BOOK OF ABSTRACTS

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Legend:

PL - Plenary Lecture
KN - Keynote Lecture
O - Oral contribution
P - Poster

INDEX OF ABSTRACTS

PLENARY LECTURES

KEYNOTE LECTURES

S1- ANALYTICAL METHODS AND MONITORING

ORAL

POSTERS

S2 - MARINE AND AQUATIC CHEMISTRY

ORAL

POSTERS

S3- SOIL CHEMISTRY

ORAL

S4- ECOTOXICOLOGY

ORAL

S5- NEW MATERIALS AND CLEAN TECHNOLOGIES

ORAL

POSTERS

S6- WATER AND WASTE TREATMENT

ORAL

POSTERS

S7- ATMOSPHERIC CHEMISTRY

ORAL

POSTERS

URBAN AREA

S8- BIODEGRADATION AND BIOREMEDIATION

ORAL

POSTERS

S9- PHOTOCHEMISTRY AND PHOTOCATALYSIS

ORAL

POSTERS

S10- ENVIRONMENT AND CULTURAL HERITAGE

POSTERS

COMMERCIAL PRESENTATION

Abstracts

PL 1

RECENT TRENDS IN THE LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY ANALYSIS OF EMERGING CONTAMINANTS IN ENVIRONMENTAL SAMPLES

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Over the last 20 years liquid chromatography-mass spectrometry (LC-MS) techniques have advanced dramatically in their sensitivity, specificity and reliability. Detection of sub-ppt concentrations is becoming routine for many organic analytes and methods achieving detection of a few hundred femtograms of some analytes have been reported. Such progress is mostly due to development of hyphenated LC - tandem or hybrid MS techniques, which are today the methods of choice for the determination of trace organic analytes in environmental samples. Swift growth in the use of LC-MS/MS for the analysis of organic contaminants in environmental matrices has been compelled by the need for high-quality data on their occurrence in the environment at very low concentration levels.

A wide range of so-called “emerging” or “new” unregulated contaminants have emerged as an environmental problem and became a hot topic for environmental analytical chemists.

This presentation will give an overview of liquid chromatography-mass spectrometry methods used for the determination of trace organic contaminants in environmental samples. Among the organic contaminants the focus is given on several groups of emerging contaminants that raised most concern as environmental contaminants and therefore attracted attention of a research community: pharmaceuticals, drugs of abuse, perfluorinated compounds and nanomaterials. Various aspects of current LC–MS methodology, using tandem and hybrid MS instruments, including sample preparation, are discussed. Some recent trends in the analysis of selected emerging contaminants will be discussed in details such as (i) automation through coupling of sample preparation units and detection systems (ii) employment of fast-LC methods using short, narrow bore columns, high mobile phase flow-rates and ultra-high pressures, (iii) application of multi-residue analytical methods for tracing down different therapeutic categories up to low nanogram per liter levels.

PL 2

PHOTOINDUCED AND PHOTOCATALYZED REACTIONS IN AQUATIC SYSTEMS

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Environmental pollution is the due to the balance of anthropogenic pressure and chemical processing by the environment. Many natural transformations are induced by light with the concurrent role of DOM, iron and other metal complexes, salts, and inorganic particulate. Several reaction mechanisms studied by our group in aquatic systems will be exemplified, including OH-,DOM- and metal oxide- mediated degradation, nitration, and chloruration, in rain, lake, ground, estuarine and marine waters.

Although photocatalysis is often invoked as a possible ways of reducing the anthropogenic pressure, more important is that the conceptual framework used in photocatalysis improves and supplements that for natural processes cited above. The study of primary reactions and the formulation of a simple model for the rate will clarify the basis of the often complex photocatalytic process, which is affected by physical parameters (catalyst surface area and texture, size of particles...), and chemical parameters, as the very nature of the substrate, and the presence in the reaction medium of species affecting the photoreactivity either directly (such as Cl^-) or indirectly by surface adsorption (F^-). Emphasis will be put on the role of absorption and complexation to the surface. The confinement to the surface favors the back reactions, which are the cause of the low quantum yields.

The active species involved in photocatalysis (holes trapped, OH radicals, electrons, HO2, singlet oxygen) and surface texture affect both the type of degradation products and the kinetic performance of the system. Partial oxidation and formation of byproducts could occur, as well as concurrent oxidation/reduction reactions and catalyzed hydrolysis. Some recent improvements in the light harvesting, the actual research needs and some established applications of photocatalysis are finally sketched out.

PL 3

THE ADVENT OF MESOSCOPIC SOLAR CELLS

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The field of photovoltaic cells has been dominated so far by solid state p-n junction devices made e.g. of crystalline or amorphous silicon, profiting from the experience and material availability of the semiconductor industry. However, there is an increasing awareness of the possible advantages of devices referred to as "bulk" junctions due to their interconnected three-dimensional structure. Their embodiment departs completely from the conventional flat p-n junction solid-state cells, replacing them by interpenetrating networks. The lecture focuses on dye sensitized mesoscopic solar cells (DSCs), which have been developed in our laboratory. Imitating natural photosynthesis, this cell is the only photovoltaic device that accomplishes the separation of the optical absorption from the charge separation and carrier transport processes. It does so by associating a molecular dye with a film constituted of tiny particles of a wide band gap semiconductor oxide (1-3). The DSC has made phenomenal progress, present conversion efficiencies being over 12% for single junction, 16 percent for tandem cells and 10.4 % for cell modules, rendering the DSC a credible alternative to conventional p-n junction devices (4). Commercial mass production of flexible DSC modules has started in 2009 on the megawatt scale. These solar cells have become viable contenders for large-scale future solar energy conversion systems on the bases of cost, efficiency, stability and availability as well as environmental compatibility.

References:

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KN 1

BY-PRODUCTS OF DRINKING WATER DISINFECTIONS: STATE OF THE ART IN THEIR ENVIRONMENTAL MONITORING

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The concern from the global community about world water issues has largely increased, in the last decades, to such an extent that a World Water Council has been established in 1996 to promote, as its mission, awareness, and trigger action on critical water issues.

Since the discovery of chlorination by-products in disinfected drinking water in 1974, numerous toxicological studies have been conducted that show the potential health risk of disinfection by-products (DBPs). Although many DBPs are present in drinking water, they are often grouped into the following categories: trihalomethanes (THMs), haloacetic acids (HAAs), and inorganic disinfection by-products (bromate and chlorite) based on their molecular structure, and chemical properties. These classes are currently regulated under the Stage 2 Disinfectant (D)/DBP Rule released by U.S. EPA (January 2006).

The development of analytical techniques of higher sensitivity and of increased capabilities of identification of unknown species, allowed in the very last years, the scientific community, to pose attention to the “emerging contaminants”, newly recognized contaminants that have not historically been considered as such which are present in the environment on a global scale.

In this lecture, mainly focused on HAAs, the current trends on analytical techniques for their determination will be discussed. Significant advances achieved by liquid chromatographic (LC) methods will be overviewed, with particular attention on those relying on ion chromatographic mechanisms that represent the majority of the improvements attempted by LC in the last decade.

KN 2

TRANSFER OF DIFFUSE POLLUTING SUBSTANCES FROM LAND TO WATER

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A great challenge for environmental chemistry lies in understanding the fate and transport of substances as they travel from soil and landscapes into waterways – the problem of diffuse pollution. Diffuse pollution can come from all parts of the landscape such as agriculture, forestry and urban systems and involves a range of substances from nutrients, pesticides, metals, pathogens to colloids and sediments. The main global concern for diffuse pollution is with nutrient (principally phosphorus (P) and nitrogen (N)) transfer from agriculture to rivers, lakes and estuaries, where they contribute to eutrophication and result in the proliferation of undesirable algae and a general decline in the biodiversity. This talk will illustrate the problem using the example of diffuse pollution of water from P and sediment/colloids arising from agriculture. It will examine the concept of the transfer continuum, a conceptual model to approach the problem focussing on sources, mobilisation, delivery and impact, embracing a range of issues that cross many scales. In agriculture P comes from a range of sources, principally fertiliser and animal feeds that contribute the main bank of P in the soil system. There are forecasts that global supplies of fertiliser P are set to run down in coming decades and so a contemporary challenge for food production and diffuse pollution management is in better utilization of current banks of *in situ* soil P for food production, especially organic forms such as myo inositol phosphate. Assessments of soil organic P pools using NMR are now available to help plan better utilisation of soil P and thus the control and understanding of diffuse pollution.

KN 3

CHEMICAL SPECIATION OF METALS IN SEAWATER

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Biogenic metals in the marine system, like iron, copper, zinc and cobalt, occur in seawater complexed with organic matter, with only a tiny fraction as the inorganic metal. Little is still known about the composition of the metal complexes or the ligands themselves. Speciation is usually carried out by cathodic stripping voltammetry which includes a titration with the metal from which the excess ligand concentration and complex stability can be derived. Here we compliment such measurements of copper complexation in coastal waters with pseudopolarography: in this technique the thermodynamic stability of the already complexed fraction is explored using electrochemical means only. Inert complexes are thus separated from the labile species. Microwire electrodes are used with an extremely thin diffusion layer, which improves the resolution between the inert and labile species. Novel data treatment will be used to quantify the ligand concentration of the labile species. Results will be presented for measurements in samples from the Irish Sea.

KN 4

ASSESSING SIDE EFFECTS OF ENGINEERED NANOPARTICLES

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Nanotechnology can design, characterize and produce materials at nano-dimensions. At this scale, the materials' physical properties change and become very useful for a vast range of applications in medicine, cosmetics, electronics, energy production etc. Given the excitement associated with all of the nanotechnology applications, evaluating the potential hazards related to exposures to nanoscale materials and its products has become a new area of research. The nanoparticle-related biological effects depend on particle surface area, numbers of particles determinations and in a large part also to their surface chemical characteristics. Much evidence suggests that nanoparticles first interact with cell membranes and subsequently they provoke a cascade of cellular events which sooner or later result in toxic effects. To answer the question about safety of nanoparticles a variety of *in vivo*, *ex vivo* and *in vitro* methods were developed. The reported nanotoxicity data are sometimes controversial, therefore the debate emerged whetere the existing toxicity tests used for other chemical are appropriate also for products of new technologies. The consensus on this issue is not reached jet. In this presentation some most commonly used toxicity tests will be presented and the advantages as well as disadvantages of using same test for nanoparticles as for dissolved chemicals will be listed. Examples on nanotoxicity of most frequently used metal oxides nanoparticles (TiO_2, ZnO and CeO_2) will be given. In conclusion, a broad international effort (NanoValid: FP7) to discover and validate the nanotoxicity tests to assess biological potential of nanoparticles to humans and environment will be presented.

KN 5

PHOTODEGRADATION OF PHENYLUREA HERBICIDES UNDER SIMULATED ENVIRONMENTAL CONDITIONS

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Degradation processes of some ring-halogenated and side-chain-substituted derivatives of phenylurea under simulated environmental conditions have been studied and compared. Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], which is used as a herbicide, has been investigated in most detail. Besides its microbiological degradation by selected fungi and bacteria, kinetic and mechanistic studies of different photochemical transformations have been carried out including direct photolysis in aqueous solution and on dry solid supports (soil components such as quartz sand, clay and goethite), photoinduced decomposition in aqueous solutions of iron(III) salts as well as photocatalytic degradation in colloidal solutions of Q-TiO_2 nanoparticles.

In the course of direct photolysis in water, entirely chlorines on benzene ring were substituted by hydroxyl groups whereas the proportion of two isomeric primary products strongly depended on irradiation wavelength. In the case of other investigated degradations, only oxidative transformations of the aliphatic side chain of phenylurea derivatives were observed using HPLC. Based on the identification of several degradation products, a detailed picture of side-chain reactions proceeding via two successive oxidatative demethylation steps could be established. Degradation proceeded according to first-order kinetics, which means that the system remained in a photostationary state with respect to hydroxyl radical concentration during the whole reaction sequence. Therefore, the kinetics of side-chain attack can be assumed to remain fairly constant as the reaction proceeds. Quantitative kinetic analysis revealed that the side-chain reactions represent only 30 % of the total photodegradation of diuron, the remainder being due to reaction on the benzene ring leading to ring-opening products, which escaped HPLC detection.

In order to get more information on the relative amount of ring vs. side chain reactions, laser flash photolysis was used. Hydroxyl radicals were generated by photoionization of $[Fe(CN)_6]^{4-}$ in neutral aqueous solution and subsequent reaction of e^-_{aq} with N_2O; they then reacted either with $[Fe(CN)_6]^{4-}$ to give $[Fe(CN)_6]^{3-}$ or with the phenylurea derivative on the ring or at the side chain. The first two of these reactions could be followed by formation of the products ($[Fe(CN)_6]^{3-}$ and OH adducts).

Experimental kinetic data for varying reactant concentrations were fitted by nonlinear regression. As a result, the rate constant for reaction of hydroxyl radical on the ring was found to decrease with the number of Cl substituents while that for reaction at the side chain increased with the number of abstractable H atoms. For diuron, the OH-attack on the benzene ring proceeded two times faster than on the dimethylurea group that fully corresponds to the results obtained for its photocatalytic degradation under continuous irradiation.

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KN 6

FERTILIZERS, HETEROCYCLIC COMPOUNDS, EUTROPHICATION AND CLIMATE CHANGE

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What we know as civilization and lifestyle has started to change. Control of the climate change will be the driving force for the technological developments of the 21st century. A brief evaluation of the developments, in historical perspective, reveals that concerns over famine has lead to developments in agriculture; demand for sustainable agriculture was achieved with the fertilizers and pesticides. This was a human centred, single sided "development model" which was ignoring reaction of environment to the anthropogenic impact.

Excessive utilization of the natural resources and release of nutrients into the reservoirs has triggered fast ageing of ecological systems and some of the by-products of civilization (CO_2, N_2O, and CH_4) have been listed among the major contributors of the global warming. For the first time in human history a concern for anthropogenic impact over natural cycles is pronounced.

Within this cyclic turmoil, affords to minimize the impact of anthropogenic activities on the environment is continuing and treatment technologies evolving faster.

New technologies in chemical, electro-photo chemical, separation and even in traditional coagulation processes are evolving to remove persistent pollutants of water and wastewater treatment processes, in recent years. Biological treatment technologies (i.e. anoxic ammonium-oxidizing) are still among the most cost and removal efficient approaches. Production of sustainable energy is also considered seriously in these emerging wastewater treatment technologies, in addition to increasing removal performances.

The need for fast and accurate detection of very low contaminant levels in complex environmental matrixes is increasing, for removal and monitoring applications.

Efficiency will be the key concept in the water and wastewater treatment, in 21st Century.

KN 7

ATMOSPHERIC AEROSOLS – SOURCES, PROCESSES, AND IMPACT

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Atmospheric aerosol particles are liquid or solid particles suspended in the atmosphere. Generally, the sizes of aerosol particles are in the range 0.001 - 100 µm. Sampled aerosol particles are also called particulate matter (PM). Most legal standards are related to PM_{10} (particles with an aerodynamic particle diameter $d \leq 10$ µm). Atmospheric aerosol particles are produced by a large variety of sources, and are either emitted as primary particles (i.e., they are directly emitted as particles into the atmosphere) or formed by secondary processes (i.e., by transformation of emitted precursor gases). Depending on the conditions, the latter may either result in homogeneous nucleation of new particles or condensation of species on the pre-existing aerosol. The mechanisms of new particle formation are still subject of debates, especially on the role of various types of molecules such as organics in the nucleation process [1].

Atmospheric aerosols are of interest mainly because of their effects on health and climate. Concerning health, many epidemiological studies have shown a link between increased mortality/morbidity and increased PM_{10} or $PM_{2.5}$. Concerning climate, aerosol particles scatter and absorb light (known as the direct effect on climate), and modify cloud properties (with a variety of effects known as indirect effects). These effects are influenced by the chemical and physical properties of the aerosol particles, which makes these properties important to be measured [2].

References:

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KN 8

MICROBIAL POPULATION IN CLOUDS: POTENTIAL ROLE IN ATMOSPHERIC CHEMISTRY

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Recent studies showed that living microorganisms, including bacteria, fungi and yeasts, are present in the atmospheric water phase (fog and clouds) and their role in atmospheric processes may have been underestimated. This paper is focused on the microorganisms present in clouds and on the role they could play in atmospheric chemistry processes. The life cycle of microorganisms *via* the atmosphere is examined, including their aerosolization from sources, their integration into clouds and their wet deposition on the ground. Then, a short description of the microorganisms that have been found in clouds and their variability in numbers and diversity is presented, emphasizing some specific characteristics that could favour their occurrence in cloud droplets. In the last section, the potential role of microbial activity as an alternative route to photochemical reaction pathways in cloud chemistry is discussed. First experiments showed that a great number of microbial strains had the enzymatic potential to degrade carboxylic acids (acetate, succinate, and formate) present in clouds. Second, to realistically evaluate the implication of microorganisms in the chemistry of clouds, temperatures encountered in clouds have been taken in account as a factor controlling the enzymatic activity. Further work was thus focused on the determination of precise biodegradation rates at lower temperatures (5 °C and 17 °C) corresponding to temperatures measured at the puy de Dôme summit
(http://wwwobs.univbpclermont.fr/observ/chimie/DATA/pdd_Choix.html).
In addition experiments were performed on a microcosm mimicking the cloud water composition. Under these conditions the relative contribution of microbial and radical activities ($OH^{\bullet}$ and $NO_3^{\bullet}$) has been quantitatively evaluated. Clearly, measured biological and chemical reaction rates are in the same range of order. More, biotransformation processes could even be the main sink for organic acids during nighttime.

Amato, P., Ménager, M., Sancelme, M., Laj, P., Mailhot, G., Delort, A-M., 2005. Microbial population in cloud water at the Puy de Dôme: implications for the chemistry of clouds. Atmospheric Environment 39, 4143-4153.

KN 9

TECHNOLOGIES FOR UPGRADING BIOLOGICAL TREATMENT OF PHARMACEUTICAL RESIDUES

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Several technologies, both biotic and abiotic, are available for the removal of pharmaceutical residues from wastewaters. Biological treatment mimics natural processes, where microorganisms use suspended and colloidal organic matter to obtain carbon for cellular synthesis and energy for cell activity. Abiotic treatment is when a chemical is altered or removed by non-biological mechanisms either physically (sorption, air stripping, membrane filtration) or chemically (ozonation, sonolysis and different advance oxidation treatments including combinations of ozonation, UV irradiation and peroxide addition, photocatalysis). The addition of abiotic treatments can increase the efficiency and result in either mineralisation, which is favourable, or the formation of more stable transformation products with different physico-chemical properties and toxicity.

This presentation covers the main treatment technologies applicable for upgrading existing biological treatment for the removal of pharmaceutical residues. As a case study, the elimination of carbamazepine and two of its stable metabolites, acridine and acridone, in a pilot biological wastewater treatment plant under aerobic and anoxic conditions and in a coupled anoxic-aerobic reactor system will be presented. The same compounds were also exposed to abiotic treatments: UV-radiation and oxidation with chlorine dioxide, where the most successful method for carbamazepine removal was shown to be UV treatment, while acridine and acridone were more susceptible to biological treatment. On the basis of our results a coupled treatment technology involving an initial UV treatment step followed by biological treatment, is proposed.

KN 10

SOLID AND LIQUID PRODUCTS OF BIOMASS/SYNTHETIC POLYMERS BLENDS PYROLYSIS AS ENERGY AND CHEMICALS SOURCE

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The catalytic and non-catalytic pyrolysis processes of biomass/synthetic polymer blends were carried out at 500°C. The subject of this work was to investigate the influence of the type of biomass and polymer as well as the type of catalyst on yield and properties of solid and liquid products.

It was stated that the composition of the blend as well as the presence of catalyst influence not only the products yield but also affect properties of char and bio-oil formed during co-pyrolysis process. Depending on the composition of sample and the presence of catalyst, the pyrolytic oil and char yield were in the ranges of 20.8-50.3 % (m/m) and 16.8-51.0 % (m/m), respectively.

It was stated that there is an only slight influence of synthetic polymer addition to biomass on the chars basic properties, i.e. ultimate and proximate analyses. The high heating value of char from cellulose and lignin is as high as 28.7 and 29.7 MJ/kg, respectively and increases up to nearly 31 MJ/kg for chars obtained from biomass/polymer blends.

Bio-oils analyses by means of CHNSO, FT-IR, GC/MS showed that the composition of starting biomass/polymer blends influences the quality and composition of liquid product of pyrolysis. The presence of synthetic polymer and/or catalyst influences the formation of different types of valuable chemicals during pyrolysis (hydrocarbons, phenols, furan's derivatives). It was also found that fuel properties (for example calorific value, density, viscosity) of bio-oils strongly depend on the composition of the biomass/polymer blend and the presence of catalyst during pyrolysis process.

KN 11

DECAY MECHANISMS ON HISTORICAL BUILDINGS IN RELATION TO ATMOSPHERIC POLLUTANTS

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The rapid increase in industrialization and urbanization, which took place in the district of Mestre and Marghera at the beginning of fifties of the last century, sharply increased air pollutant concentration in the atmosphere. Contemporaneously stonework built several centuries ago started to deteriorate very quickly as a consequence of increased air pollution.

In most Venetian monuments studied, stone decay was mainly ascribed to the transformation of calcium carbonate into calcium sulphate. To explain the mechanism of stone decay and black crust formation it is important to focus our attention on the stone-atmosphere interface in order to estimate qualitatively and quantitatively the new-formation products and try to correlate them with the different decay features commonly observed on the facade of monuments. Characteristic marking patterns, defined in terms of *black and white areas*, were frequently observed and were generally correlated to different degree of decay due to the diverse mechanism of deterioration involved.

A simplified model of stone decay was proposed and tested on several Venetian monuments by analysing samples taken from different areas showing diverse extent of deterioration.

White washing areas are strongly influenced by washing action of rainwater which prevent any deposition of carbonaceous particles and are characterized by a continuous and slow removal of calcium carbonate and re-precipitation of calcite.

In places sheltered from the rain, dirt can accumulate as incoherent stratification or as incrustation strongly bound to the surface. These surfaces are black due to the deposition of carbonaceous particles which are incorporated in a gypsum crystals network which is growing, mainly in a perpendicular shape, with respect to the calcium carbonate substrate. A close observation of sheltered areas shows two different morphologies of deterioration which are defined as *dirt accumulation and dirt wetting.*

Dirt accumulation takes place far from rain washing areas and is characterized by black superficial deposits that grow on the surface due to the collection of atmospheric particles and to the transformation of calcium carbonate into gypsum.

Dirt wetting takes place at the interface between running water and the more sheltered areas and is characterised by a thick and hard crust having a rough and spongy appearance, growing upon the original surface and forming a greater amount of gypsum due the moisture migration from the nearby washed areas.

Observations carried out on many Venetian monuments have shown that each lithotype decays differently according to their textural and structural differences.

The results obtained showed that in compact limestone, such as Istrian stone, the gypsum formation affect the stone only on the surface. On the contrary on marble a different mechanism of decay takes place: the decohesion of calcite crystals, due to thermal changes, is favouring the penetration of sulphuric acid solution in the intergranular space, thus causing the transformation of calcium carbonate into calcium sulphate, not only on the surface, but also inside the marble.

KN 12

CHEMISTRY FOR ART: MATERIALS FROM RENAISSANCE TO CONTEMPORARY

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The science provides a powerful tool to solve many problems in the field of cultural heritage and can be used to suggest appropriate procedures for conservation and restoration of artworks. Recent technological developments in microelectronics and fiber optics have led to the development of portable scientific instrumentation to carry out non-invasive *in-situ* measurements. This has enabled the Perugia Centre of Excellence SMAArt to assemble a mobile laboratory MOLAB, which is a European infrastructure in the CHARISMA project. An extensive study on the state of conservation of Michelangelo's *David* with a non-invasive approach will be discussed. Scientific investigations offer the possibility to establish in great detail the painting techniques of ancient masters. The investigations of the underdrawings of the Rocks (London, National Gallery) will be discussed and the palette of the painter *il Perugino* will be presented. This Renaissance artist, besides using traditional pigments of the sixteenth century, also experimented with metal powders, such as bismuth or bronze, or minerals with metallic lustre, or even powders of transparent uncoloured glass, in the effort to reach more sophisticated chromatic effects. The multi-technique approach of MOLAB has been adopted for investigations in modern and contemporary art. Six oil paintings and five water colours by Cezanne, all exhibited at the *Courtald* of London, have been investigated. The study concerns the differences and similarities of the palette of the artist throughout his long career. The study of *Victory Boogie Woogie*, (*Gemeentemuseum* in Den Haag) allowed for the identification of the pigments used by Mondriaan in his last unfinished masterpiece and allowed for a consideration of the building of the painting's construction, revealing earlier phases of the composition. The investigations of twenty paintings by Burri (*Fondazione Palazzo Albizzini Collezione Burri*, Città di Castello, Perugia) allowed for the characterization of the execution techniques and materials used by the artist in the period 1948-1976. Gino de Dominicis' monumental sculpture, *Calamita Cosmica*, was investigated by employing a combination of non-invasive and micro-invasive techniques. The sculpture was found to be comprised of a polyester core, to which five subsequent layers of varying composition had been added.

O 1

APPLICATION OF ASSOCIATED MULTI-COMMUTATION FLOW SYSTEMS (MCFS) AND MULTI-PUMPING FLOW SYSTEMS (MPFS) FOR CHEMILUMINESCENT SCREENING OF PHARMACEUTICALS AND PESTICIDES IN ENVIRONMENTAL ANALYSIS

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The developments of flow injection analysis (FIA) have resulted in promising flow concepts such as sequential injection analysis, bead injection lab-on-valve and multi-commutation among others. In this evolution, propelling and insertion units markedly constrains the potentialities of flow analysis procedures. Multi-pumping flow systems (MPFS)[1] have recently been proposed as a new concept for sample and reagent handling and for improving the automation degree of flow procedures. Multi-pumping flow systems (MPFS) is a recent analytical approach based on the use of multiple solenoid actuated micro-pumps strategically positioned in the flow manifold. It permits the design of flexible miniaturised networks for flow analysis based on a time-pulse-counting strategy, which facilitates the synchronisation of the added reagents. The result is a versatile full automated system, easy to program *via* software. Moreover, the excellent cost-effective, precision, accuracy and the proved robustness and miniaturisation features suggest that MPFS could be advantageously used for fulfil the requirements for developing portable fieldwork instruments for *in situ* environmental analysis.

