Wagner-Onsager-Samaras (WOS) theory, the resulting water excess is negative. A similar analysis was done on solutions of unsymmetrical electrolytes and on mixtures of salt and organic molecules. For all the systems, the water excess was negative. So, water was repelled towards the solution bulk, whereas ions probably took place between the bulk and a layer of organic molecules. The reverse situation seems appears at the silica / solution interfaces. Given the importance of such behaviours about the transfer between environmental compartments, these observations called for a more detailed model.

CHLORINATED PARAFFINS IN THE CZECH ENVIRONMENT

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Chlorinated paraffins (CPs) are the new groups of persistent organic pollutants. CPs are the complex mixtures with a chlorination degree between 30 – 70 %, and carbon chain lengths of C10-C13 (short-chain CPs), C14-C17 (medium-chain CPs) or C>17 (long-chain CPs). Chlorinated paraffins are used commonly as the high temperature lubricants in metal working industry, and as the flame-retardant plasticizers. Short chain chlorinated paraffins were classified as the Category 3 of carcinogens.

Sediment, soil, and air samples were taken over the Czech Republic during the years 2001 – 2005. Chlorinated paraffins were detected in the sediment and soil samples, mainly in the sampling locations surrounding the industry. Low volatility potential of CPs from the soils as well as low CP soil contamination caused that CPs were not found in the air samples. Medium chain chlorinated paraffins prevailed in all of samples. Average chlorination degree of SCCPs was deduced from the mass spectra to be 65%. Chlorinated paraffins were detected in the different environmental matrices at the following maximal concentrations: 347 ng.g⁻¹ d. w. for SCCPs, and 5 575 ng.g⁻¹ d. w. for MCCPs in the sediment samples; 138 ng.g⁻¹ d. w. for SCCPs, and 202 ng.g⁻¹ d. w. for MCCPs in the soil samples; CPs were not detected in the air.

This project has been carried out as a contribution to the ongoing national POPs inventory in the Czech Republic, which is focused on the new types of persistent industrial substances.

SOIL-AIR EXCHANGE: FROM THE LABORATORY TO THE FIELD EXPERIMENTS

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Soil-air equilibrium partitioning has an important impact on the environmental distribution and fate of many POPs, and laboratory simulation of volatilization from the soil surfaces is often needed for the successful fate modeling. A series of experiments focused on determination of the rate of volatile loss of PCBs and selected pesticides from the enriched soil surfaces were conducted in a volatilization glass chamber under laboratory conditions. At the same time, field experiments measuring the air concentrations above the contaminated soil surfaces were performed. Both, active and passive air samplers were employed in this study, and correlation between the POPs content in the soil, and in the air were studied.

The soil-air partitioning was assessed by calculating fugacities in the soil and air (f_S and f_A). Fugacities were calculated using the air and soil concentrations measured in the laboratory and field experiments and the results were expressed as a fraction of the total fugacity in soil: $f_S/(f_S+f_A)$. A fugacity fraction of 0,5 indicates a soil-air equilibrium while fugacity fractions $>0,5$ and $<0,5$ indicate the net volatilization and deposition from the gas phase, respectively.

The fugacity calculation provides the information about the tendency of a chemical to move from one compartment to another. It is an important parameter to predict the fate and transport of chemicals in the environment.

SILICONE RUBBER AS A REFERENCE PHASE TO STUDY SEDIMENT-WATER INTERACTIONS

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Passive sampling technique has been used successfully for environmental monitoring. Besides the semi-permeable membrane devices (SPMDs) recently the use of single phase materials for passive sampling is becoming more popular. In this research relevant properties of single phase materials like low density polyethylene (LDPE), polyoxymethylene (POM), polydimethylsiloxane (PDMS) or silicon rubber (SR) and exact polymer were estimated. Diffusion coefficients of Naphthalene (Naph), Fluoranthene (Flu), Benzo(a)pyrene (BaP) and Dibenz(ah)anthracene (DBahA) in all mentioned materials were measured. The higher diffusion was estimated for all SRs comparing to LDPE and exact. POM didn't show any diffusion for BaP and DBahA. Other properties that are characteristic for each material like resistance to solvents, glass transition temperature (Tg), oligomers release, solubility in materials, approximate estimation of permeability were evaluated in correlation with diffusion coefficients.

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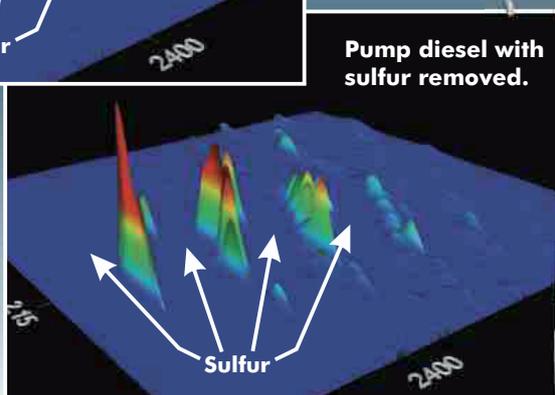
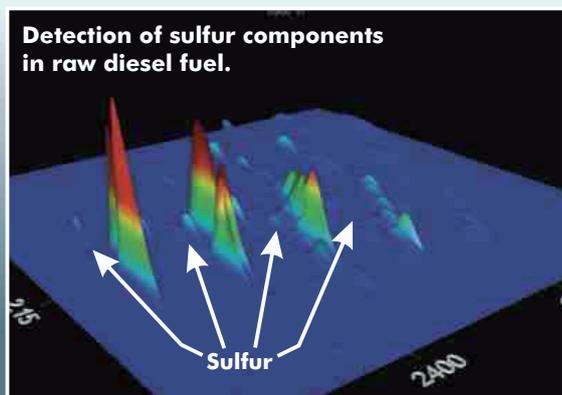
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