The aim of the work is to exploit the analytical features of MCFS and MPFS for developing a fast screening test for the forward development of MPFS-chemiluminescence (CL) systems able to determine pharmaceutical and pesticides compounds. CL detection was selected attending the excellent limits of detection, sensibility, and linear dynamic ranges observed. The experimental screening comprises over 180 different molecular structures and representative members of the most important families of pesticides and pharmaceuticals. All compounds were tested for common chemiluminescent system employed in direct chemiluminescence procedures, namely, MnO_4-, Ce(IV), $Fe(CN)_6^{3-}$ and N-bromosuccinimide.

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O 2

CONTAMINATION PROBLEMS OF THE GREY WHALES

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Sea mammals constitute the basis of the food ratio of Eskimos and coastal Chukchas, while it reaches 30% (100 kg/year/pers) for the inland Chukchas. In fact, their reliance on whale meat is so crucial that natives from Alaska and Chukotka have been granted aboriginal subsistence rights by the International Whaling Commission. Last years whale hunters have claimed a strong artificial odor prevents them to consume the whales. To identify the nature of the odor and to estimate the level of contamination of the Gray whales samples of blubber and tissues were delivered to the laboratory of organic analysis of the Moscow State University in 2004, 2007 and 2009.

Since volatile organic compounds (VOC) are responsible for the appearance of the smell GC-MS screening analysis of the samples was carried out. "Purge-and-trap" technique for volatile and liquid-liquid extraction semi volatile pollutants were used as sample preparation means before the GC-MS analysis. Several hundreds compounds were identified. Aldehydes dominated among volatile contaminants. The unpleasant smell of these compounds is well known. Since the levels of hydrocarbons in the "stinky" whales were much higher than in the clean ones their oxidation should bring to the carbonyl compounds. Acetone, benzene, toluene, diphenylsulphide are other candidates to cause the unpleasant pharmaceutical smell of the "stinky" whales.

The array of persistent pollutants remains pretty stable during last years. The blubber of whales is an ideal substance for the accumulation of lipophilic compounds (PAH, PCB, organochlorine pesticides). All these pollutants were detected in all the samples at reasonable levels. One of the blubber samples surprisingly contained 13 chlorinated PAH with 1 - 4 CI atoms. Earlier they were reported in tap water, air in the cities, automobile exhausts, smoke of the waste incinerators, waste waters of pulp and paper mills, sediments. The latter source is the most probable cause of the contamination of the Gray whales, as these animals feed (552 kg of plankton daily) filtrating sediments.

O 3

HEAVY METALS IMPACT TO ENVIRONMENT QUALITY OF ZETA PLAIN

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The area of Zeta Plain is the most populated area of Montenegro with a large population, traffic and a significant concentration of industrial plants, especially Aluminum factory. The pollution emitted by the above-mentioned sources differs in type, scope and quantity; therefore the effects are manifested in all parts of the environment.

The aim of this study was to determine the content of heavy metals, lead, cadmium, copper and zinc in soil samples, food and plant materials in order to determine the influence of the pollution sources on the environment in Zeta Plain, using plants as bio-indicators of soil contamination. At the same time bioavailability of studied metals, the mechanism of their adoption and risk assessment were analyzed by the calculation of bio-concentration factor (BCF) and transportation index (Ti).The determination of heavy metals content was performed using the technique of atomic absorption spectroscopy.

Obtained results showed that for twenty soil samples taken from Zeta Plain, it can be concluded that the concentration lead increased in fourteen soil samples, which is probably a result of the influence of traffic. Concerning cadmium, zinc and copper there was no contamination in the investigated soil sample. The lack of regulations prevents the qualification of the contamination degree of wild plants with heavy metals. Obtained results showed that the concentrations of the investigated heavy metals in all locations are higher in the soil than in plants. Also, the results showed that the contents of Pb, Cu and Zn exceed MAC values in all the investigated samples of vegetables, and samples taken near the Aluminum Factory Podgorica are more contaminated, while the content of Cd in vegetable samples is below MAC. On the basis of calculated values of Ti, which is in all samples of vegetables, for all metals, higher than 1, it can be concluded that the contamination of the samples originated from the air, considering that the BCF values are within the allowable limits.

Key words: Zeta Plain, heavy metals, BCF, Ti

P 1

COMPLEX ANALYTE SYSTEMS AND THE ROLE OF SENSORS FOR THEIR ELUCIDATION

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The monitoring of composting process to ensure its maturity is a complex problem because of the involvement of hazardous chemical profiles emitted out of the process and also due to the fact that these profiles are so random that human panels are usually unable to correctly elucidate them. But it is substantially important to measure those profiles due to the following reasons: i) to measure and avoid environmental hazards linked to the process because of these emissions to the surrounding living communities, ii) the correct information is extremely useful for predicting the maturity of the product which in turn leads to the precise maintenance of the soil ecosystem which otherwise can be ruined because of the presence of unwanted chemicals. Hereby, this process monitoring is performed using a sensor array equipped with integrated electronic circuitry and consisting of six channel quartz crystal microbalance (QCM) resonator. Different stages of composting for various plant materials were assessed using this array and GC-MS was used in connection for validation. Initial stages of composting yielded some alcohols and esters while in later stages, terpenes were in dominant quantity. This is in complete agreement of the process as carbohydrates degrade at the start while waxes and lipids decompose in the last days of composting. Additionally, results from sensor system were in good comparison to the GC-MS in spite of huge difference in working and maintenance cost.

P 2

ZINC SPECIATION IN PLANTS AND FATE OF ZINC SPECIES IN THE HUMAN DIGESTIVE TRACT

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Zinc speciation analysis is crucial in different fields of research including environmental chemistry, where limited information is available on zinc species in plants and the fate of these species in the human digestive tract, especially since zinc deficiency is recognized as a nutritional problem worldwide. In this work iceberg lettuce (*Lactuca sativa*) and pumpkin seeds (*Cucurbita pepo*) will be subjected to zinc speciation analysis via size-exclusion chromatography hyphenated with ICP-MS, after extraction of the species using "gentle" extractants, and in vitro gastrointestinal extraction tests (PBET) to account for the stability and potential uptake of zinc in the human digestive tract.

Analytical results show that pumpkin seeds and iceberg lettuce have different Zn species fingerprints (in water extracts) with a high (ca. 70%) low-MW fraction (ca. 500Da) in iceberg lettuce and a high (ca. 70%) intermediate/high-MW fraction (>10,000Da) in pumpkin seeds. When these Zn species are subjected to conditions simulating the human stomach (pH ~ 1) they break down completely. This disproofs conclusions of Zn speciation studies done in the past (on plants which are used for nutritional purposes) that low-MW Zn species may have nutritional importance. However, these findings open up a wide range of further interesting research possibilities, especially in the case of pumpkin seeds, where results evidence that anti-nutrients (e.g. naturally present phytate) can reduce the uptake of Zn by complexing with Zn^{2+} in small intestines (pH ~ 7).

Key words: Zinc, Plants, Characterization, Speciation, Physiologically Based Extraction Tests, Bioaccessibility, Nutrition, Deficiency.

P 3

COMPARATIVE STUDY BETWEEN PROBE FOCUSSED SONICATION AND CONVENTIONAL STIRRING IN THE EVALUATION OF CADMIUM AND COPPER IN PLANTS

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In the literature, ultrasound (US)-assisted extraction has been used for metal ion extraction in plants due to its unique properties of decreased extraction time, minimal contamination, low reagent consumption and low cost. However, very few papers present a sound comparison between probe-focused sonication and conventional stirring in the evaluation of metal ion extraction in plants. In this study, ultrasonic-assisted digestion has been evaluated and compared to magnetic stirring for total copper and cadmium determination by atomic absorption spectrometry in biological samples (plants, plankton and mussels). The same experimental conditions of sample amount and particle size, extractant solution and extraction time were applied for both extraction methods, in order to truly compare their effect on metal ion solubilisation. Different extractants were used, from mild to strong extractants, as well as enzymes and detergents, common used in speciation schemes. To gain further insight in this issue dried and fresh plants were tested. The results obtained indicated that ultrasound-specific properties did not contribute to the enhancement of metal ion solubilisation from the dried and powdered biological samples under study, even when the extraction was incomplete. Cell integrity in those samples was disrupted when they were immersed in aqueous solution due to the hydration process and osmotic tension in cell walls, while the enhancement due to US for the same purpose was negligible. In this sense, the application of sonication to render soluble metal ions from dried biological material, as widely used for many authors (based on the assumption that ultrasound energy enhanced the solubilising action of the extractant), does not present any advantage.

P 4

THE MONITORING OF A FORMER CONTAMINATION CAUSED BY URANIUM MINING IN LICOMERICE (CZECH REPUBLIC)

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The work has been focused on the development of the former uranium mining site located in Licoměřice, using a methodolgy for an uranium determination in water using orthogonal time-of- flight inductively coupled plasma mass spectrometry.

The analytical procedure for determination of uranium in water using o-TOF-ICP-MS method was processed including optimizing of measurement conditions. The limit of detection was defined as 89,95 ng/l of uranium. 67 samples taken both, from former mining sites and non-mining sites were analysed.

The highest concentration of uranium has been found in samples taken in the mining water treatment area in Licomerice. Emission limits for uranium were specified in resolution SUJB Praha č.j. 9156/4.3/00 agreed on 17.7.2000. The recording level of uranium emission limits has been exceeded in case of 10 water samples, the controlling level of emission limits has been exceeded for 5 water samples and the emergency lever of emission limits has been for 4 water samples. According to appendix 3-government resolution no. 61/2003 Sb., the imission limit allowed for the contamination with uranium in surface water, has been exceeded for 4 samples.

As the uranium concentration has been showing the lowering tendency during the miningwater treatment process, the recultivation and remedial measures taken by a state owned company-DIAMO in former mining site Licomerice can be considered as efficient.

The work was carried out under the financial support of the research plan MSM0021627502.

P 5

VOLTAMMETRIC DETERMINATION OF FOLIC ACID USING LIQUID MERCURY FREE SILVER AMALGAM ELECTRODE

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Mercury is due to its good electrochemical properties still one of the most used electrode material in electrochemical analysis. Mercury electrodes have many advantages but one serious disadvantage - toxicity of liquid mercury. That is why new non toxic electrode materials are looked for. Yosypchuk and Novotný introduced in 2000 silver solid amalgam electrode (AgSAE) which is made from non toxic silver amalgam. This electrode is used in some modifications and especially p-AgSAE (polished AgSAE), which was used for our measurements as a working electrode, contains no liquid mercury.

Folic acid (FA) is essential vitamin which is necessary for DNA and RNA biosynthesis, red blood cells formations and methylation processes in human body. The aim of our work was to investigate voltammetric behaviour of FA and its determination in real samples. All measurements were carried out in 3-electrodes set up in acetate buffer (pH 5) using differential pulse voltammetry. Some statistical parameters like the limit of detection (LOD = 5.9×10^{-10} mol.l^{-1}) or the relative standard deviation of 5 repeated determinations (RSD = 1.5 %) were calculated. The standard addition method was successfully used for determination of FA in two types of vitamin preparations and two kinds of fruit juices. It was found that p-AgSAE can replace mercury electrodes in voltammetric analysis of FA.

Acknowledgement: Financial support was provided by the Ministry of Education, Youth and Sports of the Czech Republic by the Research Centre LC06035 and by the project MSM 0021627502.

Reference: Yosypchuk B., Novotný L., Electroanalysis 14 (2000), 1733-1738.

P 6

DEVELOPMENT OF INTEGRATED PROTOCOL OF CHEMICAL AND BIOLOGICAL ANALYSIS FOR THE DETERMINATION OF STEROID ESTROGENS IN ENVIRONMENTAL SAMPLES

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Steroid estrogens are potentially harmful pollutants found in the environment in concentrations sufficient to affect living organisms, especially when chronically exposed. For quality risk assessment, not only chemical analysis that allows identification of sample composition, but also an estrogenicity assay that characterizes activity of the sample should be applied. In present study chemical sample characterisation using gas chromatography-mass spectrometric detection (GC-MSD) and biological characterisation using an ER-Calux® estrogenicity assay are integrated into a single protocol. For this purpose, routinely used DMSO was replaced with ethyl acetate in the ER-Calux® assay what enabled simple integration of both methods and the use of the same sample extract. Due to the high sensitivity of the ER-Calux® assay only a small amount (10 %) of the sample extract is used, while the remainder is available for chemical analysis. The method performance was tested by mixtures of standards in environmentally relevant concentrations of natural (estrone, 17β-estradiol and estriol) and synthetic (17α-ethinylestradiol) steroid estrogens. The results obtained from the ER-Calux® assay were compared to the calculated estrogenicity determined by GC-MSD. A good linear correlation (r^2=0,94) and an ideal slope (y=0,96x) were achieved which proves the successful integration of the two methods. An integrated protocol provides complete information about the sample, avoids duplication of sample preparation, reduces uncertainties due to limited preparation steps and still enables low LOD and LOQ of chemical analysis. For these reasons, it is a powerful tool for determining steroid estrogens and total estrogenicity in the environmental samples, together with reduced labour time and low consumption of used material and chemicals.

P 7

INFLUENCE OF ENVIRONMENTAL CONDITIONS ON THE ACCUMULATION OF PAHs IN VARIOUS PASSIVE SAMPLERS

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Over the last twenty years, several passive samplers have been developed to improve the monitoring of contaminants in aquatic systems. The amount of contaminant *in situ* accumulated during long periods of exposure enabled the determination of a time-weighted average concentration in water, provided exchange kinetic parameters are known. The aim of this work was to improve the knowledge of the influence of the environmental conditions on accumulation kinetics in passive samplers. The impact of the water velocity and the presence of biofilm at the surface of the sampler have been more particularly assessed. PAHs have been chosen as model hydrophobic compounds. Three passive samplers have been studied: semipermeable membranes devices (SPMDs) and polymeric membranes (LDPE and PDMS). A stainless steel channel of 6 m length has been constructed with 3 successive sections with different width and controlled velocities (0.02 to 0.09 m/s) and has been fed with wastewater at different stages of the treatment. Kinetics have been determined with passive samplers previously spiked with Performance Reference Compounds and exposed for two weeks. Dissolved concentration has been measured three times during the exposition period. A relation has been observed between the water velocity and the accumulation or elimination kinetics for all passive samplers tested regardless of the water composition. For SPMDs, the presence of biofilm at the surface has not strongly influenced exchange kinetics.

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P 8

DETERMINATION OF ATRAZINE IN SURFACE WATERS BY COMBINATION OF POCIS SAMPLING AND ELISA DETECTION

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Antibody based detection techniques such as ELISA (enzyme linked immunosorbent assay) represent a simple screening tools which can be used in both laboratory and field settings. Sampling and clean up procedures prior to target detection play a key role in the immunoassay application. Conventional methods for the monitoring of surface water rely on discontinuous grab or composite sampling. These approaches are shown to be effective for documenting the occurrence of pollutants but they provide only information about concentration levels at the time of sampling and thus may miss episodic events. On the other side, the passive sampling devices offer a cheaper and more effective procedure for measuring time-weighted average analyte concentrations in the aquatic environment over time. In this study, passive POCIS technology was applied for surface water sampling (in selected localities of the Czech Republic) whereas ELISA was used as a detection technique for atrazine. Analysis of 28 samples collected continuously from streams around small waste water treatment plants (WWTPs) by POCIS pest and POCIS pharm devices in the course of 21 days showed that atrazine concentrations were in most cases higher in down-stream samples than in up-stream samples. In another experiment, samples from 7 localities in the Brno agglomeration and inlet and outlet from the city WWTP were collected using POCIS pest device during two years. There was found atrazine decrease in samples from the most localities. High atrazine levels (120 – 605 ng per POCIS) were determined in samples collected on the outlet from WWTPs. Comparison of the atrazine ELISA with LC-MS/MS showed a good correlation of results.

This study was supported by Ministry of Education, Youth and Sports of the Czech Republic (project ENVISCREEN 2B08036).

P 9

UNCERTAINTY EVALUATION AND IN HOUSE METHOD VALIDATION OF THE HERBICIDE IODOSULFURON-METHYL-SODIUM IN WATER SAMPLES BY USING HPLC ANALYSIS

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A method for separation and quantitative determination of the iodosulfuron-methyl-sodium in water samples by high performance liquid chromatography (HPLC) was developed and in-house validated in order to demonstrate its performance for monitoring of heterogeneous photocatalytic elimination of the herbicide iodosulfuron-methyl-sodium from water. Surface and ground water samples were used to demonstrate its selectivity, detection and quantification limits, linearity, trueness and precision. In addition, stability of iodosulfuron-methyl-sodium was studied in function of temperature and time. Method accuracy was quantified through measurement uncertainty estimate based on method validation data. The paper gives practical and easy to follow guidance on how uncertainty estimates can be obtained from method validation experiments. It shows that, if properly planned and executed, key precision and trueness studies undertaken for validation purposes can also provide much of the data needed to produce an estimate of measurement uncertainty. Our analytical protocol allowed us to quantify iodosulfuron-methyl-sodium in ground water and surface water in concentration level between 2.50 – 50.0 μmol L^{-1} with satisfactory recoveries (99% – 104%) and repeatability lower or equal than 0.3% for all the matrices. We also estimated within-laboratory reproducibility over three months period, which was 0.7%. We proved that the method was specific for determination of iodosulfuron-methyl-sodium in the relevant matrices. Measurement uncertainty of results was evaluated to be 3.4% with 95% confidence level.

P 10

MONITORING OF NITRATE AND NITRITE NITROGEN IN WASTE WATER BY USING ON LINE UV SPECTROMETRIC METHOD

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Monitoring water and waste water quality parameters is currently a subject of growing concern throught the world. Monitoring of waste water quality is among other purposes essential for waste water treatment plants design, for their optimization and controll, and for improving process undertanding. Nitrate, the most abundant form of inorganic nitrogen, is formed in waste water treatment process during the nitrification step when waste water is aerated. Continuous minitoring of nitrate is desired during both the nitrification and denitrification steps. Standardized methods are proven to give reliable and comparable results of waste water quality parameters, but are mainly based on sample collection and retrospective analysis, which makes their application to real-time monitoring and process control very difficult. On-line detection of pollutants in waste water is recognized to be the best practice for continous water quality monitoring, as it eliminates contaminants due to sample handling, minimizes the overall cost of sample collection and analysis, and increases monitoring capability enabeling in time results and appropriate control of the processes in waste water treatment plants. A method is proposed for on-line UV spectroscopy and data analysis are applied to determine nitrate and nitrite nitrogen (NO_x-N) in various waste water matrices. Comparison with standard analytical method was performed. Sensor calibration with pure substance reference materials delivered sufficient resuls for characteristic municipal waste water matrix, but for waste water with substantual industrial contribution and for landfill leachate matrix match calibration was required to enhance trueness. The described method concept is well suited for on-line monitoring.

P 11

CORRELATION BETWEEN OZONE AND TOTAL VOCs IN PRINTING ENVIRONMENT

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In this study the concentration levels of ozone and total volatile organic compounds (TVOCs) were measured during working time in a screen printing facility of Novi Sad in order to investigate the workers exposure level of TVO compounds and to identify correlation between ozone and TVOCs in printing environment.

The air sampling was conducted in press department, including two different types of screen printing machines: semi-automatic and automatic. Air samples were collected and analyzed *in situ* for 4 times, once per 2 hour, during working time of 8 hr by ozonometer, Aeroqual Series 200, Aeroqual Ltd. and mobile gas chromatograph Voyager, Photovac, Inc. The ozone concentrations were from 0.12 to 0.45 ppm for semi-automatic printing machine and 0.81 to 0.92 ppm for automatic screen printing machine. The TVOC concentrations were from 25.53 to 30.10 ppm for semi-automatic and 10.02 to 19.07 ppm for automatic screen printing machine.

Analysis of the experimental data showed that ambient ozone concentration slowly increases with the increasing of TVOCs concentration and light intensity during screen printing process. The ozone concentration levels are above the permissible exposure limit (PEL) for 8-hour TWA (time-weighted average) recommended by the OSHA (Occupational Safety and Health Administration), while the TVOC concentrations were much below the PEL prescribed by the OSHA. In the Republic of Serbia, the Regulation of permitted concentration levels of TVOCs and ozone until now has not adopted.

Keywords: ozone, total volatile organic compounds (TVOCs), exposure level, screen printing process, printing industry

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P 12

IR SPECTROSCOPIC STUDY ON INDICATOR SPECIES OF LICHENS FOR DETECTION OF NITROGEN DIOXIDE IN ATMOSPHERE

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Nitrogen dioxide is one on the main atmospheric pollutants and its content grows rapidly. Interacting with water in the air NO_2 forms nitric acid, which is one of the components of the acidic rains. The goal of this work is identification of NO_2 in the atmosphere by means of IR spectroscopic study of indicator species of lichens. Object of this study are samples of different lichens: *Xanthotia parietina* (L.) Belt., *Hypogymnia physodes* (L.) Nyl., *Parmelia sulcata* Tayl., *Evernia mesomorpfa* (Flot.) Nyl. The experiment is performed in 1 l glasses containing 40 ml of HNO_3 of different concentration (0.5, 1, 3, 6, 9 %). The lichen is fixed to the inner part of the lid tightly closed just after replacing the sample. The experiment is conducted at room temperature (22–25^{0}C) during 7 days. Then the lichen samples are dried at 30–35 ^{0}C for 3 h and used for preparation of pellets with KBr to record IR spectra on “Equinox 55” spectrometer (“Bruker”) at 4 cm^{-1}, 32 scans.

By this way an attempt to reproduce interaction of vaporous HNO_3 with the components of the lichen is done. As a result a number of absorption bands appeared in IR spectra of the lichens (1381 cm^{-1} –ν_sO-NO$_2$, 874 and 779 cm^{-1} –δO–N–O) can be attributed to alkylnitrates, which formation is possible due to interaction of the acid with hydroxyl groups of lichenan. Qualitative estimation of the spectroscopic data is performed. It is established that in such conditions resistance of *P. sulcata* and *Ev. mesomorpfa* is very similar. Changes in the chemical composition are accompanied by morphological transformations.

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P 13

STUDY OF QUANTITATIVE AND QUALITATIVE VARIATION AT DIFFERENT STAGES OF PLANT GROWTH AND IN VITRO ANTIBACTERIAL ACTIVITY OF *PEROVSKIA ABROTANOIDES KAREL*

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Perovskia is a genus belonging to the *Lamiaceae* family which is allied to *Salvia*, *Nepeta* and *Rosmarinus*. *Provskia* is represented in Flora Iranica by only three species. *Perovskis abrotanoides Karel*, is an aromatic erect herb which is used in Iranian folk medicine as an analgesic in rheumatic pains The essential oil components of the leaves were isolated by hydrodistillation from *Perovskia abrotanoides Karel*, at different stages of plant growth. The oils were studied by gas chromatography mass spectrometry (GC/MS). Some of major components in the leaf oils were: camphor (17.59-26.74%), 1,8–cineol (14.67-24.39%), α-pinene (2.64-3.65%), 3-carene (6.22-18.55%), camphene (2.20-4.84%), caryophyllene (5.43-9.62%), and α-humulene (4.03-7.79%). The results show that the oil yield and the major constituent's percentage of the flower were different at different stages of plant growth. The essential oils of *Perovskia abrotanoids Karel* leaves were tested against two strains of gram positive bacteria (*Bacillus cereus, Staphylococcus aureus*) and two strains of gram negative bacteria (*Escherichia coli, Klebsiella pneumonia*). The average minimal inhibitor (MIC) and minimal bactericidal concentration (MBC) of essential oils were tested against the organisms by agar dilution.

P 14

STUDY OF VOLATILE ORGANIC COMPOUNDS OF *TEUCRIUM POLIUM* JUICE AND FRESH PLANT FROM DIFFERENT REGIONS USING HEAD SPACE SOLID PHASE MICROEXTRACTION (HS-SPME) GAS CHROMATOGRAPHY MASS SPECTROMETRY(GC/MS)

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Variation in chemical composition of essential oils, in particular and extracts of medicinal plants may be observed due to the origin the environmental conditions and the developmental stage of collected plant materials. Despite the huge analytical potential of these techniques they suffer some drawbacks: the need for highly sophisticated and costly samplers for automated injections, long preparation time, and often the need for sample heating to release volatiles. Heating accelerates further degradation of analyzed compounds. Solid phase microextraction technique (SPME) a solvent-free extraction technique eliminates some of these disadvantages. This technique proved to be an effective tool for detecting low levels of derived flavour compounds. The flavor components of the aerial and juice were isolated by HS-SPME from *Teucrium polium* , from different regions of plant growing Proviences. The volatile components of the plant were studied by gas chromatography mass spectrometry (GC/MS). Some of major components in the juice were: camphor (45.59%), yomogi alcohol (11.59%), dihydrocarvone trans (7.83%), carvone (7.23%), thymol (4.45%), bornyl acetate (3.35%), and 1,8-cineole (2.51%). The results show that the juice flavors and the major constituent's percentage of the fresh plant were different at different regions of plant growth. The results show that camphor is about half of the volatiles in the juice and fresh plant. This compound is readily absorbed through the skin and produces a feeling of cooling similar to that of menthol. It used in medicine as a stimulant, a diaphoretic, and inhalant.

P 15

STUDY OF THE VOLATILE COMPOUNDS IN *ARTEMISIA ABROTANUM L.* FROM IRAN USING HS/SPME/GC/MS

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The aerial parts of the plant *Artemisia abrotanum L.* were collected in August 2010 from Damavand (Tehran Province of Iran). It is air dried in a shadow place. A headspace solid-phase micro-extraction (HS-SPME) method followed by gas chromatography–mass spectrometry (GC/MS) was used for the analysis of volatile compounds in the leaves of *Artemisia abrotanum L.* The dried plant was powdered and the aroma compounds of a 0.05g were isolated by HS-SPME fiber in 15 min. The chemical compounds of the plant were investigated by gas chromatography mass spectrometry (GC/MS). A total of 64 constituents, representing more than 99% of volatiles were identified. The main compounds, were isobornil acetate (19.56%) , eucalyptol (14.81%), (+) trans- chrysanthenyl acetate (12.76%), *α*- cubene (9.70%), borneol (9.06%), caryophyllene (7.03%), camphor(6.83%), *γ*-elemene (2.16%), bicycle[2.2.1]heptan-3-one, 6,6-dimethyl-2-methylene (1.73%) and copaene (1.37%). This herbal medicine traditionally uses as anti- infectious, anti- bacterial, gastric tonic, digestive and stomachic in Iran. Consequently, this fast and simple method can be used for the analysis of the volatile compounds emitted from *Artemisia abrotanum L.* plant.

P 16

IMPACT OF URBAN TRUCK FARMING ON SOIL CHARACTERISTICS IN TROPICAL CLIMATE (GABON)

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The fast demographic growth observed in developing countries generates an important increase in truck farming in urban zones. As other many anthropic activities, truck farming can be associated to soils overexploitation and organic and inorganic contamination. This situation is amplified due to the lack of landworkers information and needs of intensive growth methods in these countries. This combination of factors can finally induce to soils deterioration. Additionally, soils and vegetables contamination by metals can not be neglected.

The present study was focused on urban areas of Libreville, Gabon. The aim of this work was to analyze truck farming impact on soils properties in tropical climate. The presence of metals in soils (Cd, Cu, Fe, Mn, Pb, Zn) and their mobility potential was determined as well.

Six sites were selected based on exploitation time which was between 3 and 30 years. From each site, samples (cultivated soils) and referential (non cultivated soils) were collected at the surface layer (0-20 cm) in triplicates as minimum. Physico-chemical characteristics (pH, granulometry, CEC, organic matter, Kjeldhal nitrogen, exchangeable phosphorus…) were analyzed, as well as total metal concentrations (aqua regia mineralization method) and metals mobility potential (EDTA extraction, BCR method). The results have shown that the implemented cultivation methods lead to an important soils acidification (down to pH = 2) and to a general decrease of metals concentrations, organic matter and nutrients in cultivated soils. In the majority of samples collected, the proportion of metals mobility has been lower in cultivated areas than in referential (% of total metal).

P 17

HYDROCHEMICAL INVESTIGATION OF THE NITROGEN SPECIES OF THE DANUBE BETWEEN RAJKA AND KOMÁROM (1848-1766 rkm)

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In the present work, the hydrochemical investigation of the nitrogen species (NH_4^+-N, NO_2-N, NO_3^--N, organic nitrogen and total nitrogen) of the Danube River was studied based on the measured chemical data originated from the sampling sections located at Rajka, Medve and Komárom (1848, 1806 and 1766 rkm) under the authority of the Inspectorate for Environment, Nature and Water of the North Transdanubian Region (Hungary). The quantitative changes of the nitrogen species as a function of time and longitudinal section were examined in the period of 1989-2008.

During the above twenty years approx. 11000 chemical data of the nitrogen parameters were measured by the regular water qualifications. At the beginning this meant 26-52 water sampling at all the three sampling stations while in the last years its number decreased to 12 samplings a year. The inorganic nitrogen contents were analysed by spectrofotometric methods according to the valid Hungarian standards. The organic nitrogen content was determined by the Kjeldahl method.

The results have revealed that the concentration of the total nitrogen content has been decreased in the long run. In the last two decades the amount of the ammonium has decreased significantly while the amount of the nitrate and nitrite has decreased only to a smaller extent. The concentration of the organic nitrogen has decreased in the second half of the examined period.

Keywords: Danube, hydrochemistry, nitrogen, spectrofotometry, Kjeldahl

P 18

ASSESSMENT OF WATER QUALITY IN A TROPICAL WETLAND TO MAINTAIN LOCAL WATER SECURITY

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This paper analyses the impact of environmental degradation and climate change on the water quality in a wetland and assesses how low-cost, environment friendly technologies improves the water quality. Climate change and anthropogenic impacts highly degraded the water quality in the Vembanad-Kol wetland in Kerala, south India, leading to serious shortage of reliable water. Because of the input of untreated industrial, agricultural and domestic wastes and mixing of brackish water due to failure in a project, water in the region became unfit for human use and aquatic life. Routine analysis of water sample from selected ideal locations for twelve months showed that presence of organic and inorganic pollutants are very high, water quality is much below safety limits and serious health hazards could be expected in near future. Hardness of water shows that water is totally unfit for human use. Amount of dissolved oxygen has become so low that organisms such as fish and frog disappeared from most of the region. Vector-borne and water-borne diseases affected thousands. Change in rainfall seasonality and failure in the project to multiple crop production by controlling salinity intrusion affected natural flushing of water. Rainfall is becoming more seasonal, causing erosion and sedimentation in water bodies and making parts of the wetland dry for a few months. However, experiments in the test plot with local technology using locally available plants capable of purifying water, locally available material like charcoal and lime shell, and locally made cheap aerators prove that condition can be made better without much investment, provided, the human impact is also minimised. Deepening and cleaning of the canal to enhance water circulation and erosion control using local plants made a lot of changes. Guidelines for the protection of wetland under a changing climate and environment have been provided.

P 19

ICP-MS AND ICP-OES ANALYSIS OF HORSE HAIR

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For a monitoring the environment influence of the organism health, exposure to pollution or accumulation in the body), hair analysis (horsehair, fur, wool etc.) has been recently more widely used. Hair are commonly analyzed both to demonstrate elements, and various organic substances of the organism intoxication. It is suitable matrix mainly for the identification of persistent and bioaccumulation substances, because hair are known to accumulate metal concentrations over time, thus containing a higher concentration than found in blood, serum or urine sample. The hair matrix is non-invasive, readily available, can be easily transported and does not require special storage requirements.

The aim of this work was to find a suitable process for preparing and consequential analysis horse hair using inductively coupled plasma optical emission spectrometry and orthogonal time of flight inductively coupled plasma mass spectroscopy methods. Several techniques of acid washing were tested. The simple using of a mixture of nitric acid and Triton X-100 and consequential water rinsing in an ultrasonic bath was found to be effective. Proper conditions for a microwave digestion were found. Working conditions for oTOF-ICP-MS analysis were optimized including a selection of working isotopes, concentration of calibration standards and selection of internal standards. Detection limits of the method for 52 elements analysed were found in the range from 60 ng/kg to 6 µg/kg. Matrix elements (Ca, K, Mg, Na, P, S) and Zn Cu, Fe were determined using ICP-OES method. Accuracy of analysis was verified using the certified reference material Human Hair NCS ZC 8100.

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P 20

POLYCYCLIC AROMATIC HYDROCARBONS IN AIR: SOURCES AND HEAVY METALS CORRELATION ANALYSIS

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The polycyclic aromatic hydrocarbons (PAHs) are important environmental pollutants because of their carcinogenicity and mutagenicity properties. PAHs and their derivatives are produced during the incomplete combustion and pyrolysis of fossil fuels (domestic, mobile, industrial, agricultural). The aim of this study was to determine the range of concentrations and possible sources of PAHs in Zumarraga, north of Spain from January to June 2010. Out of the 16 EPA PAHs, six were evaluated (fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene). The sampling was carried out with low volume collectors IND with PM_{10} inlets and Whatman quartz microfibre filters (QMA 1851-047). PAHs were obtained through a process of solid-liquid extraction with n-hexane in an ultrasonic bath. The extracts were evaporated with nitrogen and reconstituted with acetonitrile. The chemical analysis was carried out by UPLC-FL (Waters Acquity UPLC H-Class). The total concentration of PAHs varied from 0.3 to 38.7 ng m^{-3} where the individual concentration was highest for benzo(b)fluoranthene (14.5 ng m^{-3}). The relationship between PAHs, PM10 and metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Ba, Ce, Pb) was studied by principal component analysis, and three main components were extracted. The first suggets as possible sources of PAHs the industrial emissions. The second is a different kind of industrial source while the third component is due to the traffic.

P 21

GLOBAL DISTRIBUTION AND FATE OF DDT

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Dichlorodiphenyltrichloroethane (DDT) and its major metabolites (DDE, dichlorodiphenyldichloroethylene, and DDD, dichlorodiphenyldichloroethane) are persistent, toxic, and bioaccumulative, and have the potential to undergo long-range-transport, hence pose a hazard to the environment and human health. Though banned since decades for use in agriculture and forestry, DDT is currently at least regionally increasingly introduced into the environment from old stocks, due to illegal use, as impurity of another pesticide (dicofol), and for vector control purposes. Degradation rates, and DDT's solubility, however, are insufficiently known, and the total global 'life cycle' had not been described comprehensively so far. Lifetimes of *p,p'*-DDT, -DDE and -DDD in air, deduced from observations at a high mountain site correspond to $k_{OH} < 1.5 \cdot 10^{-12}$ cm^3 $molec^{-1}$ s^{-1}, i.e. are partly significantly lower than estimated. By global multicompartmental modelling of the atmospheric and oceanic transports of DDT and DDE the global total environmental 'life cycle' (1950-2000), geographic and multicompartmental distributions, and the influences of atmospheric lifetime and water solubility on the distributions are assessed.

P 22

COMPARATIVE ANALYSIS OF TRACE ELEMENTS ACCUMULATION IN THE SUMMER LEAVES OF COMMON URBAN DECIDUOUS TREES IN SOFIA AND BELGRADE

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This study comprises parallel investigations on some trace elements accumulation in leaves of selected common trees from urban areas of Sofia and Belgrade, the two capitals of neighbouring European countries. The assay took place in July of 2009, aiming to cover the maximum of the physiological activities of tree species (birch, maple, linden, horse chestnut) during the vegetation season. The results of chemical analyses (ICP-OES and ICP-MS) were obtained both on unwashed and washed leaf samples. Though leaves were only shortly washed (rinsed for one minute twice with double distilled water), for some elements, there was a significant difference in leaf contents between washed and unwashed leaves (most pronounced for Pb, also evident for V, Cr and Cd). Some element concentrations (Cr, Ni. V) in leaves were higher in Belgrade (B) than in Sofia (S), while others were lower (As, Cd, Co, Pb) in B. In the two investigated cities, the same species (birch, maple, linden, horse chestnut) exhibited different element accumulation levels. The results of this study indicated that evaluation of species validity for biomonitoring is a complex task, and that the species specificity has no predominant influence on trace elements accumulation in leaves, and other factors may prevail.

P 23

VOC EMISSIONS IN OFFSET PRINTING PLANTS

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Volatile organic compounds (VOCs) are organic chemical compounds that have high enough vapor pressures under normal conditions to significantly vaporize and enter the atmosphere. Printing inks and coatings used in the commercial graphic printing industry contain VOCs in varying amounts, depending on the type of ink, the drying and printing processes, substrates and end-use application requirements. Mean VOC concentrations in four different printing plants that use distinct types of vegetable based and water based inks and solvents were monitored for the purpose of quantifying the various VOCs in these areas and to relate the results with conventional printing processes. In each site VOCs were monitored during one workweek. They were sampled and analysed by mobile GC Voyager Photovac. Concentration levels of BTEX were often below limit of detection. Concentration levels of isopropanol and acetone were in range 232 – 4630 ppb and 144 – 1813 ppb, respectively. BTEX concentrations and concentrations of the other VOCs founded in printing work environments of “ecological” printing plants were below the limits considered by the Serbian law and recommendations prescribed by NIOSH (National Institute for Occupational Safety and Health).

Key words: volatile organic compounds, printing industry, ecological printing plats

P 24

o,p´-/p,p´-ISOMERS OF DDT AND ITS METABOLITES: AN APPROACH FOR LINKING SUBSTITUTION ISOMER RATIOS WITH ENVIRONMENTAL PROCESSES AND SOURCES

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Recent publications related to isomer-specific analyses were carefully reviewed for linking substitution isomer ratios with environmental processes and sources. Despite more than 2000 references related to DDT only 102 report isomer-specific data.

Only for two Superfund Sites source related isomer specific data are available, mostly for the routinely analysed six congeners. The o,p´-isomers are mostly lacking in biota samples illustrating the estrogenic interference with hormone activity, despite a more recalcitrant behavior in abiotic samples.

The global distribution of DDT and dicofol (an DDT-related acaricide) is evident. The actual sources of DDT are vector control in subtropic and tropic regions, the application as antifouling agent in China and the co-contamination by dicofol.

An outlook focuses on future research fields and unattended relationships and recommends the inclusion of o,p´-isomers in analytical scheme as an easy basic information for further tracking the global distribution as well as the enantiomeric analysis for differentiation of environmental effects.

P 25

COMPARISON OF THE RIVERS JUZNA, ZAPADNA AND VELIKA MORAVA (SERBIA) AND LONG-TERM TREND DETECTION

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The Morava river system contains 3 rivers: Juzna (Southern) Morava and Zapadna (Western) Morava which combined form Velika (Great) Morava. None of them is international river and their total drainage basin has 37,444 km². Mouth of Velika Morava is in Danube River, downstream of Smederevo and Belgrade.

Analyzed data was collected between years 1992 and 2006 from 18 sampling stations (6 on each river). Among more than 30 eco-chemical parameters, 15 was chosen (discharge, pH, nitrates, phosphates, total P, COD, BOD-5, UV extinction at 254nm, dissolved oxygen concentration and saturation, suspended matter, ignition residue and loss, dry matter and electrical conductivity) for statistical analysis based on their importance and quality of collected data. They were divided in four groups: nutrients, oxygen parameters, organic load and overall dissolved and suspended matter load.

Statistical analysis was performed using median values instead of arithmetic means. This way influence of misrepresentative extreme values determined due to unusual ecol. incidents, errors in sampling, lab. analysis, data transcription etc. was minimised. Existence of temporal and spatial trends was examined. Spatial trends were analyzed either by comparing yearly medians from place to place, or by comparing median values of measurements made in specific month between selected locations (seasonal spatial trends).

Every sampling location is checked for existence of time trend whether parameters change from year 1992 to 2006. Also changes between months from January to December were followed. In this case, trends are better described by quadratic function than linear.

Average values from last sampling location of Juzna and Zapadna Morava were compared with av. values of first and last sampl. location at Velika M. for the purpose of determination of tributary influence and Velika Morava self purification potential and contaminant pressure. Spatial and temporal trends of selected eco-chemical parameters were compared between 2 tributaries and Velika Morava.

P 26

SLOVENIAN OLIVE MILL WASTES: A POTENT SOURCE OF BIOACTIVE PHENOLS

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The interests in natural product research for drug discovery purposes have greatly expanded since 1980s [1] with particular emphasis on recovery of value-added compounds from plant materials and/or their processing products [1-2]. Concepts like this have also found application in various agri-food waste matrices, including the one of olive oil production. In fact, olive mill wastes have been already confirmed as a valuable source of different bioactive phenols [2], important targets of food and pharmaceutical industries [1] attributed to their antioxidant properties.

In recognition of waste recycling importance, the present study was undertaken in an environmentally friendly aspect to determine the phenol profile of Slovenian olive mill wastes, along with their antioxidant activity assessment. Thus, two olive waste matrices (wastewater & pomace) were screened for a potent presence of bioactive phenols, in a search for a low-cost alternative source of natural antioxidants within a sustainable framework of an ongoing eco trend.

HPLC-DAD/MS analyses confirmed the presence of several phenols in both samples of olive mill wastes, including hydroxytyrosol, tyrosol, verbascoside, luteolin, comselogoside, caffeic acid and their corresponding glycosides/isomers. While the total phenol content in a solid olive reside i.e. pomace was rather low (9.2 ± 0.7 mg g^{-1} DW), a much higher values were obtained in liquid i.e. wastewater sample (47.6 ± 0.1 mg g^{-1} DW) as determined by Folin-Ciocalteu analysis. However, simple regression analysis ($r = 0.88$) also revealed a strong contribution of total phenols to overall antioxidant potential of samples tested, indicating that Slovenian olive mill wastes could present a promising source of screening hits, like hydroxytyrosol, tyrosol and verbascoside, associated with highest antioxidant activities, and hence of highest commercial value.

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P 27

IDENTIFICATION OF SO_2 IN INDUSTRIAL AREAS BY MEANS OF INFRA RED SPECTROSCOPIC ANALYSIS OF *HYPOGYMNIA PHYSODES* (L.) NYL.

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Modern towns concentrate different technogenic objects, which are the sources of various ecotoxicants. It is urgently necessary and important to detect each of them. In this work a novel approach based on IR spectroscopic analysis of lichens allowing to identify sulfur containing pollutant (SO_2) in the samples and to evaluate its biological effect on the lichens is suggested. The method combines advantages of lichenindication and IR spectroscopy**.**

Samples of *Hypogymnia physodes* (L.) Nyl. lichen collected in industrial districts of Tver with various type and level of atmospheric pollutions are studied. For IR spectroscopic measurements pellets of the lichen samples (~ 2,5 mg) with KBr (~ 0,75 g) are prepared. Spectra are recorded on FTIR spectrometer “Equinox 55” (“Bruker”) with 4 cm^{-1} resolution and 32 scan.

Essential difference caused by influence of the pollutants has found in IR spectra of the samples from various places. Absorption bands of different intensity at 1313, 782, 666 and 514 cm^{-1}, which correspond to sulfons (-R-SO_2-R) are discovered in spectra of the studied samples. Sulfons are formed in the lichens due to a long term influence of SO_2 of low concentrations that is confirmed by the results of numerous modeling experiments. Qualitative estimation of the spectroscopic data coincides with the results of lichenindication. It is found that high content of the sulfons characterizes the samples from highly polluted areas. Experimentally proved that the approach can be applied for detection of SO_2 among different atmospheric ecotoxicants.

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P 28

MULTI-PUMPING FLOW DETERMINATION OF AUXIN HERBICIDES COUPLED WITH CHEMILUMINESCENCE DETECTION

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Chemiluminescence (CL) has been established as a valuable detection technique in flow analysis. CL based flow procedures present a number of advantages: they do not require an external energy source, they are very sensitive and present wide dynamic ranges and low detection limits, the response is almost inmediate and the instrumentation is relatively simple and cheap. On the other hand, the use of micro-solenoid pumps in pulsed flow chemistry is a vialable alternative for automated analyses. Furthermore, the pulsed pattern flow related to the propelling units used, ensures a fast and efficient sample-reagent interaction that leads to a better reaction zone homogenisation. Moreover, increased sample throughput, reduction of sample and reagents consumption and easier management of solutions are significant improved over classical FIA methodologies.

In the present communication a multi-pumping flow manifold based on the utilisation of multiple solenoid-actuated micro-pumps is proposed. The active device incorporates the liquid propelling units, the sample insertion port and commuting elements. Reconfiguration of the flow manifold is performed by using software settings, without physical alteration of the instrument manifold. The pulsed flow system allows an easy control of insertion and mixing patterns for sample, oxidant and sensitizers´ solution. Chemical and flow parameters, namely, medium and concentration of oxidant, influence of sensitizers, as well as the number of pulses and insertion pattern for sample and oxidant solutions were optimised. The resulting fully automated multi-pumping flow system was applied to the direct chemiluminescent determination of Indol-3-ylacetic acid and 4-Indol-3-ylbutyric acid auxin plant growth regulator herbicides in technical formulations and environmental samples.

P 29

CONCENTRATION AND DETECTION OF PLANT AND HUMAN VIRUSES USING CIM MONOLITHS AND REAL TIME qPCR

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Human and plant viruses can be present in lakes, rivers and public water supplies under a variety of circumstances, such as natural disasters or bioterrorism. Apart from these reasons, animal and plant viruses can make their way to environmental waters also by faecal contamination (enteric viruses) and by release from plant roots or infected leaves (several plant viruses). In order to detect viruses in such samples concentration prior to detection is essential. We have combined the high potential of CIM monolithic supports for viral concentration with the high potential of real time quantitative PCR for virus detection. In this presentation we will show the particular cases of the human Rotavirus (icosahedral) and plant Pepino mosaic virus (filamentous) concentration, and the implementation of such detection system to on-site detection format.

P 30

DEVELOPMENT AND VALIDATION OF MULTI-RESIDUE ANALYSIS OF PHARMACEUTICALS IN WATER BY ONLINE PRECONCENTRATION - LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY

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The impact of pharmaceuticals towards aquatic and ground ecosystem is still poorly known. However, some cases were showing pharmaceutical effects on ecosystems (feminization of fish, high mortality of vultures caused by diclofenac[1]).

To increase the knowledge of pharmaceuticals in water bodies is therefore very important as they may represent a potential environmental problem. The characterization of pharmaceutical contamination requires powerful analytical method able to detect compounds at very low concentration (few ng/L).

Multi-residue analytical methods have been reported in literature. A step of sample preparation with Solid-Phase Extraction is often necessary before the analysis itself. This step is crucial and time consuming. In our work, a multi-residue chromatographic method (liquid chromatography - triple quadrupole mass spectrometry using positive and negative electrospray ionisation) has been developed and validated for 40 multi-class pharmaceuticals and metabolites in drinking and surface waters. The extraction step has been performed online (EQuan system developed by Thermo Fisher Scientific). Pharmaceutical compounds included in the method have been selected according to several criteria: lipid regulators, antibiotics, β-blockers, non-steroidal anti-inflammatories, anticancer drugs, etc. The poster presentation will show the development and validation of the method. A performance discussion will also be proposed with respect to pharmaceutical properties.

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P 31

DETECTION OF VOLATILE CHLORINATED HYDROCARBONS BY CRYOFOCUSING GC-ECD SYSTEM

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Chlorine is one of the most abundant elements in nature, which undergoes a complex biogeochemical cycle. Chlorine bound in some substances is partly responsible for atmospheric ozone depletion and contamination of some ecosystems. As due to international regulations anthropogenic burden of volatile chlorinated hydrocarbons (VCH) in atmosphere decreases, natural sources (plants, soil, abiotic formation) are expected to dominate VCH production in the near future. Examples of plant VCH production are methyl chloride, and bromide emission from (sub)tropical ferns (Saito and Yokouchi, 2006), chloroform, 1,1,1-trichloroethane and tetrachloromethane emission from temperate forest fern and moss (Laturnus and Matucha, 2008). Temperate forests are found to emit in addition to the previous compounds tetrachloroethene, bromoform and bromodichloromethane (Hoekstra et al., 1998). VCH are taken up and further metabolized. As an example see the formation of trichloroacetic acid from tetrachloroethene in spruce chloroplasts (Forczek et al., 2008). The aim of this work is to identify the formed VCH in temperate forest ecosystem by a cryofocusing/GC-ECD detection method, hence filling a gap of knowledge in the biogeochemical cycle of chlorine.

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P 32

SIZE DISTRIBUTED URBAN AEROSOL MASS CONCENTRATIONS OF BELGRADE (SUMMER-AUTUMN 2008)

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This work focuses on the size-segregated aerosol chemical composition observed during the summer-autumn 2008th. Within the SIMCA project (INTERREG/CARDS-PHARE Adriatic New Neighborhood Programme) size-segregated aerosol was sampled using 6 -stage High Volume Cascade Impactor. During the measured campaign were taken 32 samples every 6th day. Sampling duration for each sample was 48 hours. Particle size distribution in the size range 0.0 to 0.49*μm*, 0.49 to 0.95*μm*, 0.95 to 1.5*μm*, 1.5 to 3.0*μm*, 3.0 to 7.2*μm* and > 7.2*μm* in urban area of Belgrade were measured. Aerosol mass concentrations are determined by gravimetric measurements (m_{GM}). One-fifth of filter sample were extracted in 5 mL of ultra-pure water and analyzed by ion chromatography Metrohm for Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}.

The obtained results were done with the precisions 8% for Cl^-, 2% for NO_3^-, 2% for SO_4^{2-}, 3.2% for Na^+, 18% for NH_4^+, 24% for Ca^{2+}, 3% for Mg^{2+} and 8% for K^+.

The first results are shown two peaks: at 0.56*μm* and 9.77*μm* for particles, two peaks: at 0.50*μm* and 4.2*μm* for SO_4^{2-}, three peaks at: 0.32*μm*, 1.2*μm* and 5.01*μm* respectively for NH_4^+ and three peaks at: 0.30*μm*, 1.2*μm* and 4.79*μm* respectively for Ca^{2+}.

P 33

COMPARISON BETWEEN CLASSICAL AND IMPROVED POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLER (POCIS) FOR ALKYLPHENOL POLYETHOXYLATES

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The European Union (EU) adopted the Water Framework Directive in 2000 and aims to improve and protect the quality of the aquatic environment and its resources. The EU member states should gradually reduce releases of substances classified as "priority" substances and phase out substances classified as "priority hazardous" and set up monitoring networks. The objective is to achieve good water status by 2015. In order to better control the release in aquatic systems of "priority", "priority hazardous" and emerging substances, it is necessary to develop new sampling tools that can overcome the grab sampling. Despite its usefulness, grab sampling is not representative of a heterogeneous medium with spatial and temporal variability. Passive sampling tools can obtain a Time Weighted Average (TWA) concentration during the deployment period. The TWA aqueous concentrations can be estimated from the amount of substances accumulated in the sampler during exposure. The Semi-Permeable Membrane Devices (SPMDs) and the Diffuse Gradient in Thin Film (DGT) are widely used and well calibrated. On the contrary, Polar Organic Integrative Sampler (POCIS), still require laboratory development before exposure in aquatic systems.

Calibrations of POCIS were conducted in the laboratory in a tank contaminated with a flow through system under controlled temperature and hydrodynamic conditions. In classical POCIS alkylphenol polyethoxylates were firstly accumulated in the hydrophilic PolyEther Sulfone (PES) membrane then in the receiving phase. After 15 days, these compounds were always present in the membrane with a significant concentration. In another calibration adapted POCIS-like were used with a hydrophobic Low Density PolyEthylene (LDPE) membrane and others with nylon membrane which are more suitable for the akylphenol polyethoxylates. These calibrations allowed the comparison of the uptake rate constants obtained with classical and adapted POCIS.

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P 34

A NEW DILUTION TUNNEL FOR THE EXPERIMENTAL DETERMINATION OF EMISSION FACTORS FOR PM AND ORGANICS FROM DOMESTIC BIOMASS BURNING

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Domestic biomass burning is receiving great attention from regulators and modelers, due to its significance as PM and PAHs emission source, and hence as contributor to environmental concentrations of these pollutants. Producers are also interested in testing stove and fireplace for assessing technologies and proposing innovation. Despite of these driving forces, no international PM emission testing standard has been issued yet. A brief review on available “in stack” and dilution tunnel methods for determining primary PM and condensable compounds will be presented, with special emphasis on $PM_{2,5}$ determination. Temperature for PM collection, fuel loading in the case of wood logs and choices if sampling transient phases (start / end of the combustion) still remain matter of debate.

An improved version of US-EPA 5G method using HEPA filtered and controlled dilution air and multi stage PM_{10} and $PM_{2.5}$ impactor has been developed in the frame of the LENS project, funded by the Italian Ministry for Education, University and Research. First results about PM, OC/EC, PAHs, levoglucosan and VOCs from recent design commercial pellet stoves will be presented and compared to US-EPA 5G and to direct in stack sampling. Further experiments on wood stoves are planned. Mismatch with emission factors considered in air quality source inventories and relevance of these uncertainties on scenarios assessment will be commented.

P 35

SIMULTANEOUS DETERMINATION OF TCS, TCC AND PARABENS IN WASTEWATER SAMPLES

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Triclosan (TCS), triclocarban (TCC) and parabens (MeP, EtP, PrP, BuP, IsoBuP and BzP) are used as antiseptic and preservatives in personal care products. They are “down the drain” contaminants, with recognized endocrine disruption function, released into the aquatic environment mainly via urban wastewater treatment plants and combined sewer overflows (McAvoy et al. 2002, Aguera et al. 2003, Canosa et al. 2006, Chu and Metcalf 2007). TCS has been shown able to accumulate in the algae (Orvos et al. 2002). TCC implies a chronic toxicity in fish at a concentration of 90 mg/L (Ying et al. 2007). Recently, parabens, with an EC50 between 5 and 30mg/L for Daphnia magma, have been considered toxic (Bazin et al. 2010). However their environmental levels are not sufficiently monitored. The lack of data on these compounds in France prompted us to determine their levels and their distribution between dissolved and particulate phases in urban areas. The analytical protocol for their determination in the dissolved phase of wastewater has been validated. It consists in a SPE extraction followed by an UPLC/MS/MS analysis. The overall method recovery for spiked samples of wastewater is between 84 and 105 % according to the analytes. The analysis of the particulate phase is under validation. Concentrations have been determined in the effluents of the five emissaries of Seine Aval WWTP, which drains influents of 6,000,000 inhabitants in Paris area, with a daily capacity of 1,780,000 m^3/day.

Keys words: TCS, TCC, Parabens, Wastewater, and UPLC/MS/MS.

P 36

ATRAZINE, DEA AND DIA RESIDUES IN GROUNDWATER OF THE REPUBLIC OF SERBIA (2007-2009)

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With the objective to check the presence of atrazine and its metabolites, deethylatrazine (DEA) and deisopropylatrazine (DIA) in the groundwater, the monitoring programme was carried out on the whole teritory of the Republic of Serbia. The sampling was performed during spring and autumn, over the period from 2007 to 2009, in the localities where the atrazine-based herbicides were intensively applied for a number of years. In total there were 327 samples of groundwater of the first welling-up collected. The atrazine and its metabolites were extracted with methanol by means of ENVI-C18 (47mm) disc, and the residue level of the studied compounds was analysed with GC/MSD. The studies carried out in spring 2007 deteremined the presence of atrazine and one or both metabolites in 79% samples of groundwater before the application of herbicides. The average value of the atrazine residues was 0.18μg/dm^3, DEA 0.14μg/dm^3 and DIA 3.22μg/dm^3. By re-sampling in autumn of the same year the increase in the atrazine residue level (0.21μg/dm^3) and the metabolites (DEA 0.15μg/dm^3 and DIA 3.52μg/dm^3), was found as the result of the atrazine application. By the decree of the Ministry of Agriculture, Forestry and Water Management - Plant Protection Administration of the Republic of Serbia of 31/12/2007, the herbicides which contain the active substance of atrazine are prohibited. In the groundwater sampled in spring 2008, the average value of the atrazine residues was 0.19μg/dm^3, DEA 0.16μg/dm^3 and DIA 3.57μg/dm^3, while in autumn the average atrazine value was 0.22μg/dm^3, DEA 0.18μg/dm^3 and DIA 3.92μg/dm^3. During 2009 the studies were repeated only in the localities in which the presence of the residues of atrazine and/or its metabolites was previously confirmed. The decrease in the average level of atrazine residues (0.12μg/dm^3) and the increased content of its metabolites (DEA 0.51μg/dm^3, DIA 4.01μg/dm^3), as the result of the prohibited atrazine application, were confirmed.

P 37

DETERMINATION OF URANIUM ISOTOPIC COMPOSITION OF WATER AND CALCITE BY TIMS AND ICP-QMS. APPLICATION TO THE STUDY OF WATER TRANSFER AND WATER/HOST ROCK INTERACTION IN KARSTIC SYSTEMS. CASES STUDIES IN FRANCE

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The analysis of the uranium isotopic composition ($\delta^{234}U$) of percolating waters and calcite in karstic systems can be used as an indicator of time/mode of water transfer within the host rock and soil. $\delta^{234}U$ in percolating water in caves also varies with host rock or soil heterogeneities, with zones displaying a $^{234}U/^{238}U$ ratio out of equilibrium, due to the source of uranium (for instance depleted uranium zone that have leached for long time).

Here we present and compare two analytical procedures for uranium purification and isotopic ratios analysis using isotope dilution.

The first one, classical, includes an iron co-precipitation step and a purification of the uranium fraction on anionic ion exchange resin prior to the analysis of isotopic ratios by thermo-ionisation mass spectrometry (TIMS). The second one, without iron co-precipitation, uses UTEVA resin for uranium separation and allows the analysis of uranium ratios by inductively-coupled plasma-quadrupole mass spectrometry (ICP-QMS). This last protocol is less time consuming, and allows $\delta^{234}U$ reproducibility (2σ) of 3-4‰.

We present cases studies of U analysis of water and calcite (speleothems) from French caves displaying large $\delta^{234}U$ variations (-500 to 3000), and we suggest an interpretation of the variability observed for each case.

P 38

ASSESSMENT OF THE PERFORMANCE OF A POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLER (POCIS) TO SAMPLE VOLATILE ORGANIC COMPOUNDS (VOCs) FROM THE DISSOLVED PHASE

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Volatile organic compounds occur at trace levels in surface waters. It has been shown that they might have biogenic sources like coming from forest soil organic matter and marine algae, but their main way of introduction to the aquatic system is traceable to the industrial development leading to their discharge from petrochemical plants and solvent factories, and to agricultural practices since they are used as fumigants or solvents for pesticides (xylenes).

The determination of VOC concentration levels in the dissolved phase is generally done by analyzing spot water samples with static or dynamic headspace techniques, or using Solid Phase Micro Extraction. Passive sampling tools such as Semi-Permeable Membrane Devices have been used to sample VOCs from air, but to our knowledge, no or few works using passive sampling monitoring for volatiles in water have been reported.

The present study presents an attempt to evaluate the performance of POCIS to sample volatiles from water. For this purpose, a flow through sealed exposure system was conducted, and replicate POCIS were retrieved periodically in order to determine VOC sampling rates. Different extraction protocols to extract volatiles from the OASIS-HLB phase using SPME technique were also developed.

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P 39

TWO COMPLEMENTARY APPROACHES TO PERFORM THE ENVIRONMENTAL MONITORING OF THE METHYL TERT-BUTYL ETHER (MTBE) FUEL ADDITIVE

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Since 1979 the tetraethyl lead was eliminated from the gasoline composition to reduce the lead emission from the gaz combustion of cars and was replaced by the Methyl tert-Butyl Ether (MTBE) and Ethyl tert-Butyl Ether (ETBE). These compounds are added to gasoline to improve the fuel motor performance increasing the octane indices.Consequently the addition of MTBE/ETBE into the gasoline has largely increased and has been generalized across the world inducing a risk for the environment.

In this context MTBE/ETBE can contaminate largely the water compartment, in particular groundwaters which are exposed by the omnipresence of the fuel service pumps and the high solubility of this compound.

In this study, two complementary approaches were developed to determine the water concentration of the MTBE and the ETBE (Ethyl tert-Butyl Ether). In one hand the solventless extraction technique, headspace Solid Phase Micro Extraction (SPME), was applied to determine easily the water concentration at the ng/L level. In another hand the passive sampling approach was introduced with a POCIS laboratory calibration performed over 19 days. The passive sampler calibration illustrated the integrative properties of the device for these additive substances. Their Sampling rates were also determined with the respective accumulation curves into the receiving phase, allowing the estimation of time weighted average concentrations in the environment.

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P 40

ELECTROCHEMICAL BEHAVIOUR OF MODIFIED CARBON PASTE ELECTRODES BY USING SCHIFF BASE LIGANDS FOR TRACE METALS ANALYSIS

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The application of modified carbon paste electrodes (MCPE) in Analytical Chemistry has attracted considerable attention in recent years. These electrodes are widely used mainly for voltammetric measurements because of inexpensive, with low background current, wide range of used potential, easy fabrication and rapid renewal. Various chemically active species have been used into CPE.

Hydrazones are an important class of reagent widely employed for spectrophotometric determination of metals. Being good analytical reagents, they can be used for its application in the determination of heavy metals by stripping voltammetry. The aim of the present investigation was to develop news MCPE modified with some hydrazones as 2-hydroxybenzaldehyde benzoylhydrazone, 2-hydroxybenzaldehyde N-ethylthiosemicarbazone, pyridoxal salicyloyl hydrazone and 2-acetylpyridine salicyloyl-hydrazone, synthesized in our laboratories by simple condensation of aldehyde and hydrazide. Well-defined peaks were obtained for measuring of different metals as Ag(I), Cu(II), Ni(II) or Cd(II) by using DPASV-MCPE. The analytical performances were evaluated (% modifier in the past, preconcentration time, metal concentration,...) and the suitability of MCPE for water analysis were optimized for Ag analysis at ppt levels because it is a tracer of sewage pollution and one of the most toxic elements to aquatic bacteria, phytoplankton and invertebrates.

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P 41

ELECTROCHEMICAL STRIPPING ANALYSIS OF NANOMOLAR LEVELS OF COPPER IN NATURAL WATER

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In recent years, there is a huge potential for the development of voltammetric environmental trace-metal analysis, particularly in the field of trace metals in aquatic matrix where other techniques are much more limited.

In this work, a new sensitive method for determination of copper in natural water using 2-hydroxybenzaldehyde benzoylhydrazone (2-HBBH) as a selective complexing ligand has been developed. This reagent produced electrochemical signal for different metals such as Cu(II), Pb(II), Cd(II) and Bi(III) depending on the pH of supporting electrolyte among other variables. The peak currents for metals were adequate for trace analysis but stripping voltammogram overlapping of Cu(II) and Bi(III) was found. This study tries to solve the interfering effects that copper and bismuth exhibit on the adsorptive cathodic stripping voltammetric determination of each other. This problem has been previously mentioned in other papers using different AdCSV systems, but to the best of our knowledge there are only a couple of reports that solve this problem. With the proposed method, the determination of Cu(II) in the presence of Bi(III) was possible by pH variation (pH 3.5). The instrumental and chemical factors were optimized using experimental designs. Analytical parameters such as repeatability, linearity and accuracy were also investigated. The detection limit for copper in the experimental conditions was found to be around 10-10 M. The method was validated with certified reference water samples showing good concordance with the certified values. It was also applied to synthetic samples and real water samples with satisfactory results.

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P 42

ANALYSIS OF METALS IN SEAWATER USING A PORTABLE VOLTAMMETRIC SYSTEM

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As a result of the OSPAR convention (1998) and The Water Framework Directive of the European Parliament (2000/60/EC), the concentrations of metals and their inputs into seawater must be monitored by each country of the European Union. While some metals act as micronutrients for marine species, most metals are toxic at high concentrations. Metal speciation is also crucial: both bioavailability and toxicity are highly dependent on speciation. The use of anodic and cathodic stripping voltammetry can permit the determination of both the total concentration of a given metal and the concentration of uncomplexed metals. This project is using existing voltammetric methods to develop a portable and semi-autonomous voltammetry system capable of making measurements of multiple metals simultaneously in marine waters over a tidal cycle using ASV, and of carrying out speciation analysis using CSV. Laboratory tests to optimize mercury drop size and deposition time, and diminish multiple metal and salinity influences were conducted using natural seawater spiked with Cd, Cu, Pb and/or Zn. Results from a deployment of the instrument in semi-automatic mode at an aquaculture research station in the west of Ireland (MRI Carna) are described. The suitability of the use of a mercury drop electrode versus a gold wire working electrode is discussed. This work has been funded by Science Foundation Ireland (SFI).

P 43

ENVIRONMENTAL ASSESSMENT AND ANALYSIS OF HEAVY METAL POLLUTION IN SEDIMENTS NEAR SOHAR PORT AND USE OF SEA CRABS AS A BIO-INDICATOR

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The industrial area centered on Sohar Industrial Port (SIP) was established in 2000 as the third major industrial area in the Sultanate of Oman, with initial operations starting in 2005. SIP contains a range of petrochemical companies such as Oman Refinery, Oman Polypropylene, Oman Aromatics, Oman Methanol, and Sohar Fertilizer, as well as metal-based industries, such as Sohar Aluminum and Vale.

The only recent analytical investigation on heavy metals sediments in and around the area was conducted in 2005, and no significant results were found at that time. Therefore, there has been no research to date that has investigated any time history of heavy metal concentrations in and around SIP, and their environmental impact.

The aim of this study is to investigate the chemical composition of sediments near Sohar Port. Thirteen heavy metals (V, Cr, Mn, Ni, Cu, Se, Hg, Cd, Pb, Zn, Fe, Al and As) will be analyzed by using microwave digestion followed by ICP-MS. This study will cover four stations: Harmul northwest of SIP, Majees southeast of SIP, Zafaran south of SIP, and one station within the SIP. Data will be collected for two years and at two different periods each year. Local crab species will be used as a bio-indicator of any pollution in the marine environment by heavy metals. Concentrations of accumulated heavy metals in crabs' bodies will be determined by atomic absorption spectrophotometry. Research in the past has shown that marine crabs accumulate certain heavy metals in their bodies and therefore can be used as monitors in determining the impact of heavy metal pollution on ecosystems.

P 44

DETERMINATION OF ORGANIC POLLUTANTS IN PRUT RIVER BY GC/MS SYSTEM AFTER CONCENTRATION ON A PASSIVE SAMPLING DEVICE

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The anthropogenic contaminants present in river water may include complex mixtures of common consumer products. The fate of such contaminants in surface water is largely unknown, and therefore the development of robust analytical methods for detection, identification and quantification are crucial

Traditional water samples represent only those contaminants present at the time of sampling[1]. Transient occurrence of selected contaminants in wastewater may result in temporal changes in the chemical quality of effluent discharged to neighboring streams. Repetitive sampling to accommodate episodic events and/or transient occurrence can be physically, logistically, and financially difficult, especially in remote areas. Without sufficient repetitive sampling, it may be impossible to formulate estimates on the time-weighted average (TWA) concentrations of the contaminants of interest. Passive samplers offer an attractive alternative to traditional sampling methods as grab or composite water samples.

In this study, we compared the polar organic chemical integrative sampler (POCIS)[2] to traditional water sampling methodologies, as grab or composite water samples for the detection of organic river-related compounds including herbicides, drugs, fragrances, plasticizers, and other components of industrial, domestic, and agricultural origin. The samples were collected from preselected sites situated on Prut River, border between Ukraine and Romania (31 km) and then the border between Romania and Moldova (711 km). The analyses were performed by GC/MS system.

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P 45

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS ASSOCIATED WITH URBAN AEROSOLS BY LC- GC

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Polycyclic aromatic hydrocarbons (PAHs) are the products of incomplete combustion or pyrolysis of carbonaceous material at high temperature (1). PAHs are a wide group of organic compounds have been found in urban air. The sources of PAHs into the atmosphere can be divided into two groups; 1) natural sources; such as forest fires and volcanic activities, and 2) anthropogenic sources including; power plants, waste incineration, industrial processes, and combustion of fossil fuels in automobile engines (2). The anthropogenic sources are known to have the major role in releasing of PAHs into the urban atmosphere (3).

In the present work, airborne particulate matter from the atmosphere of the city of Isfahan was collected on quartz fiber filter (Whatman QM-A) by a Greasby, Model PS2 high-volume air sampler. The exposed filters were extracted by carbon dioxide supercritical fluid extraction (SFE), using 10% methanol as modifier under 400 atm. Pressure. A united chromatographic technique (LC-GC) was developed for analysis of PAHs. A Varian 9001 HPLC pump with two (250 mm x 1 mm, i.d.) stainless steel columns in series was linked to a Varian GC model, CP-3800 equipped with a BPx5 column (25m x 0.32 mm, i. d..) analytical column and flame ionization detector. The system was used for analysis of PAHs in the standard reference material (SRM-1649) and also in the local airborne particulate matter and showed that the system is quite reliable. Finally the system was used for continuous determination of PAHs in Isfahan city atmosphere.

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P 46

MERCURY AND ITS ALKYLDERIVATIVES IN FRESHWATER FISH FROM ARTIFICIAL LAKES IN THE CZECH REPUBLIC

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Mercury and its derivatives belong to the most dangerous pollutants in global scale. Due to their toxicity together with bio-accumulative and bio-magnification properties, mercury compounds, especially their alkylderivates, represent a serious risk for man being on the top of food chain. Because of this reason, great attention is paid to monitoring of mercury and its derivatives in all environmental compartments.

This study deals with the determination of methylmercury and inorganic mercury levels in fish tissues. The fish originated from three various artificial lakes was analyzed. Brno Dam Lake is situated in relatively contaminated part of the Czech Republic, Karolínka Dam Lake is in relatively clean area of Beskydy Mountains, and Koryčany Dam Lake is in the area of Chřiby Hills. The fish available at the market in the town of Brno were also analyzed for comparison. For the determination of total mercury content the AMA-254 instrument was employed. For the detailed analysis of mercury species the method based on leaching of fish tissues using potassium hydroxide, derivatization of leachate with potassium tetraphenylborate and subsequent isolation of mercury derivatives by SPME, followed by gas chromatography with electron capture or mass spectrometric detection was used. The limit of detection of GC-MS method was established to 25.4 ng/g for methylmercury and 128.69 ng/g for inorganic mercury. Recovery was set to 75.5 % - 83.6 % for methylmercury and 45.6 % - 53.0 % for inorganic mercury. In real fish samples, methylmercury concentrations within the range of 136 – 655 ng/g and inorganic mercury levels between 52 – 219 ng/g. The total content of mercury in analyzed samples varied within the range of 15 – 1700 ng/g.

P 47

ACCUMULATION OF HEAVY METALS BY AQUATIC MACROPHYTES IN THE MARANO AND GRADO LAGOON (ITALY)

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Approximately 3% of the Italian territory is included in the National Priority List of Polluted sites. An example is represented by the "Laguna di Grado e Marano" which lies in Friuli Venezia Giulia (NE Italy). It includes about 4,200 ha of dry land and ca. 6,800 ha of wetlands and lagoons. The main pollutant, occurring particularly in wetlands and lagoon, is represented by mercury. However, heavy metals and organic pollutants were recorded as well.

During Summer 2010, a survey was performed with the objective to observe, if any, the bioaccumulation of heavy metals in the tissues of *Cymodocea nodosa*, *Zostera marina*, *Zostera nolti*, aquatic macrophytes commonly found in the lagoon. Samples of sediments and specimens of macrophytes, were collected and analyzed for the heavy metal content (Cd, Co, Cd, Cu, Hg, Mn, Ni, Pb and Zn).

The in concentrations, with the exception of Hg, were quite low. The Hg levels found in the sediments were comprised within the range 610-12,997 μg kg^{-1}. In *Cymodocea nodosa* and *Zostera marina*, Hg was mostly accumulated in the *leaves*; the average Hg concentrations were, respectively, 44.5 and 61.8 μg kg^{-1}. The opposite was found in *Zostera noltii*, being the leaf concentration of Hg (183 μg kg^{-1}) more than doubled when compared to the root concentration (71 μg kg^{-1}). For all the species, the bioconcentration factor was very low (<<1).

P 48

APPLICATION OF TIME RESOLVED LASER-INDUCED FLUORESCENCE MEASUREMENTS AND LASER INDUCED BREAKDOWN SPECTROSCOPY FOR ANALYSIS OF ENVIRONMENTAL CONTAMINANTS

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Aim of this presentation is to show possibilities of use of combined time resolved laser induced fluorescence (TR-LIF) and laser induced breakdown spectroscopy (LIBS) system for analysis of environmental contaminants. The TRLIF/LIBS system is implemented in our laboratory in Belgrade.

A detailed description and some of the preliminary results of our TRLIF/LIBS are given in [1-4]. Shortly, pulsed excitation is provided by a tunable Nd-YAG laser system (Vibrant model 266 made by Opotek, Inc.) with pulse duration of 5.4 ns, pulse repetition rate of 10 Hz and energy per pulse of up to~350 mJ. This system incorporates the optical parametric oscillator (OPO) that is pumped by the fourth harmonics of the Nd:YAG Brilliant laser at 266 nm. The output of the OPO can be continuously tuned over a spectral range from 320 nm to 475 nm. The laser induced fluorescence in the samples is recorded using streak scope (Hamamatsu model C4334-01) with integrated video streak camera. The fundamental advantage of the streak scope is its two dimensional nature, that is especially important in measuring time-resolved fluorescence spectra. The data is acquired using HPD-TA software.

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P 49

SOIL SALINITY CHANGE DETECTION IN SHAHINDEJ USING REMOTE SENSING

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One of the main environmental problems which affect extensive areas in the world is soil salinity that is one of the most common land degradation processes all regions, where precipitation exceeds over evaporation. Nearly 25% of all irrigated land is salt-affected, and this proportion tends to increase in spite of considerable efforts dedicated to land reclamation. This requires careful monitoring of the soil salinity status and variation to curb degradation trends, and secure sustainable land use and management .Traditional data collection methods are neither enough for considering this important environmental problem nor accurate for soil studies. Remote sensing data could overcome most of these problems. Although satellite images are commonly used for these studies, however there are still needs to find the best calibration between the data and real situations in each specified area. Shahindej area, North West of Iran was selected as a field study of this research. Landsat satellite images for this area were used in order to prepare suitable learning samples for processing and classifying the images. Electrical conductivity of all samples was measured. Seven reflective bands of TM satellite images taken from the study area in 2009 were used for soil salinity classification; the classification was carried out using common algorithms based on the best composition bands.

Keywords: Soil Salinity, Remote sensing, Satellite Images, image processing, Shahindej, TM satellite

P 50

EVALUATION OF CONTENT OF PCB AND PBDE IN PLANT BIOINDICATORS

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Contamination in the environment is usually assessed on the basic of plant and animal bioindicators. Plant bioindicators include needles of coniferous plants and moss. Needles of coniferous plants and moos belong to a group of „detectors“, i.e. naturally occurring species that react not only to changes in the environment.

Moss can be found almost everywhere: from the coast of Arctic seas through tropical zones to Antarctica. Conifers are wooden trees or shrubs that usually live many years. Moss and needles are recommended as bioindicators to monitor the levels of persistent organic pollutants (POPs). POPs released in the environment, can be transported by air or water into remote regions far from the original source of contamination. In addition, POPs show high stability in all components of the environment. They enter the air from various industrial sources such as power stations, heating plants, incineration plants and also from local domestic fireplaces, etc. Air-borne POPs may occur as vapour or may bind to the surface of solid dust particles.

Our study particularly focused on PCBs and PBDEs which belong to a group of pollutants that spread easily into the environment by means of remote transport. The levels of PCBs and PBDEs in plant bioindicators (needles of coniferous plants, moss) were determined using gas chromatography combined with an electron capture detector. The main aim of this study was to find out whether the selected bioindicators are suitable to assess the level of environmental contamination with PCBs and PBDEs. The highest levels of PCBs were found in the Norway spruce (Picea abies). PCB-28 congener was the most frequently detected congener, but congeners PCB 153, 138 and 180 being also detected. Polybrominated diphenyl ethers were not detected using the method chosen. The selected type of a bioindicator was not therefore found suitable to determine the level of environmental contamination with PBDE.

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P 51

EX-SITU ANTIMONY FILM ELECTRODE FOR SIMPLE MEASUREMENT OF SELECTED ORGANIC COMPOUNDS OF ENVIRONMENTAL IMPORTANCE

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Recently, a new promising metal film electrode, the antimony film electrode (SbFE), has been introduced and shown to be electroanalytically competitive with the well known mercury and the already established bismuth film electrodes [1]. SbFEs have found application in anodic stripping voltammetry [1,2], as well as in cathodic adsorptive stripping voltammtery of metal ions [2]. On the other hand, in contrast to BiFE [3], the application of SbFE for the determination of organic compounds has not been studied yet. Since analytical electrochemistry methods offer simple and inexpensive measurements convenient for on-field applications, it is essential to examine the potentialities of SbFEs for the detection of selected organic compounds of environmental significance.

In this work we report on the SbFE, prepared ex-situ on the surface of a glassy carbon electrode, for direct cathodic voltammetric measurement of a family of neonicotianamide insecticides with thiametoxam (TMO), chlotianidin (CLO) and dinotefuran (DNF) as model representatives. The conditions of ex-situ antimony film deposition (electrode pretreatment procedure, plating potential and plating time) were investigated and optimized using electrochemical and microscopy (SEM) techniques. Several important parameters for the direct cathodic voltammetric measurements of target insecticide analytes, such as pH and solution composition, voltammetric mode and protocol, etc., were thoroughly examined. Based on this study the optimum calibration and analytical data were selected and are discussed in this contribution.

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P 52

LIQUID CHROMATOGRAPHY WITH THERMAL LENS SPECTROMETRIC DETECTION – A HIGHLY SENSITIVE TECHNIQUE FOR DETERMINATION OF NEONICOTINOID INSECTICIDES IN ENVIRONMENTAL SAMPLES

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An analytical method was developed for the determination of trace amounts of four neonicotinoid insecticides: thiamethoxam, imidacloprid, acetamiprid and thiacloprid by liquid chromatography coupled with thermal lens spectroscopy technique. This multiresidue-analysis method is based on a HPLC reversed phase separation (C_{18} column), isocratic elution and collinear dual beam TLS detection. The TLS measurements were made on a pump-probe TLS spectrometer in a 8 μL flow-through (1 cm path-length) quartz cell at 244 nm excitation laser wavelength [1]. The working conditions, especially the composition of the mobile phase, and the TLS parameters, such as modulation frequency and lock-in amplifier time constant were optimized. The retention times of thiamethoxam, imidacloprid, acetamiprid and thiacloprid were found to be 4.4, 5.7, 6.5 and 8.5 min and the LOQs were 50, 89, 10, and 25 μg/L, respectively. In all cases, the linearity of detector response was checked in the range of LOQ-1000 ng/cm^3. The LOD for imidacloprid compared well with that obtained by the same method using a diode-array detector (DAD), while the LODs for the other investigated neonicotinoids provided by TLS technique were up to 8.5 times lower compared to DAD. The applicability and versatility of developed trace level analysis was tested and confirmed on spiked pepper, honey, and river water, samples as well as homogenates from woodlice fed on contaminated food.

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P 53

SEMI-SPECIFIC BOD BIOSENSORS FOR PULP AND PAPER INDUSTRY WASTEWATER ANALYSIS

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Biochemical oxygen demand (BOD) is widely used universal parameter to describe organic pollution in water and wastewater. Compared to standard BOD measurements, a faster method is based on BOD biosensors. Unfortunately biosensors often fail to estimate BOD resulting from specific refractory compounds found in industrial wastewaters. More precise BOD measurements can be carried out using semi-specific microbial sensors. Semi-specific microorganisms have certain compounds or compound groups that they can use as an energy source in addition to universal substrate spectrum. Thereby semi-specific microorganisms are able to oxidize refractory compounds found in industrial wastewaters, which would be undetected by universal biosensors.

As the pulp and paper industry wastewater consists in a large proportion of cellulose fibers (40-60% of dry solids) the cellulose–degrading bacteria of *Bacillus subtilis* (isolated from decaying sawdust) and *Paenibacillus sp*. (isolated from rabbits manure) were used to construct semi-specific biosensors. Their suitability for the use in semi-specific BOD biosensors for the analyses of pulp and paper industry wastewater was compared with non-specific *Pseudomonas fluorescens* biosensor.

BOD measurements carried out in cellulose-spiked OECD synthetic wastewater showed the biosensor's suitability for measurements in wastewater containing cellulose. Semi-specific biosensors were able to detect cellulose added to the OECD synthetic wastewater and good correlation was acieved between sensor-BOD and BOD_7 while non-specific *Pseudomonas fluorescens* biosensor failed to do so. All biosensors underestimated the BOD_7 of different synthetic wastewater samples containing other refractory compounds (fat, phenol, milk products) to which biosensors were non-specific.

P 54

VOLTAMMETRIC CHARACTERIZATION AND DETERMINATION OF CLOTHIANIDIN USING A CARBON PASTE ELECTRODE

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In the present study, electrochemical characterization of the neonicotinoid insecticide *Clothianidin* (CLO) is described followed by its determination at a tricresyl phosphate-based carbon paste electrode (TCP-CPE) when using differential pulse voltammetry (DPV). Various experimental parameters such as the carbon paste composition, electrode conditioning, effect of dissolved oxygen, and pH-value of the supporting electrolyte were investigated in order to achieve the optimal signal-to-noise characteristics for detection and quantification of the analyte of interest. Besides analyses of model solutions, the new DPV method was applied to monitor the disappearance of the parent compound during its TiO2assisted photocatalytic degradation. Important kinetic data for CLO were also obtained and evaluated, showing that the respective voltammetric procedure provide reliable results that agreed well to those of the reference HPLC / DAD method.

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P 55

THE ULTRASENSITIVE REAL-TIME DETECTION OF THE VOLATILE ORGANIC COMPOUND WITH THE NANOCRYSTAL-RELATED SEMICONDUCTOR SENSOR

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Volatile organic compound (VOC) discharged from the house and daily necessaries volatilizes easily in the indoor air because the normal temperature normal pressure and causes the health hazard by the low concentration. Then, the development of a practicable gas sensor without the preprocessing can detect the VOC gas in high sensitivity in the locale is hoped. Semiconductor sensor is one of the front runner and is built in various home electric appliances. In the present study, the sensitivity of this sensor to VOC at the ppb level was verified, and the high sensitivity factor was examined multilaterally. Especially, the aging time of tin oxide precursor solution examined nano crystalline of the tin oxide and influence on sensitivity. The resistance of two spit type interelectrode was measured as sensor resistance. In addition, the structure of the made sensing body was evaluated with scanning electron microscope (SEM), X-ray diffraction (XRD), and atomic force microscope (AFM). When the tin oxide on the sensor chip was observed with AFM, it was understood that the size of the average particle was about 17 nm. On the one hand, crystalline size of SnO2 ,estimated from the three main diffraction peaks, was 7.5, 7.4, 7.6 nm, respectively. It was suggested that the particle that had been observed from this with AFM be not monocrystalline but be a polycrystal. In addition, the size of the particle increased to about 30 nm by 4-8days at the aging time of the precursor solution. The sensor sensitivity has decreased remarkably along with it. It is a high sensitivity factor of the sensor that the occupation proportion in the space charge layer in each particle is high, and is thought that the smaller the size of the particle is, the higher sensitivity is. Moreover, a plain response was shown to ppb order VOC, and it was proven that the practicality was an extremely high sensor though sensitivity humidity (RH=60%) below decreased more under dryness.

P 56

CONTENTS OF PSEUDOTOTAL METALS IN ALLUVIAL SEDIMENTS FROM DANUBE RIVER, SERBIA

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We determined the pseudo total concentrations of metals presented as a sum of extracted concentration after five sequential extraction steps. The pseudo total metal concentrations were found to be (mg kg^{-1}) for Mn: 666; Fe: 25,852; Mg: 16,193; K: 2,063; Ni: 32.4; Zn: 72.2; Pb: 15.0; Cu: 26.0 and for Cr: 15.9. Correlation analysis and two multivariate analysis methods (Principal Component and Cluster Analysis) were helpful in determining the associations between the pseudo total extracted fractions of metals and with elemental carbon, hydrogen, nitrogen, sulfur, total inorganic and organic carbon. These correlations will help us to identify substrates of trace metals in different oxic/anoxic condition. The correlation results of the trace metals and Fe, K, Mg and Mn suggest their adsorption, mainly onto Fe and Mn (hydro) oxides and K alumosilicates, whereas correlations of metals with sulfur indicate that they were precipitated as Fe-sulfides.

P 57

EVALUATION OF PASIVE SAMPLERS TO MONITOR MICROENVIRONMENT CONCENTRATIONS OF OZONE

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The low cost passive method including fundamental analytical procedure for ambient ozone determination was validated. Different factors affecting method performance were examined, *i.e.* precision, accuracy, recovery, uncertainty, limits of quantification, applicability and costs. The validation was performed comparing passive samplers versus a) reference continuous UV-photometric ozone analyzer and b) reference passive samplers analysed in the outsourcing reference laboratory.

The overall precision of the passive method was 13.2 % expressed as pooled relative standard deviation (RSD_{pool}). The accuracy was estimated in terms of recovery, *i.e.* as the ratio of the observed values (passive measurement) to the reference values (both reference continuous analyzer and reference passive samplers) for different exposure time, *i.e.* 1, 2, 7 and 14 days, and different time periods of exposure, *i.e.* winter and summer, respectively. The relative standard uncertainty of 0.048 was calculated from the standard deviation of the mean recovery values. The individual component of the uncertainty were derived from the accuracy and precision and gave the expanded uncertainty of 0.28 using a coverage factor ($k=2$, $p=0.05$). The overall correlation between the results using linear regression gave the correlation factors of $R^2=0.84$ and $R^2=0.53$, respectively. The limit of quantification of applied passive method (LOQ) was 2 $\mu g/m^3$, taken the lowest concentration in the linear range and calculated for 7 day exposure time. The limit of detection was calculated as 3 times the standard deviation of the blanks. The validated method enables cost-effective spatial and temporal measurements in those locations, where ozone is significant problem and where continuous monitoring is not practical or not possible.

P 58

PHOTOACOUSTIC SPECTROSCOPY APPLIED TO METHANE MEASUREMENTS IN THE ATMOSPHERE

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In the last decades the concentration of methane, a greenhouse effect gas coming from multiple sources, has rised up to 1.75 ppmV in the atmosphere. For this reason, its monitoring has become very important, especially in countries with large livestock production. The low concentration value of methane turns its detection very difficult for most of the methods of measurement. Therefore, in this paper, we study the detection by means of modulated photoacoustic spectroscopy, based on an optical parametric oscillator tuned at 3019 cm^{-1}, which corresponds to the ν_3 stretching vibrational mode. We developed a photoacoustic detection system which uses a rectangular acoustic cavity, with high quality factor, external acoustic shield and CaF_2 windows in Brewster angle. This design allowed reducing noise and, this way, achieving a detection limit adequate to measure environmental methane concentrations.

The band head of the ν_3 mode coincides with absorption bands of water; this may be a problem if we consider that the linewidth of the OPO is around 6 cm^{-1}. So, we study the possibility of measuring the environmental methane concentration taking in account this overlapping of bands and the spectral characteristics of the radiation. In a previous work, we proofed that the acoustic signal from methane-air is lower with respect to mixtures with nitrogen due to slow collisional relaxation rates of oxygen. Based on this background, in this work we investigate the influence of the energy exchanges in presence of water molecules on the amplitude of the signal and test the benefit of adding water to the sample in order to reduce the oxygen relaxation time and, consequently, increase the signal. This study aims to prevent the use of sample filtering that could give place to a lower concentration value than the real one, due to non-selective adsorption of gases.

P 59

AN INVESTIGATION OF THE EFFECTIVE FACTORS ON THE RELATIONSHIP BETWEEN ECONOMIC GROWTH AND ENVIROMENTAL CHEMISTRY

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The process of economic development in recent decades has been such that in which environmental issues are one of the most important concerns of politicians and lawmakers. Nowadays, different countries, beside their national policies and operations, try to control the environmental pollution concerning international level. Therefore, an investigation of the relationship between economic growth and environmental pollution can be applicable, because it may be used as a base for national and international environmental policies.

Therefore, in this study,a panel data approach was used to analyze the effect of economic growth, technical, preferential and political changes on the important air pollution factors in the 56 selected countries with different developments levels, including Iran during the period 1995 to 2005.The results indicate that despite the positive effect of the economic growth on the environmental pollution, technological advances has played an important role in the reduction of sulfur and nitrogen dioxide,and in improvement of the political indices in the reduction of carbon dioxide as the air pollutant.

P 60

WATER POLLUTION BY MUNICIPAL SOLID WASTE OF THE ABOMEY-CALAVI WET ZONES, BENIN

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Waste management is an environmental challenge as well in industrial nations as those in limited resources. In Benin (West of Africa) wet zones are often banked up by household waste. The aim of present study was to identify various forms of pollutions engendered by these practices. 25 samples were collected in 5 points: well far from wastes filling (reference), 2 in a wet zone (well and surface) without wastes, 2 in a wet zone (well and surface) with wastes. Physico-chemical, chemical and microbiological characterizations of the 125 water samples were determined. Whatever depth, turbidity increased in samples collected in filled wet zone in comparison to unfilled ones. Dissolved oxygen concentration was twice lower in filled wet zone samples than in unfilled ones. Nitrate concentrations oscillated between 49.8 mg/L in samples collected in filled wet zones and 18.85 mg L^{-1} in wells situated on unfilled wet zones; all these values are superior to that admitted by the standards Beninese and the World Health Organization (10 mg L^{-1}). The rather low contents in Cu, Cr, Ni, Cd, Mn, and Fe, in waters collected in wet zones indicated on one hand no metallic pollution and on the other one an imbalance of ecosystem engendered by municipal solid wastes present in wet zones. The microbiological analyses revealed presence of faecal coliforms and *S. sciuri* more important in wet zones filled than in unfilled ones. Analytic results confirmed organic pollution due to filler waste in wet zone. Particularly organic matter degradation was observed in samples collected in wet zone containing wastes. No significant difference was noted between well and surface. The filling of the wet zones by the waste constitutes an ecological risk. Moreover, it represents a public health problem by chemical and microbiological pollution because people live around wet zone and drink water collected in wells.

P 61

SIMULTANEOUS PROFILING AND QUANTITATION OF PHOSPHONIC ACIDS

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Alkyl phosphonic acids are formed from the hydrolysis of certain chemical warfare agents (CWA), which include highly lethal G and V class nerve agents. While use of CWAs is banned by the Chemical Weapons Convention, the threat remains if deployed to a food or water source. CWA hydrolysis products represent a viable screening target since they exhibit greater stability in food matrices. Sensitive and selective detection of phosphonic acids with a hybrid triple quadrupole linear ion trap allows compound specific targeted scans capable of revealing an entire class of CWAs per sample.

Five phosphonic acids (MPA, EMPA, IPMPA, CHMPA, and PMPA) were used to evaluate polarity switching and how simultaneous collection of quantitative and qualitative data affect quantitative data quality.

P 62

RAPID SCREENING OF ANTIMICROBIAL BREAK DOWN PRODUCTS UNDER SIMULATED ENVIRONMENTAL CONDITIONS BY LC/MS/MS

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The escalating number of Pharmaceuticals and Personal Care Products (PPCPs) that have been detected in our waterways is a concern that has come to the attention of several regulatory agencies as well as the general public. Several approaches to monitor and screen these compounds have been developed, but few methods exist to characterize the environmental breakdown products of PPCPs in the environment. Here we present a rapid approach to screening environmental water samples using typical degradents such as heat, oxidation, and UV light to look at the breakdown products of three antimicrobial agents. This technique uses data dependent scanning functions in the mass spectrometer as well as advanced software tools to aid our screen for degradent products of environmental PPCPs.

P 63

DETERMINATION OF SILVER IN WATER BY FLOW INJECTION ANALYSIS WITH TLS SPECTROMETRIC DETECTION

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In the present century the disinfection of water is of prime importance both for the animal world and humans, since the purity of it affects the health and life span. The commonly used techniques for water disinfection are those that arise from the chemical treatment of it by chlorine-containing compounds, ozone, fluorine or iodine. They are low cost but the toxic carcinogenic by-products may be formed as a result of their use. Because of that, over the recent years, much attention has been directed to the use of silver nanoparticles as disinfection agent since it does not produce any taste, odor or color in the treated water as well as no by-products are formed. The only disadvantage is that silver, once absorbed, is held indefinitely in the body tissue, what in case of repeated exposure to it may lead to blue-gray discoloring of skin (argyria). Therefore the concentration of silver species in water supplies must be monitored. Unfortunately, none of the existing methods are suitable for that purpose because they are not sensitive enough to satisfy the requirements associated with the both recommended dose for germicidal efficacy for silver in water and the maximum contaminant level (MCL) of it. Thus, in this work, a new technique was developed in which a flow injection analysis (FIA) coupled to collinear dual beam thermal lens spectrometric (TLS) detection was used for determination of colloidal and ionic silver in water by exploiting the reduction reaction with BH_4^-. This method was found to be fast, simple and sensitive. For the optimal experimental conditions the estimated limit of detection (LOD) was 0.8 μg/L what is over 50 times lower than the maximum contaminant level (MCL) for silver in water and 62 times lower compared to a similar method based on transmission mode spectrophotometric detection. Presented method was also successfully applied to the analysis of real samples such as river and tap water as well as water sample for the International Space Station (ISS) crew consumption.

P 64

DATA ON RECONQUISTA RIVER POLLUTION (ARGENTINA). CASE STUDY FOR RECOVERING MISSING DATA

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Reconquista river (on the border of Buenos Aires City) is one of the most polluted river in Argentina. The hypothesis was that a 10 years of data collection of about 30 different parameters on 15 different locations (6 on the river and 9 on the three incoming canals) will give enough data to draw a reliable conclusions about the origin and sources of pollution, trends of the pollution, and enable several conclusions of how to handle the revitalisation of the river. As it is often the case on the long term environmental studies and data collection it shows up that due to unforeseen circumstances (weather, malfunctions of apparatus, power break-down, etc) not all data for all variables were available for all measuring sets. If a strict approach is chosen only such sets of data that contain all variables at all locations for all recording campaigns should be taken into account. However, it immediately becomes clear that if such an approach is chosen large amount of valuable data should be discarded. Therefore, Artificial Neural Network (ANN) approach, using Kohonen ANNs for handling incomplete data set was suggested to approximate some of the missing data. In this work the Kohonen ANN used for handling the missing data within uniform multi-vatriate data collection matrix is explained, discussed, and preliminary results using the actual data are reported. In the test runs the correlation factors of up $r \sim 0.6$ between the real measurements data and the recovered ones if the former were intentionally removed from the data set, were obtained.

P 65

THERMAL LENS SPECTROMETRY APPLIED TO THE STUDY OF CYANOBACTERIA

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In recent years harmful algal blooms (HABs), have become a issue of growing interest due to their increasing frequency of occurrence and severity. Cyanobacteria HABs are particularly dangerous for the environment and human health due to the release of toxic secondary metabolites (cyanotoxins) during their senescence and decaying. The most serious concerns about cyanotoxins regard their neurotoxicity, hepatotoxicity, and their effects as tumor promoters. Moreover in 1996, fatal casualties among haemodialysis patients were reported due to water contamination and recently it has been suggested that these metabolites could play a role in neurodegenerative diseases such as Alzheimer's and multiple sclerosis disease. Since cyanotoxins can contaminate water supplies, in 2004 WHO fixed 1 μg/L as the maximum safe concentration of microcystins in drinking water. However this is only a provisional guideline and more studies are needed to assess the real safe concentration of this cyanotoxins, not only regarding drinking water but also all other possible sources of contamination (irrigation and recreational waters etc.). Powerful tools are required both as early warning systems for detecting the presence of potential harmful cyanobacteria and as sensitive methods for determining very small amounts of cyanotoxins.

In this work we investigated the applicability of thermal lens spectrometry (TLS) to determination and investigation of cyanobacteria photosynthetic pigments such as allophycocyanin and phycoerythrin, which could represent a sensitive tool for the detection of cyanobacteria in fresh waters. Particular attention was dedicated to photodegradation of pigments under irradiation by intensive laser light used for excitation in TLS and to the fluorescence efficiency at different excitation wavelengths, which significantly affects the sensitivity of TLS method. Preliminary experiment on phycoerythrin using a thermal lens microscope (excitation wavelength 532 nm, laser power 20 mW) shown that the degradation half life time of this pigment under given experimental conditions is 67 sec.

P66

HIGH RESOLUTION MASS SPECTROMETRY FOR DETECTING PHARMACEUTICALS PRESENT AS POLLUTANTS IN WATER

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The use of Liquid Chromatography coupled to tandem Mass Spectrometry (LC-MS/MS) for targeted quantitation of PPCP has been well established. More recently there is a growing interest from environmental researchers to also screen for and identify non-targeted compounds in environmental samples, including metabolites and degradates, but also completely unexpected pollutants. High resolution and accurate mass LC/MS/MS system is capable of performing highly sensitive and fast MS scanning experiments to search for unknown molecular ions while also performing selective and characteristic MS/MS scanning for further compound identification and, therefore, is the instrument of choice for this challenging task.

In metabolomic investigation the change (greek: ‘meta’) of the fingerprint of a system is systematically studied. Originally developed to study cellular processes, such as small-molecule metabolite profiles, statistical data analysis tools are suitable to also study changes in environmental systems and, thus, to identify unexpected environmental pollutants.

Here we describe the use of the AB SCIEX TripleTOF™ 5600 system for the screening for unexpected environmental pollutants applying statistical data analysis using MarkerView™ Software. The detected compounds were identified based on empirical calculation of the molecular formula, interpretation of MS/MS fragments and mass spectral library searching. The acquired high resolution and accurate mass spectra were further used to quantify the amounts of detected and identified environmental pollutants in a large set of environmental water samples.

P67

ACCELERATED LC/MS/MS FOR THE QUANTITATION AND IDENTIFICATION OF PESTICIDES, PHARMACEUTICALS, AND PERSONAL CARE PRODUCTS IN SURFACE WATER SAMPLES

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Endocrine disrupting compounds (EDC) and Pharmaceuticals and Personal Care Products (PPCP) are environmental contaminants of growing concern. In order to properly assess the effects of such compounds on our environment, especially their disruption of endocrine function in mammals and fish, it is necessary to accurately monitor their presence in the environment. The diversity of chemical properties of these compounds makes method development challenging. Presented in this work is a method which enables the quantitation of these compounds using Multiple Reaction Monitoring (MRM) and their identification using Enhanced Product Ion (EPI) scanning with mass spectral library searching using a hybrid triple quadrupole linear ion trap LC/MS/MS system (QTRAP® 5500). Extracts of water samples were analyzed and analytical data, including quantitative and confirmatory results, were reported automatically.

In a single experiment approximately 160 MRM transitions were monitored. The use of Scheduled MRM™ greatly enhances accuracy and reproducibility of LC/MS/MS detection of a large set of targeted analytes at low concentration levels. Limits of Quantitation were found in the sub 10 nanogram per liter range. In the same experiment fast confirmatory Enhanced Product Ion (EPI) scans were triggered by intelligent software using Collision Energy Spread (CES) settings. In comparison to dedicated and fixed Collision Energies CES was found to give more reproducible and richer MS/MS spectra and thus greatly enhancing the quality of library searching. Library searchable EPI spectra were generated at low nanogram per liter concentrations.

P 68

SEASONAL VARIATIONS OF NITROGEN COMPOUNDS CONTENTS IN THE SURFACE AND GROUNDWATERS OF STARA ZAGORA REGION, BULGARIA

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The present research was provoked as a result of the deteriorated ecological situation in Stara Zagora Region, Bulgaria, during the last 8 years. The aim of the study was ecological monitoring of the natural waters in Stara Zagora Region, ascertaining seasonal concentration variations during 2010, establishing of a database and correlations regarding the parameters – nitrates, nitrites and ammonium, providing a framework for sustainable management of the natural waters in the region. To accomplish this goal, the concentrations of nitrogen compounds in real surface and groundwater samples taken from four municipalities of Stara Zagora Region (Chirpan, Kazanlak, Gurkovo and Stara Zagora) were spectrophotometrically determined and the statistical significance of the data was tested. The results obtained displayed that NO_2^--N could be classified as a potential pollutant of the surface waters from Stara Zagora and Chirpan municipalities, while NO_3^--N could not be classified as a contaminant. The derived polynomial correlation between NO_3^--N and NO_2^--N concentrations in Zetyovo Reservoir, Chirpan Municipality, allowed mathematical modelling of the experimental results. The present study ascertained that the quality standard for groundwaters, regarding nitrates (50 mg L^{-1}), was exceeded in 42 % of the sampling points (shaft well in a drinking water pumping station-Gita Village; Kolyo Ganchevo-well; Cherganvo Village-well; Gurkovo City-well; Sulitza Village-well), with values in the range 64.3 - 99.6 mg L^{-1} NO_3^-, predominantly during the spring, 2010.

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P 69

THERMAL LENS MICROSCOPY FOR ENVIRONMENTAL ANALYSIS IN MICROFLUIDIC SYSTEMS-THEORETICAL SIGNAL ANALYSIS FOR BROAD BAND TOP-HAT EXCITATION

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Thermal lens microscope (TLM) coupled to lab-on-chip chemistry in microfluidic systems is a powerful tool for analyzing a variety of compounds. It was already successfully applied for the analysis of trace cobalt concentrations with the detection limit (LOD) of 0.13 zmol[1] or carbamate pesticide derivatives with LOD = 7×10^{-8} M.[2] In all these cases a laser was employed as excitation source. Therefore a very limited range of emission lines was available and the achieved selectivity was not as high as desired. This severely limits the use of such TLM systems for the practical applications. To avoid these limitations, a broad-band top-hat excitation source was introduced.[3]

In this work a theoretical model was built, on the basis of which the behaviors of the thermal lens signal under different experimental conditions in flow systems with laser and broad band source excitations were analyzed for the first time. It was found that in case of a probe-beam with smaller beam waist and a relatively large mode mismatching degree results in higher thermal lens amplitude. In addition higher resistivity to the fluctuation of the flow velocity and to the probe beam offset can be achieved. For a larger probe-beam waist, higher tolerance to the chromatic aberrations and variation of the pump-beam radius is predicted. Such theoretical analysis provides information about possible optimization of experimental parameters to achieve higher sensitivity and specific detection of various compounds in environmental and other samples.

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P 70

DETERMINATION OF POLYBROMINATED DIPHENYLETHERS AND PERFLUORINATED COMPOUNDS IN SOIL AND MATRICE FROM FIREPLACES

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Polybrominated diphenyl ethers belong among the persistent compounds, which have been classified as priority organic pollutants. In environmental compartments are observed in the past decade. Polybrominated diphenyl ethers are detected in abiotic and biotic matrices. For these studies were chosen the matrixes from seats of fire, taken in various localities of the Czech Republic and Slovakia. Their analysis should demonstrate whether they in these specific matrices remain. There were examined following polybrominated diphenyl ether congeners: BDE- 28, 47, 99, 100, 153, 154, 183. For their isolation from the matrix were used three different extraction techniques, namely ultrasonic extraction, microwave extraction and pressurized solvent extraction. For the determination was chosen method of GC / ECD. In these studies are also described basic chemical, physical and environmental properties of BDE, including other analytical methods that can be used to determine polybrominated diphenyl ethers in environmental compartments.

The other theoretical part of these studies consists of current matters regarding the presence of perfluorinated organic compounds in living environment elements. The attention has been focused on perfluoroctanoic acid (PFOA), (PFOS) and (FOSA). Physical-chemical characteristics of these organic pollutants and their toxicological and environmental aspects have been described. Possible ways of the pollutants analytical determination have been specified. The experimental part has explored effects of extraction techniques (sonication, pressurized solvent extraction, solid-phase extraction) used for PFAS separation from seats of fire soil sample. Identification of the analytes have been achieved by liquid chromatography/mass spectrometry.

P 71

ASSESSMENT OF HEAVY METAL LEVELS IN SOIL FROM AGRICULTURAL AREA OF BELGRADE, SERBIA

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The concentrations of heavy metals in soils are associated with biological and geochemical cycles and are influenced by anthropogenic activities, such as agricultural practices, industrial activities, and waste disposal. As a consequence, potentially toxic elements have accumulated in the soil profile. Analysis of heavy metal concentrations in soils is, therefore, critical for policy making orientated at reducing heavy metal inputs to soil. This paper contributes to the knowledge of the content of heavy metals in agricultural soils from the Belgrade area, Serbia. Soil samples from the most important agricultural city areas were collected from Jun to October of 2009. to determine the content of cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn). Soil samples were collected at 50 random agricultural plots under vegetable crops according to ISO Standard 10381-2. Samples preparation was done according to ISO Standard 11466 to determine heavy metal contents. Following ISO Standard 11466, extraction of heavy metals from soil samples was carried out in aqua regia, while their determination was done by flame atomic absorption spectrometry (FAAS) in accordance with ISO Standard 11047. The content of Cd, associated with fertilizers, atmospheric deposits and plant remains, do not exceed the reference values established by the Serbian national regulations. The same goes for Cu, Fe, Mn Ni and Pb associated with anthropogenic pollution, and for Zn associated with parent rocks. Besides total metal concentrations in the all investigated agricultural soils are considerably below MRLs on agricultural soils, thus the examined soils can be considered unpolluted.

P 72

ASSESSMENT OF HEAVY METAL LEVELS IN PLANT PRODUCTS FROM AGRICULTURAL AREA OF BELGRADE, SERBIA

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Heavy metals pollution has become an important issue in developed countries. Their concentrations in soils and subsequent accumulation in plants is a growing interest. Hence, regular and stringent food quality control, with an emphasis on heavy metal contamination, is going to become an imperative. This paper contributes to the knowledge of the content of heavy metals in plant products from the Belgrade area, Serbia. Plant samples from the most important agricultural city areas were collected from Jun to October of 2009. to determine the content of cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) in edible parts of plants. Samples were collected at 50 random agricultural plots in accordance with relevant Commission of the European Communities Council Directive. Samples preparation was done according to AOAC official method 922.02 to determine heavy metal contents. Following AOAC official method 975.03 determination was done by flame atomic absorption spectrometry (FAAS). The small amount of Cd was found in most of the plant samples but it mainly does not exceed 0.3 mg/kg. Copper was found in all samples mostly under 10 mg/kg. The same goes for Mn, while Ni was not detected in almost none of the samples. Iron associated with plant species as well as place and time of sampling was detected in all samples in larger amount compared with other studied metals. Lead slightly exceeds 1 mg/kg only in few samples, and Zn exceeds 30 mg/kg only in one sample. Total metal concentrations in the all investigated plant samples are below MRLs, thus the examined plants can be considered unpolluted.

P 73

ASSESSMENT OF PESTICIDE LEVELS IN PLANT PRODUCTS FROM AGRICULTURAL AREA OF BELGRADE, SERBIA

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In the light of increasing reports on pesticide contamination of food commodities consumers are becoming more aware of the importance of safe and high quality food products. As a consequence, monitoring projects, including assessment of the content of pesticide residues in plants, is going to become an imperative. The objective of this study was contribution to the determination of the pesticides pollution levels in vegetables in the Belgrade area, Serbia. Plant samples from the most important agricultural city areas were collected from Jun to October of 2009. to determine 17 compounds selected on the basis of pesticides registreted and used in plant protection in our country. Plant samples were collected at 50 random agricultural plots in accordance with relevant Commission of the European Communities Council Directive. Extraction of pesticide from homogenised plant samples was performed by QuEChERS method based on acetonitrile extraction folowed by dispersive solid phase extraction cleanup (dSPE). The recovery and quantification was done by fortification with a mix standard pesticides solution applying same analytical procedure. A gas chromatograph/mass spectrometer (GC/MS) was used as a detection and quantification device. According to results, none of seven pesticides examined in analised pepper samples were found. The same goes for four pesticides examined in analised cabbage samples, five examined in analised tomato samples, six examined in analised zucchini samples and eight pesticides examined in analised appricot samples. Only one of six examined pesticides in one of analised cucumber samples was found in amount below MRLs (bifenthrin 2.46 µg/kg). Generally, vegetable crops from examined agricultural city areas are unpolluted by contaminants used for plant protection.

P 74

ASSESSMENT OF PESTICIDE LEVELS IN SOIL FROM AGRICULTURAL AREA OF BELGRADE, SERBIA

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Pesticides constitute one of the most hazardous groups of contaminants to environment. The majority of such substances are applied directly to soil or sprayed over crop fields and hence released directly to the environment. As a consequence of an outstanding concern for human health, environmental monitoring projects including assessment of the content of pesticide residues in soil have been performed throughout the European countries. This work contributes to the determination of the pollution levels by pesticides in soils in the Belgrade area, Serbia. Soil samples from the most important agricultural city areas were collected from Jun to October of 2009. to determine 17 compounds selected on the basis of pesticides registreted and used in our country, as well as on the basis of their stability and persistent in environment. Soil samples were collected at 50 random agricultural plots under vegetable crops according to ISO Standard 10381-2. Samples preparation was done according to ISO Standard 11466. Extraction of pesticides from soil samples was performed by liquid–solid extraction procedure using methanol:acetone=1:1 folowed by purification on florisil column and elution by ethil acetate:acetone=4:1. A gas chromatograph/mass spectrometer (GC/MS) was used as a detection and quantification device. According to results, pesticides residues, in amount considerably below MRLs on agricultural soils (pendimethalin 19.76 µg/kg and metribuzin 57.19 and 11.52 a µg/kg), were found only in three soil samples, indicating that soil from agricultural plots under vegetable crops from examined agricultural city areas is unpolluted by contaminants used for plant protection.

P 75

HISTORICAL TRENDS OF PCBs, PAHs, PBDE AND ALKYLPHENOLS IN DATED SEDIMENTS FROM FLOOD-PLAINS OF THE SEINE RIVER (FRANCE)

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The Seine River basin (79,000 km², 20 millions inhabitants) is considered as representative of river basins exposed to the impacts of intense human activity due to the combination of strong human pressures with very limited dilution via the Seine River (mean flow : 290m^3/s in Paris). To obtain a chronological overview of the POP-contamination of the basin a sediment-core from flood-plains downstream Paris was collected and analysed. Hence, a 100-cm vertical core was taken close to Bouafles, 100 km downstream Paris (draining about 96 % of the basin) and then divided into 50 2-cm samples. The core was dated by gamma spectrometry of radionuclides ^{210}Pb, ^{137}Cs and ^{241}Am. Then four groups of organic contaminants were analyzed: polychlorinated biphenyls (PCBs), polycyclic aromatic compounds (PAHs), polybromodiphenyl ethers (PBDEs) and alkylphenols (APs). The objectives of this work were i) to determine the concentration and the historical contamination for each family and congener and ii) to compare these historical profiles to the production and consumption patterns. Results show a very high contamination caused mainly by the industrial and urban activity of Paris region. Moreover the temporal profiles clearly underlined strong behaviour differences between pollutants over the period considered (1940-2004). For example, PAHs and PCBs concentrations respectively peaked at the end of the 1950s and in the 1960s and then sharply declined. On the contrary PBDEs peaked around 1990. Globally, the historical profiles fit with the production and consumption patterns for most contaminants. To better understand the time profiles, the next step will more precisely examine their evolution in relation to the evolution of the Seine basin and especially of the Paris region, regarding its urbanization and/or industrialisation.

P 76

ENZYMATIC FIA-TLS METHOD FOR DETERMINATION OF BIOGENIC AMINES

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Biogenic amines (BA), which might appear in foodstuffs due to poor hygienic conditions or microbiological contamination of water, have been implicated as causative agents in a number of food poisoning episodes. Due to their potential toxicity, they are of big concern to susceptible and disease affected persons. To prevent undesirable consequences, control of BA in food requires highly sensitive, selective and rapid methods for their determination.

The aim of this work was the implementation of an enzymatic reaction between immobilized transglutaminase (TG), BA and a glutaminyl donor in a FIA system. During the enzymatic reaction, already optimized in batch mode, ammonia is released and detected with indophenol method using a thermal lens spectrometer (TLS) built in-house. The advantages of the newly developed screening assay for BA, include no need for time consuming (about 1 hour) derivatization of BA, as commonly performed in HPLC[1] or capillary electrophoresis,[2] and improved sample throughput (10 samples/hour). The LOD for BA achieved at present is still relatively high (between 2×10^{-4}M for putrescine and 7×10^{-4}M for cadaverine). However, the results from batch mode measurements with non-immobilised TG, which showed LODs comparable to other methods,[1,2] indicate that up to 1000-times improvements in sensitivity are possible and could be achieved by increasing the amounts of immobilized TG and by adding organic solvents such as acetonitrile to improve the sensitivity enhancement of TLS in water. This should provide 100-times lower LODs in comparison to the enzymatic method relying on transmission mode spectrometry.[3]

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P 77

APPLICATION OF CHROMATOGRAPHIC METHODS FOR THE CZECH BEER AUTHENTICITY STUDY

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Beer has been traditional beverage in Bohemia for hundreds of years. It is considered not only as refreshing drink, but it is also healthy, nutrishing and tasty drink, which could even improve the health state of human being. Typical features of the Czech beers, which are well known and appreciated by consumers in many countries, are its characteristic full and very rich mild bitter taste and rich and stabile foam, which prevents the beer against quick oxidation during drinking. The typical properties of the Czech beer are the results of advanced and carefully realized brewing technology and high and rigorously controlled quality of the raw materials, mainly barley, malt, hop, and water used for brewing.

The typical taste of the Czech beer is caused by the presence of large number of sensorically active compounds; some of them are active even in trace concentrations. Therefore, the analysis of beer components belongs to analytical challenges. In our study we focused on two groups of minority beer components: bitter compounds and volatiles. Using advanced chromatographic separation techniques (orthogonal two-dimensional gas chromatography with mass spectrometric detection for volatile compounds, liquid chromatography with electrospray ionization and tandem mass spectrometric detection for bitter compounds) we tried to specify the characteristic features of distribution of compounds under study in the Czech beers and possibilities of distinguishing them from the beers produced outside the Czech Republic.

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O 4

UNDERSTANDING MARINE POLLUTION IN THE GULF OF ALIVERI, CENTRAL GREECE: IMPACT ON SORPTION DUE TO BLACK CARBON PATRICLES AND SALINITY

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The Gulf of Aliveri is a small gulf receiving the waste and outfall of industrial activities such as power generation and cement production. The beach sediments next to the power station formed as a result of anthropogenic activities. These anthropogenic deposits originate mainly from combustion and waste dumping processes. In the present work, marine sediments and water samples were taken from the Gulf of Aliveri. The sediment samples were found to contain varying percentages of coal, lignite, and char particles. Although, polycyclic aromatic hydrocarbon (PAH) concentrations found in the sediments were comparable to background concentrations in the Mediterranean Sea, the pyrolytic to petrogenic ratio was high for sediment samples and low for water samples. In order to better understand distribution of PAHs in marine systems with heterogeneous sediments sorption experiments were performed in both synthetic fresh and salt water for the different carbonaceous materials and also for the heterogeneous sediments. Phenanthrene was used as the model PAH compound. Due to salinity, various effects are observed for the different carbonaceous materials on the capacity and also on the degree of nonlinearity. Each material presents a different sorption pattern and various effects due to salinity are observed (e.g. coal sorption isotherm becomes linear in the presence of salinity whereas for lignite no significant difference is observed). The cumulative behavior of the sediments is explained based on the carbonaceous materials behavior and on the organic petrography characterization. Changes of the materials surface properties and of the porosity due to salinity are also considered. These results will then be compared to in-situ sorption data.

O 5

THE EFFECT OF ALGAL-EXUDED ORGANIC LIGANDS ON METAL BIOAVAILABILITY IN SEAWATER

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Aquatic organisms produce organic ligands via the active release of photosynthates, degradation of senescent cells, rupture of cells due to grazing, and cell lysis by pathogens (Fogg 1983, Sundin 1995). The release of organic ligands has important implications for metal toxicity in seawater, as such ligands are able to bind metals, altering their toxicity. While it is widely accepted that these ligands binds free metal ions, reducing their availability, some studies have concluded that they increase metal bioavailability (Campbell et al. 1997). It is postulated that organic ligands bind the algal cell wall resulting in increased membrane permeability of metal complexes and hydrophilic substances (Boullemant et al. 2004, Vigneault et al. 2000). The same binding also increases the negative charge at the algal surface (Slaveykova et al. 2003, Lamelas et al. 2005). This may result in the formation of a ternary complex between dissolved organic ligand, metal, and algae. Hence, it is at present unknown to what extent algal exudates may affect metal bioavailability. This work describes species-specific ligand profiles which were observed for five macroalgae (*Laminaria hyperborea, Fucus spiralis, Fucus vesiculosus, Ascophyllum nodosum,* and *Pelvetia canaliculata)* as a function of exposure to multiple metals (Cd, Cu, Pb, Zn) and a range of environmental conditions. Phenolic and CDOM exudation were estimated by measurement of the absorbance of water at 274 nm (Wiencke et al. 2007) and 440 nm (Hulatt et al. 2009), respectively. The determination of total dissolved metal, thiol, humic acid, and fulvic acid concentrations of the culture solutions by cathodic stripping voltammetry (CSV) are discussed. This work has been funded by Science Foundation Ireland (SFI) and the Irish Research Council for Science, Engineering and Technology (IRCSET).

O 6

WATER DISINFECTION WITH ELECTROLYSIS METHODS

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It is known that in water supply systems develop microbiological pollution, which significantly affects the quality of water. There are different water treatment methods to reduce microbiological contamination, among which electrolysis methods have a considerable potential. This method is easily managed, can be automated and is environmentally friendly. Additional chemicals are not necessary because the main disinfecting agents are produced from the naturally occurring ions found in water itself (mainly from chloride ions). Electrolysis process efficiency is affected by material of electrodes used in electrolysis apparatus.

Water treatment with electrolysis was performed in an electrolytic cell with special TinO2n-1 ceramic electrodes and *Escherichia coli* bacteria were used as a model organism for disinfection experiments. In order to clarify the impact of electrolysis process on water treatment, the model solutions containing chloride ions with the initial concentration less than 1 mmol/L were electrolyzed at the conditions (j = 8,3 mA/cm2, pH 7± 0,2, to = 25oC). Viability of the bacteria *E. coli* was determined by modified DVC and FISH methods.

It was determined that, if electrolysis of solutions with different initial concentrations of chloride ions is done, the amount of released chlorine increases with extending the time of electrolysis and the chloride ion concentration.

If chloride ions are present in concentration range, which is common in raw water, using TinO2n-1 electrodes in the electrolysis process it can create enough amount active chlorine to kill more than 99% of *E. coli* within 15 minutes. A practically applicable simple model for prediction of disinfection efficiency with electrolytic cell has been proposed.

P 78

NITROGEN SOURCES AND CYCLING IN THE GULF OF TRIESTE (N, ADRIATIC)

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The sources of nitrate were determined using stable isotope approach in Slovenian part of the Gulf of Trieste and its main river tributaries Rižana and Dragonja. The sampling was performed in May 2010. In the river Rižana no impact of municipal sewage or agriculture on the nitrogen cycling was observed at the time of sampling. On the other hand higher nitrate concentrations and elevated $\delta^{15}N_{NO3}$- values were found in the river Dragonja, and were the consequence of leaching into the river of organic fertilizers from agricultural land. The relation between the isotopic composition of nitrate and its concentration showed that nitrate at most marine sampling locations was the result of mixing between marine and terrestrial origins of nitrate. The impact of nitrification was observed only at the sampling location »K« (Bay of Koper, 0.5 NM off the coast, 16 m deep) at 10 and 15 m depths in relation to higher $\delta^{15}N_{PN}$ values indicating phytoplankton as the main source of particulate organic material. Variation in $\delta^{15}N_{PN}$ values was due to phytoplankton assimilation. The low value of the fractionation factor ε, averaging 1.1‰, compared to that from other studies, was probably the consequence of different phytoplankton species and different growth conditions. The carbon isotopic mass balance calculation of particulate organic material revealed the higher contribution of allochthonous particulate matter from freshwater inflows. The proportion of allochthonous vs. autochthonous particulate matter decreased with depth.

P 79

DIMETHYLTHALLIUM - A NEGLECTED ENVIRONMENTAL CONTAMINANT IN SURFACE WATER

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Thallium has been considered as toxic metal in many environmental studies for decades. Its occurrence in water, sediments, soil and air particulate matter in partially elevated concentrations is commonly the result of anthropogenic emissions related to mining and metal processing activities. For numerous heavy metals the formation of organo-metal compounds and its release to the environment is known due to technical applications (e.g. butyl tin compounds) or bioalkylation (e.g. dimethyl mercury). Although biomethylation of thallium species is known for decades information on its occurrence in the environment are scarce. Solely one study (Schedlbauer&Heumann, 2000) detected dimethyl thallium in the marine environment at levels of 0.5 to 3.2 ng/L using positive thermal-ionization isotope dilution mass spectrometry, a very complicated and demanding analytical approach.

However, the absence of environmental information on methyl thallium species is related to the lack of appropriate but simple analytical methods for its accurate detection at a natural abundance level. Hence, in our study a LC-MS based approach for the sensitive and accurate determination of dimethyl thallium has been developed. Using synthesized reference material and internal standard material (dibutyl thallium) a direct measurement of pre-concentrated surface water samples with high reproducibility and high sensitivity was achieved. Further on, the developed method was applied on surface water and sewage water samples from an area in Western Germany affected by a long lasting impact of lead/zinc mining and metal processing activities. Maximum values of up to 40 mg/L demonstrated, that dimethyl thallium plays an important role in the environmental distribution and fate of thallium, which has been neglected so far.

Schedlbauer OF, Heumann KG (2000) Appl. Organometall. Chem. 14, 330-340

P 80

CONTAMINANT INPUTS FROM LARGE COASTAL CITIES INTO THE SEA: THE CASE OF MARSEILLE (SW FRANCE)

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Marine pollution is one of the priority issues of the Mediterranean environment and comes from multiple sources including large coastal cities which are considered as hot spots. The METROC (Ifremer) project objectives are to assess bulk and net chemical contaminant fluxes related to large Mediterranean coastal cities, with the Marseille area (SW France) as the first studying site. The present study especially aims to assess the inputs of chemical contaminants to the coastal environment derived from direct urban discharges (sewage network, urban watercourses) and wet weather effluents. The contaminants of interest are metallic (Cd, Pb, Hg) and organic (PAHs, PCBs, PBDEs), by distinguishing the dissolved and the particulate fractions, in addition to physico-chemical parameters (*e.g.* pH, conductivity, turbidity), inorganic/organic carbon contents and dissolved organic matter fluorescence measurements. The method of the fluxes determination results from (i) the determination of contaminant concentrations by collecting water samples in Marseille study area, and (ii) the hydrological data provided by the territorial managers (*e.g.* water discharge). The collection of water and particles samples started in 2009 at 4 to 12 different sampling sites and regarding the various weather conditions (dry/wet periods). First results show that urban watercourses display relatively high concentrations of dissolved metallic contaminants during dry weather period (*e.g.* Pb: 0.128-13.2 $\mu g.L^{-1}$; Hg: 1.7-30.2 $ng.L^{-1}$) due to anthropogenic influences. During storm events, the calculated fluxes for the dissolved metallic contaminants (*e.g.* Pb: 0.8-348 $g.h^{-1}$) and the suspended matter (0.5-19 $t.h^{-1}$) show a high temporal and spatial variability due to the extreme variations of hydrological flow and chemical characteristics in Mediterranean areas.

P 81

DYNAMIC OF CONTAMINANT INPUTS TO THE SEA FROM LARGE COASTAL CITIES: THE CASE OF MARSEILLE (FRANCE)

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Among all the possible sources of marine pollutions, impact of large coastal cities is one of the most worrying, especially in the Mediterranean Sea, due to the rapid population increase all around the coasts. These inputs, partly diffusive and strongly linked to weather conditions (e.g. episodic intensive rain events leading to important land weathering) have to be studied in details to be compared to other sources as large river or atmospheric inputs. In the framework of 2 programs (GIRAC-PACA, ANR MARSECO), study of direct inputs of the Marseille city to the Mediterranean Sea is in progress. In dry conditions, the main water inputs of the agglomeration consist in the mixing of treated wastewater with 2 urban rivers, directly discharged to the sea by an outlet. Aims of this study were to determine the organic carbon and trace metals bulk fluxes to the sea, and to characterize their behaviour in the freshwater/seawater mixing zone. Different campaigns were carried out in 2010, with water sampling in urban effluents and along sea profile/transect. Samples were analyzed for physico-chemical parameters, organic carbon and metals concentrations (dissolved/ particulate), and fluorescence properties. The obtained results showed that concentrations of some contaminants in city effluents overpass by order of magnitude the sea levels. It leads to a non-negligible contamination of the water mass close to the effluent outlet. An important expansion of this impacted zone is expected during wet conditions, especially after extreme rain event. Dynamic of most of the studied species appears to be conservative with salinity in the freshwater/seawater mixing zone. This unexpected result probably has to be attributed to the fast water mixing, minimizing particulate/dissolved repartition. These measurements will be confronted with the results of a dissolved/particulate transport model developed by IFREMER for the prediction of contaminants dispersion in the open sea.

P 82

NEW GLOBAL OCEAN CONTAMINATION DERIVED FROM DEBRIS PLASTICS

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Plastics have been recognized to be chemically stable and physically durable. Plastics are as a source of global contamination of new harmful chemicals into the ocean.

Since late eighties, some chemicals such as phthalic acid esters(PAE) ,nonylphenol (NP)or bisphenol-A(BPA) which are possibly eluted from plastic, were often detected in rivers and oceans although their source and elution pathway are not clear.

Plastics have a long history of the studies on chemical stability like anti-aging or weathering of polymers. However, there is little known on plastic decomposition in the nature. And there is no kinetic data of plastic decomposition at living life or natural environment. We developed a novel method to determine kinetic parameters of plastic decomposition at low temperature and confirmed the generation of harmful chemicals from plastics at 30 – 50 °C.

The results at the low temperatures indicate that polystyrene (PS) undergoes decomposition at 30 °C and generate styrene oligomer. Analytical results of sea sand and water shows the new contamination of these chemical progresses over the world. The results provide us the doubts in the stability and durability of plastics and chemicals emission in use and at disposal.

P 83

DIFFUSE POLLUTION BY PERSISTENT ORGANIC POLLUTANTS AS MEASURED IN PLASTIC PELLETS SAMPLED FROM VARIOUS BEACHES IN GREECE

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Through transportation accidents or intentional releases, plastic pellets (small granules 1-5 mm in diameter) are widely distributed in the ocean all over the world. They are hydrophobic organic materials and thus they are a favourable medium for persistent organic pollutants to absorb to. Pellets demonstrating a certain degree of erosion are expected to have enough contact time with the water pollutants and thus, reach sorption equilibrium with the water phase. The program International Pellet Watch, where plastic pellets were collected by different researchers throughout the world, has resulted in maps for the global distribution of persistent organic pollutants (POPs) in coastal waters. These maps demonstrate that using beached plastic pellets as passive sampling media it is possible to identify pollution hot spots in a global map. In the present study plastic pellets are used to determine the diffuse pollution of selected Greek beaches. Samples of pellets were taken from these beaches. The pellets were extracted and PCBs, DDTs, HCHs, and PAHs were measured. Although, there was no control on the release of the plastic pellets or their fate in the sea, there were differences observed among sampling sites related to their pollution. Plastic pellets collected in beaches in the Saronikos Gulf demonstated much higher pollutant loading than the ones collected in a remote island or close to an agricultural area. Based on data collected in this study and international pellet watch, pollution in Saronikos Gulf, Greece is comparable to other heavily industrialized places of the world.

P 84

TRITIUM MEASUREMENT METHOD FOR THE ENVIRONMENTAL SAMPLES OF BALTIC SEA BASIN (RUSSIA)

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Tritium is present in water (liquid and vapor) as a result of natural processes in the atmosphere, as well as from fallout from past atmospheric nuclear weapons tests and the operation of nuclear reactors and fuel reprocessing plants. The form of most concern, tritium oxide (HTO), is generally indistinguishable from normal water and can move rapidly through the environment in the same manner as water. The expanding construction of nuclear industrial plants and nuclear power stations on the shores of the Baltic Sea is creating a real possibility for the introduction of radioactive wastes into the sea water and the waters of Baltic Sea basin (Ladoga Lake, St.Petersburg rivers). The problem is even more pressing because the Baltic Sea has limited water exchange with the ocean and is comparatively shallow. Tritium concentrations were measured for Baltic Sea waters and snow cover near shores of Russia, for Ladoga Lake water and for river waters of St.Petersburg city. This makes it possible to evaluate the background "global" level of tritium. The low tritium concentration in the environmental water (lower than 1.0Bq/kg-H_2O) is within the detective limit by the low background liquid scintillation counter. As for the samples close to or lower than the detective limit, the samples have to be treated. Two methods of treatment were compared: the method of distillation and method of ion-selective filters. A low-level liquid scintillation system Quantulus 1220 (Wallac, Turku, Finland) was used for measurements. The detector background is reduced by means of a passive shield (made of lead, cadmium and copper) and an active shield (based on a mineral oil scintillator) around the vial chamber. Low activity materials were used in its construction. The obtained results gave the possibility to assess the level of tritium activity in the Environmental water of Baltic Sea basin. The researches are supported by project FCP «The scientific and scientific-pedagogical specialists of innovation Rassiaб 2009-2013».

P 85

COPPER SPECIATION ASSESSMENT IN AQUATIC ECOSYSTEM AFFECTED BY HISTORICAL MINING ACTIVITIES

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The Abrud river basin, in Western Carpathians, Romania, is an aquatic ecosystem exposed to anthropogenic influences exerted by long-term mining. This study examines size and effect of copper concentrations of this ecosystem by assessing both the total copper content and ionic forms of copper in surface waters and sediments. These components were studied by sampling surface water and sediment of 10 control sites (May 2010) located in a section of river about 25 km length that has been exposed to acidic mine water spills and leaks from dumps for many decades. To calculate the partition coefficient (k_d) of copper between the liquid and solid phase suspension, liquid samples were filtered through membrane filters with porosity of 0.45 mm and were subjected to laboratory analytical determinations (spectrophotometric, chromatographic techniques) required to create a complete image of the chemical composition of the matrix. The results were integrated into the mathematical model PHREEQC to determine the weight of chemical species of copper. The results showed that in conditions of low pH (range 2.8 to 7.3) copper exist mainly as free ion. Speciation of copper in sediment was performed using sequential extraction procedure to identify the four chemical steps: (1) exchangeable, (2) Fe/Mn oxides, (3) organic matter/sulphides and (4) residual. The results showed that in sediments of the Abrud river and its tributaries, copper is bound to the exchangeable fraction (range 14.32 to 46.54%) and to the bound fraction of organic matter and sulphides (range 25.22 to 60.34%). We conclude from the results of this investigation that the sites most affected by pollution in the Abrud river are located in locations with the highest levels of the bioavailable mobile fraction.

P 86

HUMIN CONTRIBUTION TO SEDIMENTARY ORGANIC MATTER IN THE ADRIATIC SEA

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A substantial fraction of the so-called refractory organic matter in waters and sediments is constituted by humic substances (HS) which are formed from the decomposition of plant, animal and microbial tissues and tend to be more recalcitrant than their precursors. HS can play important roles as electron transfer in the anaerobic environment and in complexing hydrophobic and hydrophilic species. These properties are important with respect to the migration potential of pollutants in marine environments. The aim of this study is to evaluate the autochthonous or allochthonous origin and the contribute of humin (HM), insoluble fraction of HS, to sedimentary organic matter (OM) in order to investigate the biogeochemical features the HM formation pathway in the Adriatic sediments. Sediments cores were sampled in three sites located respectively in a coastal area of central Adriatic Sea (CCA, 0-25 cm; 35 m depth), in the middle Adriatic pit (MAP, 0-25 cm; 248 m depth) and in the southern Adriatic pit (SAP, 0-35 cm; 1150 m depth) during the SIT-1 cruise carried out in the framework SESAME project during February 2008. Organic carbon and total nitrogen and stable isotopic ratio ($^{13}C/^{12}C$) were determined in sediments and residual HS extracted. The major contribution to sedimentary organic matter is due to the HM (up to 90%) in all stations with an increase with depth along the cores, in particular in the SAP. Refractory allocthonous OM could explained the more negative values of $^{13}C/^{12}C$ (-24.7 ±0.5 ‰) determined in HM in the station more subjected to continental input (CCA), with respect to the other stations (-23.4 ±0.2 ‰ and -24.2 ±0.3 ‰, respectively for MAP and SAP) where the bacterial humification processes could play an important role in the transformation of OM during decay along water column.

P 87

COULD ANTIFOULING PAINTS CONTRIBUTE TO METALS CONTAMINATION IN SEDIMENTS OF THE SOUTHERN VENICE LAGOON?

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Harmful side effects of TBT compounds on the environment and their regulations against them have resulted in significant investment in research into development of TBT-free systems, predominantly using copper and mercury as biocides.

The Southern Venice Lagoon is a not industrialised area, but it is subjected to a high anthropic activity due to the presence of the city of Chioggia and the significantly increase in recent years of dockyards, harbour, marinas, shipping and fishing activities. Some of these activities could have contributed to contaminate the southern lagoon and its sediments by metals used as biocides in the antifouling paints. The aim of this work is to investigate the origin of the metals contamination in surface sediments. The sampling was carried out from April to September 2003 in different sites of the Southern Venice Lagoon near the town of Chioggia. Sandy silt and silt textural types were prevalent inside the lagoon. A clay component was present in reduced amount (< 7%) in all sediment samples. Positive correlation was found between the content of pelite, C_{org} ($R^2 = 0.79$ $p<0.05$) and N_{tot} ($r^2 = 0.85$ $p<0.05$), suggesting a prevailing association of organic matter within the fine sediments. Higher concentrations of metals as Cu, Zn, Pb, Sn, Ni and Hg in the dockyards and marina sites suggest their possible past and recent use as biocides in the antifouling paints. The enrichment factor (*EF*) showed highest values (EF>10) near the dockyards, harbour and marina for Hg and Cu whereas low EF values were found in the channels of the southern Venice Lagoon.

P 88

MERCURY AND HUMIC ACIDS IN THE GRADO AND MARANO LAGOON BOTTOM SEDIMENTS

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The Grado-Marano lagoon system in the northern Adriatic has been affected by relevant mercury (Hg) inputs from two distinct sources: a chlor-alkali plant has been active since the 40's whereas the Idrija Hg mine (NW Slovenia) has been supplying Hg through the Isonzo (Soča) River into the nearby Gulf of Trieste, since the 16th century. In the framework of the recently completed "MIRACLE" Project (Mercury Interdisciplinary Research for Appropriate Clam farming in Lagoon Environment), one of the subtasks was to investigate the biogeochemical behaviour of Hg in lagoon bottom sediments. The research was also focused on recognizing where Hg is potentially mobile at the water-sediment interface, and which factors can promote Hg availability for recycling and methylation. Organic matter and, especially, humic acids (HAs) are known to play an important role in complexation of heavy metals, Hg included, along with other chemico-physical parameters.

Results from surface sediments (0-1 cm) show a highly significant correlation between the methylated form (MeHg) and HAs, particularly where HAs appear at high concentrations (>5 mg/g), in the western sector of the study area (Marano Lagoon). As also reported in literature, HAs presence could represent a preliminary indication of potential methylation, which seems also confirmed by higher MeHg/Hg ratios found in those samples where Hg is basically not in association with sulfide forms (non-HgS).

P 89

VERTICAL DISTRIBUTION OF TRACE METALS IN THE KRKA RIVER ESTUARY (CROATIA) ACCESSED DGT AND VOLTAMMETRY

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Trace metal speciation in the highly stratified oligotrophic Krka River estuary (Croatia) has been studied by using *diffusive gradients in thin films* (DGT) and stripping voltammetry. Halocline in estuary is usually formed between 1.5 and 2.5 meters, and ranges from 30 cm to around 1 m. High degree of variability of physico-chemical parameters (S/T/pH/O_2), as well as of major ion composition is spotted in the halocline, causing changes not only in metal concentrations but also in metal speciation. It is considered that increased biological activity in the freshwater-seawater interface (FSI) plays an important role in control of metal speciation.

Two types of DGT devices (diffusive and restricted) were deployed for defined period (around 110 hours) at six depths. Each day, one (in winter) or two (in summer) discrete samples were taken at each depth, in order to track daily changes of metal concentrations. The same samples were used to make eighteen composite samples.

Anodic (Zn, Cd, Pb and Cu) and adsorptive cathodic (Ni, Co) stripping voltammetry were used for determination of metal concentrations, as well as for copper speciation study. DGT-labile metal concentrations were determined by HR ICP-MS.

High nautical traffic in the estuary during summer season generates significant increase of some trace metals in upper brackish layer (3-5 times for copper). Although concentration of Cu is increased in the upper layer (without pronounced change in DOC concentration), decrease in percentage of non-labile copper complexes in seawater layer suggests an existence of ligands which form stronger copper complexes in brackish layer. According to obtained metal speciation data, model projections show that in upper layer free copper concentrations could over-pass toxic level (10^{-11} M).

P 90

SILICA-GEL-BONDED MACROCYCLE SYSTEM AS SOLID PHASE EXTRACTION ADSORBENT FOR THE SEPARATION OF ARSENIC SPECIES (As^{3+}/As^{5+}) IN NATURAL WATERS

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A simple flow-based method was developed for the simultaneous determination of As(III) and As(V) in freshwater samples. A silica-gel-bonded macrocycle system, namely AnaLig® AN-02 and commonly known as molecular recognition technology (MRT) gel, was used as solid phase extraction (SPE) adsorbent. The retention, extraction and recovery behaviour of the MRT gel SPE columns (MRT-SPE) were studied in terms of pH. Fortified deionized water samples containing 100 µM of arsenic species were treated at the flow rate of 0.2 mL min^{-1}. The collected analyte were then eluted by HNO_3 (1 and 6 M) and introduced into graphite furnace atomic absorption spectrometry. Interference from the foreign ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, CH_3COO^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-) (10 mM) were studied. The accuracy of the proposed separation technique was tested with certified reference waters and spiked 'real' water samples. Satisfactory recoveries (97–102%) were observed with the spiked samples. Other characteristics to consider the MRT-SPE system for sensitive and selective arsenic species (As^{3+}/As^{5+}) separation were effortless regeneration and unaltered separation performance of the sorbent material.

P 91

PHOTOHALOGENATION OF ACETAMINOPHEN IN COASTAL MEDITERRANEAN WATERS

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A large number of experimental studies aiming at understanding the photofate of organic pollutants in fresh surface water have been published. In contrast, considerable less attention has been paid to the possible environmental significance of photoreactions of anthropogenic compounds in seawater and to the formation of potential toxic transformation products. With respect to this latter issue, the formation of halogenated organic compounds occupies a special position since they have complex diversities of biologic effects. The biotic processes are the main published and focused natural origins of halogenated organic chemicals while to date relatively little attention has been focused on abiotic chemical processes for organohalogen production. It is thought that abiotic chlorination or bromination is likely due to the formation of $Cl_2^{\cdot -}$ or $Br_2^{\cdot -}$ radical as a consequence of Fe(III) or Fe(III)$^-$ dissolved organic matter complex irradiation. However, the quantitative relevance of these processes has not been assessed yet. This work presents results of photochlorination studies in coastal seawater, using acetaminophen as model molecule. Natural seawater was sampled in the Gulf of Lyon (southern France), a coastal area with width depth around 10-20 m, characterized by a modest hydrological recycle, and subjected to noticeable anthropogenic inputs, from the city of Marseille and the Rhône river. Acetaminophen was added to the seawater as target contaminant, and the samples were irradiated under simulated solar light. The extension of direct and indirect photolysis and the formed intermediates were evaluated. The investigated compound was slightly degraded by direct photolysis but degradation mediated by natural photosensitizers formed several secondary pollutants including hydroxylated, nitrated and brominated and chlorinated derivatives. The significance of these different transformation pathways will be discussed by taking into account the water chemistry variability.

P 92

CHANGES IN CHIRAL SIGNATURE OF VENLAFAXINE AS A TOOL FOR STUDIES OF BIOLOGICAL ATTENUATION PROCESSES OF TRACE ORGANIC POLLUTANTS IN RIVERS

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The capacity of rivers for biological attenuation processes of trace polar organic pollutants are probably significant but poorly understood. Although it is possible to estimate in-stream attenuation rates from monitoring data, accurate estimates require large data sets and are complicated by uncertainties regarding assumptions about organic WWTP performances and hydrologic data. To overcome these limitations, one approach might be the use of chiral compounds, since many agrochemicals and drugs are chiral and are used as racemates. Individual enantiomer may interact differentially with other chiral molecules, such as enzymes, usually leading to different biotransformation rate of each enantiomer. The main contribution of this work is to investigate changes in chiral signatures of the antidepressant venlafaxine, its metabolite *O*-desmethylvenlafaxine and different chiral β-blockers (atenolol, propranolol, metoprolol) as valuable tools for studies of biological processes in aquatic systems. This work includes: 1) The development of a method for the simultaneous enantiomeric analysis of investigated compounds at the low ppt levels in river water samples by chiral chromatography coupled with mass spectrometry 2) Investigations on enantioselectivitity with respect to sorption and biodegradation processes by means of laboratory-scale experiments and 3) Determination of changes in enantiomeric fraction (EF) value of investigated compounds along a small (Arc River) and a large river (Rhône River). The main results are the followings: 1) Atenolol was the only compound showing an enanselective behaviour with respect to sorption. In contrast, all investigated compounds underwent enantioselective biodegradation processes but with different kinetic rates 2) Venlafaxine was the only compound which did not appear to undergo a net enantiomeric shift in WWTP. Its average EF in the small river remained unchanged with distance downstream probably due to a too short water residence time while it might show a gradual decrease in large river providing evidences for biodegradation.

P 93

UREA IN SWIMMING POOL WATER: OCCURENCE, AND REACTIVITY WITH CHLORINE

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The disinfection of swimming pool water is in most cases guaranteed by gaseous chlorine or sodium hypochlorite. In France, the concentration of free active chlorine (HOCl) in pool water must always be kept between 0.4 and 1.4 mg/L. Along with its disinfecting action, free chlorine also reacts with organic and inorganic compounds present in water. Those substances are mainly released by the swimmers (urine, sweat, dander, scales, cosmetics, ...). Urea is the main nitrogen compound in these secretions (84% and 68% of the total N content of urine and sweat, respectively) and is considered as one of the main precursor of inorganic chloramines in swimming pool water. The main objectives of this study were to investigate the reactivity of chlorine with urea and to evaluate the concentration levels of urea in swimming pool water. Chlorination experiments of were carried out in phosphate buffer solutions of urea ($[\text{Urea}]_0$: 25 µM - 1 mM), in the pH range 5-11 and at chlorine:urea molar ratios ranging from 0.5 to 10 mol/mol. The data obtained from concentrated solutions of urea (1 mM) showed that the chlorine demand of urea was ≈ 5 mol Cl_2/mol of urea and that CO_2, N_2 and NO_3^- represent the end-products of degradation of urea. Chlorination of urea solutions simulating swimming pool conditions ($[\text{urea}]_0 = 50 \mu M$) showed that the degradation rate is very slow. Analyses of urea in water samples collected from 50 municipal indoor swimming pools showed that the mean concentration of urea was about 18 µM (s.d. 11.7) and represents about 6.3% of the TOC parameter. The data also confirmed that urea is very slowly degraded by chlorine in swimming pool water.

P 94

RELATIONSHIP BETWEEN ACIDITY AND COMPOSITION OF PRECIPITATION

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Precipitation samples were collected at the coast of the south Adriatic coast, in the town of Herceg Novi. All samples were analysed for conductivity, pH, and major anions and cations (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}). The ionic species can be arranged according to decreasing amount in precipitation: $Na^+ > Cl^- > SO_4^{2-} > Ca^{2+} > Mg^{2+} > NO_3^- > NH_4^+ > K^+$. Less then 30% of precipitation samples had $pH < 5.6$ and more then 70% of samples could be characterised as alkaline. Time series, correlation analysis, neutralisation factors indicate that major neutralisation agent is Ca^{2+}.

P 95

SPREADING OF ORGANIC LIQUIDS SPILLED AT SEA

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Chemicals spilled at sea after wrecks of chemical tankers often form layers, either immediately or after mass reorganising. These layers are led by the physics and chemistry of adhesion and spreading. Steady states and kinetics of spreading can coexist.

At lab we have experimentally studied only the behaviour under equilibrium conditions: any spontaneous evolution at sea will occur to reach an equilibrium state. First, spreading ability of the organic phase onto water was characterised by the spreading coefficient obtained by measuring the three interfacial tensions (water-rich phase/air, organics-rich phase/air, water-rich phase/organics-rich phase) of four systems in mutual solubility equilibria, mixtures of water and organic liquids chosen because large quantities of them are transported by seas. All the systems have positive spreading coefficient: the organic phase has a tendency to wet the water surface, giving place to an easy evaporation. The less dense ones (n-butanol, methylmethacrylate –MAM-, methyl ethyl ketone –MEK-) are floating ; so the formation of surface layers has to be strongly expected. The densest one, dimethyldisulfide –DMDS-, is sinking and so, it is not expected to float over water, how ever transient layers can be observed: as far as DMDS is gently spilled at the water surface, and that the spontaneous layer is not too thick and heavy, the capillary forces are able to overcome the gravity forces. This is important to know how to foresee possible intense evaporation during an accident.

The second spreading case was studied by simply measuring the contact angle of an organics sessile drop lying on a glass plate in a bath of water. This angle being for each chemical, larger than 90°, we have concluded that these organics do not wet very well the hydrophilic glass surface, because they are themselves at least partially hydrophobic: conversely, they will be able to wet hydrophobic surface. So, the spreading of organic layers will depend, as usual, of the hydrophobicity or hydrophilicity of the solid in contact, rocks, sands, ship hulls, seaweeds or surface of other living beings.

Finally, we tried to find a simple but realistic equation describing the kinetics of spreading on sea surface whose essential aspects will be developed in a poster.

P 96

SPREADING KINETICS OF LIQUIDS SPILLED AT SEA

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Chemicals spilled at sea after wrecks of chemical tankers often form layers, either immediately or after mass reorganising. Although the phenomenon is apparently very similar in nature to the spreading of oils, whose spreading equations are in use, others specificities appear:

- substances transported by sea are far more diverse than oils
- many parameters are able to affect the behaviour of products spilled in large quantities, as the weather conditions, the accident location, the characteristic properties of the substances
- implied phenomena are coupled; this is the source of many difficulties in resolving behavioural equations, which makes it difficult to solve them in case of emergency.

Here is presented an attempt to take into account, in the equations describing the spreading of a liquid layer on a free surface of sea water, several physico-chemical properties all depending on the chemical nature of the products:

- their density compared to the sea water density (already taken into account in the exristing equations)
- their viscosity
- their surface tension and their interfacial tension with the water, and so, their spreading coefficient.

The new equation can be solved with the help of the following approximations:

- non-coupling of phenomena
- mechanical equilibrium et the edge of the layer.

Although rough, these approximations are reasonable and can be solved in a time compatible with emergency.

P 97

Se AND ITS SPECIES IN *MYRIOPHYLLUM SPICATUM* AND *CERATOPHYLLUM DEMERSUM* GROWING IN WATER CONTAINING Se (VI)

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The possible accumulation of Se (VI) and additionally effects of Se on physiological characteristics were studied on two aquatic plants *Myriophyllum spicatum* L. and *Ceratophyllum demersum* L. Plants were cultivated outdoors in semi control conditions and in two different concentrations of Na selenate (20 µg Se/L and 10 mg Se/L). High dose of Se (10 mg Se/L) negatively affected photochemical efficiency of PSII of both species, while 20 µg Se/L did not exert any effects on PSII. There were no effects of either concentrations of Se on the amount of photochemical pigments. Concentrations in plant tissue ranged from 0.7 to 297 µg Se/g DM in *M. spicatum* and from 0.7 to 485 µg Se/g DM in *C. demersum*. Amount of soluble Se in plant tissue increased with concentration of Se in water. Findings showed that both species could take up a great amount of Se. The present of Se compounds and their content in macrophytes will be presented.

P 98

DISTRIBUTION AND FATE OF AROMATIC ORGANIC POLLUTANTS IN SEAWATER
(THEORETICAL STUDY FOR AN ACCIDENTAL SPILL SCENARIO)

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The maritime transport of chemicals substances has increased in the last decades due to the continuous development of the chemical industry and the need to transport in massive quantities. Accidental releases can occur as a result of natural disasters, human errors, or due to technical and mechanical failures in chemical transfer and storage equipment. Gases, liquids, solids and/or packaged goods can, in case of accidents, enter the marine environment and cause dangerous situations for human beings, or be harmful for the marine environment. When gases, liquids or solids enter the marine environment various types of behaviour are possible. Substances can form gas clouds, evaporate from the surface, float on the surface, dissolve in the water column, sink to the bottom, or show combinations of these. The behaviour in the marine environment depends on the solubility, density and vapour pressure of the released chemical substance.

The present work evaluates the behaviuor of aromatic organic pollutants once they get in contact with seawater. Based on the physical properties of the organic substances and the seawater conditions, it is possible to determine their fate into the seawater. The experimental set-up was performed by using a vessel reactor with temperature and pressure control attempting to reproduce the sea conditions at laboratory scale. The rate constant of solubility was determined under different experimental conditions (pressure and temperature) and the maximum solubility was estimated as a function of the salinity concentration and the temperature. The rate of evaporation and the rate of sorption on sediments were also considered for those pollutants which theoretical behaviour was expected to reach these compartments (air an sediments). The Markov model was applied to predict the fate of the organic substances in the environment and the results were compared to the theoretical behaviour defined by the physical properties of the organic pollutants.

P 99

INTERACTION BETWEEN BISPHENOL A AND TANNIC ACID: SPECTROSCOPIC TITRATION APPROACH

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The interaction between tannic acid (TA) and bisphenol A (BPA), an endocrine disruptor, was studied by absorption and fluorescence titration techniques. The binding constants and corresponding thermodynamic parameters at different temperatures were determined. The intrinsic fluorescence of BPA was strongly quenched by TA and the quenching mechanism is attributed to dynamic and static quenching. The thermodynamic data revealed that the formation of TA-BPA complex was endothermic, entropic-driven, and spontaneous. Furthermore, hydrophobic interaction seems to be the major driving force for the formation of the nonfluorescent TA-BPA complex.

P 100

ON THE TERRESTRIAL EXPORT OF ORGANIC CARBON TO OCEANS: ARE WE MEASURING THE RIGHT THING?

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Dissolved organic matter (DOM) in the oceans represents one of the biosphere principal stores of organic C. A large proportion of this matter is drained from the continents and, thus, it is affected by the increase in dissolved organic C (DOC) concentrations observed over the past decades in rivers throughout the Northern Hemisphere. This increase has important implications for long-term C balances as well as drinking water quality, but it has proven difficult to ascribe DOC variations to a specific environmental driver (e.g., temperature increase, rising CO_2 in the atmosphere, increasing amounts of precipitations and runoff, droughts, increase in soil acidity or ionic strength, etc.). We have analysed the abundant existing data and found that some methodological problems persist (e.g., the possible sorption of 'dissolved' organic compounds onto 'particulate' inorganic colloids and particles have been ignored; a myriad of methods, giving not always comparable results, have been used to determine DOC values, methodology has been incompletely reported, etc.). However, the main problem identified in our study is that the fact that very different compounds are 'hidden' under the common 'umbrella' of DOC concentrations has rarely been taken into consideration. Sometimes, DOC is misleadingly taken as a synonym of 'humics' or refractory C (without specific measures having been made) but 'humics' are not the only type of DOM present in surface waters and not even the most abundant in many aquatic systems (e.g. oceans and many surface waters, particularly during productivity periods). We think that the standardisation of methods used for DOC determination and, especially, the simultaneous determination of DOC and some well-targeted types of DOM would significantly improve our understanding of the role of organic matter in the C cycle under present global change stressors.

O 7

KINETIC EXTRACTIONS TO MIMIC MOBILIZATION ABILITY OF TRACE METAL IN COMPOST, SOIL AND COMPOST-AMENDED SOIL

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Biological and mechanical treatment (BMT) of municipal solid waste is a wide spread practice. Meanwhile, using BMT-compost for soil amendment can represent a risk regarding contamination of soil and natural water by trace metals. As several authors have hypothesized that kinetic metal extraction data might better reflect dynamics of metals in soil, an attempt was made to use this approach to determine different pools of trace metals according to their mobilization capacity. Two extraction solutions were used, $Ca(NO_3)_2$ (0,05 mol L^{-1}) and EDTA (0,05 mol L^{-1}) at pH 7. The procedure was applied to BMT-compost, reference soil (calcosol, silty-clayey) and amended-soil (30t/ha). It was repeated on soils sampled over a six-month period after compost spreading. Extracted metal amounts increased rapidly during the first hours of the kinetic experiments, equilibrium was almost reached after 24 hours even if minor release occurred for some trace metals. Results allow to class trace metal forms in five pools according to their mobilization potential. The ratios “Quantity of metal extracted in 1h/quantity of metal extracted in 24 h” (Q_{1h}/Q_{24h}) were determined. Results suggest different metal binding energies to compost or soil constituents depending on the trace metal and highlight influence of season and BMT-compost adding on qualitative modifications of these bindings.

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O 8

ENHANCING p-CRESOL EXTRACTION FROM SOIL

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Soil washing is a potential technology for rapid removal of organic hydrocarbons sorbed to soils. In this work, p-cresol desorption with different non-ionic surfactants (Tween 80, Brij 30 and Triton X-100) was compared to cyclodextrin (HPCD) and citrate as solubilizer. All desorption experiments of the contaminated soil were performed using the batch equilibration technique at 25 °C. Solubilizer concentrations were varied between 0.5-20 g/l and liquid to solid ratio between 1 to 5 ml/g. Kinetic desorption data were obtained for 1 g/l and 2.5 ml/g. Ecotoxicity of solubilizers was evaluated by Microtox bioassay. The soil used in this work was categorized as loamy sand at neutral pH with a soil organic matter (SOM) content of 5%. Desorption of p-cresol in water or with different organic solvents (as dichloromethane, hexane, isopropanol, and acetone) was negligible in our experimental conditions. All the solubilizers used in this work show a significant extraction. The presence of the different solubilizers did not modify the natural pH of the soil 7-7.5, excepting when citrate was used as extracting agent, which was maintained about 4.2. p-Cresol extraction was accompanied by SOM desorption, this modification of the soil was minimized using HPCD and Tween 80. Asymptotic values higher than 55 % of desorption percentages were only obtained for Tween 80 and Brij 30 at 48 hours. However, Brij 30 ecotoxicity (EC_{50}= 0.49 ppm) is in the same order of that obtained for p-cresol, being this surfactant clearly ruled out. Liquid to solid ratio of 5 ml/g for Tween 80 presented the best extraction results, while concentrations higher than 0.5 g/l did not produce any effect on the desorption efficiency, because these concentrations are far from the critical micelle concentration (cmc) of Tween 80 (0.013 g/l). p-Cresol extraction by consecutive cycles was also analyzed, although more than 90 % of p-cresol extracted was obtained in the first cycle.

O 9

ADSORPTION OF ORGANOPHOSPHOROUS COMPOUNDS ON WELL-CHARACTERIZED HEMATITE, MAGHEMITE AND GOETHITE NANOPARTICLES

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Particles of iron(hydr)oxide minerals in the earths crust are highly reactive toward phosphates, and sorption of organophosphorous (OP) compounds constitutes an important part of the anthropogenic phosphor cycle. Here three different polymorphs of well-characterized nanoparticles were chosen as model systems for iron minerals, i.e. hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and goethite (α-FeOOH). Comparative studies of structure-specific sorption processes were performed using three OP compounds, namely trimethyl phosphate (TMP), triethyl phosphate (TEP) and dimethyl-methyl phosphonate (DMMP). Using in situ infrared vibrational spectroscopy OP adsorption was studied in a temperature controlled system under different conditions: Dry sorption, dry sorption under simulated sunlight and sorption with controlled humidity. The surface reactivity is shown to be dependent on OP compound, particle type and environmental parameters (humidity and sunlight). All OPs are found to adsorb on unsaturated iron cation surface sites (Lewis acids) on hematite and maghemite. In contrast, on goethite hydrogen bonding to surface OH (Brønsted acid) dominates. On the iron(hydr)oxide minerals dissociative adsorption is facile on the dry surfaces yielding methoxy and formate reaction intermediates. The reactivity increases in the order goethite < maghemite < hematite. Addition of water blocks reactive adsorption sites, whereas sunlight promotes OP dissociation on all minerals irrespective of humidity. DMMP and TMP are the most reactive OPs in dark and under sunlight illumination, respectively, while TEP is the least reactive compound. The implications of the results are discussed.

O 10

BIOGEOCHEMICAL CYCLES OF CHLORINE IN THE FOREST ECOSYSTEM: RADIOTRACER STUDY USING ^{36}Cl AND ^{14}C

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In nature, chlorine does not occur only as chloride or bound in substances of anthropogenic origin in the polluted environment but also in many hundreds of organic compounds of natural origin. Chloride deposited in the forest ecosystem from the atmosphere reacts with soil organic matter (SOM) under the mediation of microorganisms forming chloroacetic acids (CAAs), chloroform, other aliphatic and aromatic compounds and chlorinated humic substances. Chlorine in soil is thus mostly bound in organochlorines (AOX) and so involved in SOM degradation, leading to smaller SOM decay products and finally to their mineralization. Radioisotopes ^{36}Cl and ^{14}C together with radiotracer methods were used in the research of the role of chlorine in the forest ecosystem; their advantage is among other things the possibility of radioactivity budget. The results achieved in the investigations of the formation and fate of organochlorines in the Norway spruce/soil system are presented. CAAs are formed in the forest soil by enzymatic SOM chlorination (and easily microbially degraded). It was shown for the first time that chlorination of SOM yields tri- and also dichloroacetic acid; investigated was also formation of further chlorinated compounds as well as of chlorohumus. However, chlorohumus is in alkaline solution not stable, loses partially chlorine and is degraded to fulvic acids; this alkaline hydrolysis was confirmed by ^{36}Cl. The monitoring of chloride and AOX in 12 forest stands in the Czech Republic showed that only minor part of chlorine is present as chloride (ca. 60 mg/kg FH soil) and prevailing are AOX (ca. 200 mg/kg). For comparison one stand in a coastal region in southern Norway with much higher deposition of chloride was monitored. The DyDOC model for the dynamics of DOC chlorination was adapted. In this way more systematic knowledge about chlorine cycling in the forest ecosystem was gained.

P 101

BIOLEACHING OF HEAVY METALS IN CONTAMINATED SOILS UNDER THE ANAEROBIC CONDITION BY INDIGENOUS BACTERIA AND *SHEWENELLA SP.*

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A study on the bioleaching of heavy metals and arsenic (As) in contaminated soils collected from the old smelting site in South Korea was carried out under anaerobic conditions. The objective of this study was to investigate the microbial effects on heavy metals and arsenic mobilization. Two types of biogeochemical leaching tests were conducted for 28 days in batch scale. First test was performed with indigenous bacteria, and the reduction bacteria *shwenella sp. (oneidensis MR-1, algae BrY)* was used in second test. The anaerobic condition was composed of serum bottles purged out 99 % N_2 gas. Experiments were carried out in duplicate.

From the first test, indigenous bacteria was stimulated using various carbon sources and concentrations(for example, 1mM, 10mM, and 20mM glucose, and 1mM, 10mM, and 20mM lactate) to obtain the optimum experimental condition. The sterilized Distilled In Water (DIW) was injected to control the growth of indigenous bacteria for the microbial control.

In the second test, *shwenella sp.(oneidensis MR-1, algae BrY)*, facultative anaerobic bacteria, was injected to examine the redox transformation and biogeochemical behavior interaction of heavy metals in contaminated soil. 10mM lactate was used as a carbon source.

P 102

INCUBATION EXPERIMENT FOR MEASURING SOME HEAVY METAL CONCENTRATIONS OF TWO FLOOD-PLAIN SOILS

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Soil samples were collected in the east-central Hungary of River Tisza flood-plain areas in the middle of August 2003, two flood-plain soil samples were used in this study, which will be referred as Tivadar and Gergelyiugornya. Tivadar is a small village close to the River Tisza that has low degree of anthropogenic impact, upstream River Szamos mouth. Gergelyiugornya is in a direct line from the Szamos-Tisza connection (about 100 m in the flow direction). The River Szamos is of essential relevance, because there has been a very harmful cyanide and heavy metal pollution. Therefore, the objective of this study was to compare the clear Tisza sites (Tivadar) with the polluted area (Gergelyiugornya).

Soils of 10g were packed in plastic bags and in the laboratory at 25 °C were incubated for 1,7,14,21 days under water-flooding incubation. Following the incubation we measured the Fe, Cu, Zn and Mn concentrations of the soil samples by applying nitric acid and slightly acidic buffer solutions. It was found that the heavy metal concentrations with the incubation experiment in case of the slightly acid solution the iron and manganese concentrations are significantly higher in Gergelyiugornya sample while the copper concentrations are significantly higher in Tivadar sample. There was no significant difference in the zinc concentrations of the two samples. In case of strongly acid solution all the measured heavy metal concentrations were significantly (with even an order of magnitude) higher in Gergelyiugornya sample. The obtained data showed the concentration phenomena under different incubation period and this phenomenon was more pronounced at higher incubation period (2 weeks) than the lowest one (1 day).

P 103

ADVANCES IN DEVELOPMENT AND EVALUATION OF SORBENT MATERIALS FOR ENVIRONMENTAL APPLICATIONS

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The results of a call for a Global NEST journal special issue that is now in press will be presented. This special issue is edited by the authors and is entitled “Development and Evaluation of Sorbent Materials for Environmental Applications”. A short abstract of each paper will be presented along with the most interesting results. Twelve papers were submitted. They were separated into four main topics, i.e. Sorbent Materials for: a) Water and Wastewater Treatment, b) Fuel Purification, c) Soil and Sediment Remediation, and d) Pollution Monitoring. Pollutants studied include: metals (copper, cadmium), organic pollutants [micropollutants (PAHs, PCBs), dyes (Crystal Violet), pesticides (Atrazine), organic sulfur (benzothiophene, dibenzothiophene)], and nutrients (ammonia). Sorbents studied include natural material [zeolite (clinoptilolite)], modified natural (clay), synthetic, polymers, activated carbon, char, microbes (bio-sorption), metal-organic frameworks (MOF). Findings presented in the papers include originally developed hydrogels and materials with impressive sorption capacities. A complete methodology to understand interfacial mechanisms and finally, determine the exact mechanism of surface binding at the molecular scale is presented along with various applications. Challenges in flow through systems having changes in permeability changes in packed beds with pure oxides and humic acids. A thorough review paper on the addition of sorbents for soil and sediment remediation critically presents this new methodology that is developing this last decade. This review paper identifies challenges related to this methodology. Another paper addresses one of these challenges. And finally, it is presented how once sorption mechanisms and material science are understood, one can pick plastic pellet from beaches and use them as monitoring tool for organic pollutants.

P 104

EFFECT OF LONG-TERM MSW COMPOST APPLICATIONS ON METAL UPTAKE BY CUCUMBER (*Cucumis sativus* L.) PLANT AND SOIL METAL BIOAVAILABILITY

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A greenhouse experiment was carried out to assess heavy metal loading and its bioavailability on the greenhouse soil and uptake of metals by cucumber plant following MSW compost application. MSW compost was applied from 2005 to 2009 to greenhouse soil as an oven-dry basis, totaly at 100 ton ha^{-1}(MSWC$_{100}$) and 200 ton ha^{-1} (MSWC$_{200}$) levels. An uncontaminated greenhouse soil at the same location was used as a control treatment for comparison with the results. After the end of 4 years of successive MSW compost applications to greenhouse soil, the residual effects of MSW compost on heavy metal accumulation in cucumber and total and bioavailable heavy metal status of greenhouse soil were tested.

It was found that plant heavy metal contents were higher in MSW compost treated greenhouse soil than that in untreated soil. Higher levels of MSW compost applications caused higher accumulation of Zn, Cu, Ni, Pb and Cd in the leaves and fruits of cucumber plant. Concentrations of heavy metals in plants were below the phytotoxic levels. In the MSW compost treated greenhouse soil, according to background and toxicity limits, heavy metal status of cucumber leaves were ranged in normal and high levels. Although concentrations of heavy metals in cucumber fruit were below the phytotoxic threshold levels, Pb concentration was exceeded safety food metal limit value for edible vegetables by MSWC$_{200}$ compost treatments.

The greenhouse soil treated with MSW compost contained higher concentrations of both total and DTPA-extractable Zn, Cu, Ni, Pb and Cd than that of untreated soil. Results obtained for DTPA extractable metal availability indicated higher relative metal availability in MSW treated soils. Relative metal availability order of metals in MSW treated soils were Zn>Pb>Cu>Cd>Ni. Bioavailable Cd content of control soil was found below the detection limit. The amount of bioavailable metals in the greenhouse soil was significantly high for MSW compost treatments. In MSW compost treatments, total soil metal concentrations were found below the permissible pollutant limits, but the increase in available metal fractions was more marked than those of total concentrations.

P 105

THE BEHAVIOUR OF Zn ADSORPTION ON SOME CLAYEY ACID SOIL OF MALAYSIA

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The contribution of organic matter, oxides, and clay fraction to Zn adsorption in six soils from Malaysia kualambure was evaluated. After soil characterization, adsorption isotherms were obtained by adding six solutions containing between 5 and 100 mg L(-1) concentrations of $ZnCl_2$. Results obtained show that all soils have high affinity for Zn sorption. Distribution coefficients were obtained from the data of adsorption isotherms. Zn adsorption isotherms corresponding to untreated soil adjusted to Langmuir and Freundlich empirical models. Distribution coefficients allowed knowing the Zn adsorption capacity of these soils, and of the organic matter, oxides, and clay fraction. Soil organic matter is the main component that affects Zn adsorption as long as soil pH is near neutrality. At acid pH, the oxides are the main component that affects Zn adsorption, although to a much smaller extent than the organic matter near neutral conditions. So soil pH is the main soil factor that determines Zn adsorption, before any other soil property.

P 106

IMMOBILIZATION OF POTENTIALLY TOXIC METALS USING DIFFERENT SOIL AMENDMENTS

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Soil pollution with different metals and metalloides is a widespread problem all over the world and it needs to be properly solved. The in- situ immobilization of potentially toxic metals, using different amendments, is cost-effective, non invasive and promising method for contaminated soil remediation. In the present study we investigated the effectiveness of phosphate (apatite) and Slovakite (commercial mixture of dolomite, diatomite, smectite basaltic tuff, bentonite, alginite and zeolite) amendments in immobilizing Pb, Zn, Cu and Cd from contaminated soil. Three different concentrations of apatite and Slovakite (1%, 2.5%, and 5% by weight) were applied to a contaminated soil originating from an old lead and zinc smelter site in Arnoldstein, Austria. Using chemical extraction tests we examined metal phyto-availability (using diethylenetriamine pentaacetic acid (DTPA) and calcium chlorid extraction), mobility (ethylenediaminetetraacetic acid, EDTA) and exchangeable cations in soil (ammonium acetate, NH4OAc). Generaly, the effectiveness of added amendments to immobilize metals increased by increasing the amount of amendment. Metal fractionation was assessed by six-step sequential extraction. The influence of added amendments on soil microbial activities (soil respiration, ß- glucosidase, acid and alkali phosphatase and dehydrogenase activity) was also investigated.

P 107

APPLIANCE OF GEOCHEMICAL NORMALIZATION AND ENRICHMENT FACTORS FOR THE EVALUATION OF ENVIRONMENTAL CONTAMINATION WITH TRACE ELEMENTS IN SEDIMENTS

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The concentrations and pollution levels of vanadium, chromium, nickel, copper, zinc, cadmium, and lead in sediments were assessed to evaluate the environmental quality and potential contamination, using the: determination of element content, geochemical normalization method, determination of metal background values, calculation of enrichment factors (EF). The study area represented Danube alluvial sediments from the canal, which begins at the Oil Refinery Pančevo and located in the industrial zone of the city Pančevo. In this canal is placed the pipeline for wastewater and atmospheric water, which is beginning from the Pančevo Oil Refinery, and water from pipeline is pours in a canal for wastewater that flows into the Danube. The values of calculated enrichment factors indicate that on investigated locality existed minor to moderate enrichment of sediment with Cr, V, Cu, Pb, Cd, Ni, and Zn, except for one locality, where sediment is severe enrichment with Zn.

P 108

BIOSURFACTANTS FROM *L. pentosus* AS ALTERNATIVE TO CHEMICAL SURFACTANTS FOR THE BIOREMEDIATION OF CONTAMINATED SOILS

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The bioremediation of hydrocarbon contaminated sites is limited by the poor availability of these hydrophobic contaminants to microorganisms, which could be improved by using surface active compounds. Microbial molecules that are able to reduce the surface tension of media are named biosurfactants, which usually are less toxic and more effective than chemical surfactants. Consequently, during recent years efforts are being directed to explore ways to reduce the biosurfactant production cost through improving the yield and the use of either cost-free or low-cost feedstock or agricultural by-products as carbon sources. If the production cost of biosurfactants becomes competitive with the synthetic surfactants and the commercial availability of biosurfactants increases, the industrial use of microbial surface active compounds can be expected to grow in the coming decade.

The biosurfactant employed in this work was obtained from *L. pentosus* by fermenting hemicellulosic sugars (19 g/L of xylose, 9 g/L of glucose) in the same concentration than the hemicellulosic sugars obtained from trimming vines shoots. Soil was contaminated with 700, 7000 and 70000 mg/Kg of octane, and following the biosurfactant, from *L. pentosus*, was added to soil and incubated at 25 ºC.

After 15 days it was observed that soils in absence of biosurfactants only reduced the concentration of octane between 1.2 and 24 % whereas, soils incubated with biosurfactants from *L. pentosus* reduced the octane concentration between 58.6% and 62.8%.

P 109

STUDY OF PERMEABILITY AND CONTAMINANT FLOW IN GRANITOID ROCKS USING DYES

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Rock permeability has significant influence on spreading of contaminants in granitic rock environment. Even fresh granite rock contains small intergranular and intragranular spaces where the contaminants can flow. The study is involved in determination and characterisation of microstructures and diffusion velocity measurements using dyes as a contaminant analogue in ex-situ as well as in-situ granitoid environments. New method of sample preparation and observation was developed during laboratory tests.

Eight different dyes and pigments were experimentally tested as contaminant analogues. 1) Cation active water soluble dyes were used to simulate chemical contamination with sorption ability. 2) Alkali reactive water soluble dyes constitute potentially non-sorbent contaminations. 3) Fine pigments (10^{-4} m) and ultra fine (10^{-6} m) milled pigments simulated colloid contaminant particles of various sizes. The advantage of using dyes and pigments as a contaminant analogue is their easy optical detection and low risk of toxicity during in-situ experiments.

Fresh granitoid borehole cores (from depth 80-100 m) from four different localities in the Bohemian Massif were collected for laboratory experiments. Sets of samples were immersed into dye solution. Penetration lengths were measured after determined time steps. Results show differences in diffusion speed according to rock structure and mineral composition. Pictures of flow channels were taken for subsequent optical analysis. Feldspars and micas occurred to be the main minerals allowing inter- and intragranular flow.

Ultra slim borehole (ø 20 mm) was drilled into the bottom of existing 76 mm borehole in the 100 m depth at two localities. These slim boreholes will be filled by non-sorbent dye to examine diffusion velocities under lithostatical pressure. The results will be compared with laboratory experiments. In-situ experiment is planned in spring 2011.

P 110

MONITORING OF SELENIUM CONTENT IN PARENTAL ROCKS FROM THE SOUTH - EASTERN PART OF ROMANIA

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Selenium is a naturally occurring mineral element that is distributed widely in nature in most rocks and soils. In humans, selenium is a trace element nutrient which functions as cofactor for reduction of antioxidantenzymes such as glutathione peroxidases and certain forms of thioredoxin reductase found in animals and some plants (this enzyme occurs in all living organisms, but not all forms of it in plants require selenium). Selenium can be presented in both inorganic (selenite, selenate, hydrogen selenide etc) and organic forms (selenomethionine, selenocysteine and selenoproteins etc). Among them, hydrogen selenide is extremely toxic while selenomethionine is essential and nutritional to the human body.

Romania belongs to the European space where selenium abundance in the environment components is low. Inside the country areas in which the presence of this microelement is below the average determined for the whole country have been separated. One of these areas is Dobrogea. The selenium deficiency became manifest by myodystrophy incidence with sheep in the area North of Constanța. This paper is focused on the South-Eastern part of Romania, where a study was done regarding low level of selenium in rocks, these area being characterized by a natural handicap, selenium deficitary. For this purpose, we determined the total and mobile content of selenium in the parent rock (green schist, limestone, and loess). Wet digestion with a mixture of anorganic and strong acids was used for determination of rock samples regarding of total content in a oven with microwave, and for extraction of mobile content, the samples were extracted with a commun extractant, namely EDTA and Ammonium Acetate. These contents were dosed by atomic absorbtion spectrometry coupled with hydride generation (HG-AAS). Data obtained regarding of selenium content confirms its deficiency in studied area.

P 111

THE IMPACT OF GARDENING ON HEAVY METALS SPECIATION IN SOILS AFFECTED BY SMELTERS ACTIVITIES

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Heavy metals in soil are hazardous for human health when they are mobile. Their mobility in soil depends on the species they are bound to.

The main question for this research is whether or not agricultural practices influence heavy metal speciation in soils.

In order to answer this question, sequential extraction procedures were applied to soils sampled from three gardens and three undisturbed pastures from a smelter in the impacted area. Lead, cadmium and copper were analyzed by an atomic absorption spectrometer with graphite furnace. For the beginning, in order to investigate the fate and transformation of pollutants in soil, the preliminary measurements were carried out using X-ray fluorescence spectroscopy. The content of organic matter, minerals, pH, iron, manganese and calcium were also determined.

The results obtained are in concordance with the expectations. In the garden soils affected by smelters activities, the heavy metals content and mobility are influenced by the agricultural practices.

P 112

UPTAKE OF NICKEL, ZINC, CADMIUM, CHROMIUM AND LEAD BY VARIOUS *BACILLUS sp.*

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Water pollution problems, due to industrial effluents in aquatic environments, are increasing day by day as industrial effluent waste is degrading ecosystem, global water cycle and environment. Industrialization is accelerating the deposition of heavy metals in soil and water bodies. Conventional processes used for removal of heavy metals from industrial wastewaters include chemical precipitation, oxireduction, filtration, electrochemical techniques and sophisticated separation processes using membranes. This work presents some results on the use of microbes from the genus *Bacillus* for uptake of cadmium, zinc, nickel, chromium and lead ions. Maximum chromium bioaccumulations were 5.6 mol/g biomass for *B. sphaericus*, 5.6 mol/g biomass for *B. cereus* and *B. subtilis*, and 6.4 mol/g biomass for *Bacillus* sp. Maximum zinc bioaccumulations were 5.7 mol/g biomass for *B. sphaericus*, 4.6 mol/g biomass for *B. cereus*, 4.8 mol/g biomass for *Bacillus* sp. and 5.6 mol/g biomass for *B. subtilis*. Maximum cadmium bioaccumulations were 7.8 mol/g biomass for *B. cereus*, 8.6 mol/g biomass for *B. subtilis*, 11.1 mol/g biomass for *Bacillus* sp. and 11.5 mol/g biomass for *B. sphaericus*. Maximum nickel bioaccumulations were 7.3 mol/g biomass for *B. cereus*, 6.8 mol/g biomass for *B. subtilis*, 10.8 mol/g biomass for *Bacillus* sp. and 9.6 mol/g biomass for *B. sphaericus*. Maximum lead biomaccumulations were 0.7 mol/g biomass for *B. sphaericus*, 1.9 mol/g biomass for *B. cereus*, 2.2 mol/g biomass for *Bacillus* sp. and 1.8 mol/g biomass for *B. subtilis*. The different *Bacillus* strains tested presented distinct uptake capacities, and the best results were obtained for *B. subtilis* and *B. cereus*.

*Key words**:** Bioaccumulation, Bacillus sp, Heavy metals*

P 113

CADMIUM SORPTION AS INFLUENCED BY CARBONATE FORMS OF CLAY FRACTION OF SOME CALCAREOUS SOILS IN AL-HASSA

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The different carbonate forms were determined in the fine (< 0.2 um) and coarse (2 - 0.2 um) clay fraction of the three representative soil profiles in Al-Hassa Oasis at Saudi Arabia. The results indicate that the total calcium carbonate (Ct) is high (9.40 - 28.10%) and relatively higher in fine than coarse clay. The calcite ranges from 0.35 to 9.55 %, Mg calcite is found to range from 0.00 to 10.20 % and the other carbonate varies 0.24 to 17.70 %. Mg calcite is relatively higher in the fine than the coarse clay fraction.

Data of cadmium sorption by clay fraction indicate two populations of sites (I and II) having different affinity for cadmium sorption were present and fit the binary Langmuir equation. The constants related to the bonding energy in part I (K1I) were higher in fine clay than the coarse clay and correlated significantly with Mg-calcite content while the maximum adsorption values of part I were higher in the fine clay and correlated significantly with Mg-carbonate content. On the other hand, K1 and K2 for part II have no regular trend and no correlation with calcium carbonate forms.

Keywords: carbonate, Mg calcite, clay fraction, Langmuir, adsorption

P 114

HYDROGEN PEROXIDE STABILIZATION WITH CHELATING AGENTS IN SOILS FOR ISCO TECHNOLOGY

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H_2O_2 is one of the most commonly used reagents for in situ chemical oxidation (ISCO) as a promising alternative to remediate contaminated soils. It has limitations related to stability and transport. The focus of this investigation was to evaluate the potential of using chelating agents to improve the H_2O_2 stability. The chelant is able to complex metals and reduce their ability to react with H_2O_2. The oxidant stabilization ($[C_{H2O2}]_o=10g·L^{-1}$) with four different chelating agents (EDTA; Citric acid; Ascorbic acid and Gallic acid) in two concentration values (10 and 50mM) was investigated in soil slurry batch reactors at 20ºC ($V_L/W=2mL·g^{-1}$). Three loamy sand soils (S1, S2 and S3) with high soil organic matter content (SOM=15.1, 10 and 7.44%, respectively) at natural neutral pH≈7 have been used.

S1 is the soil with higher SOM and none of the chelating agents improve the H_2O_2 stability. Mainly, its high oxidant demand is due to the presence of natural SOM and inorganic reductants that consume H_2O_2. For S2 and S3 the three acid chelating agents were able to reduce significantly the H_2O_2 decomposition. The H_2O_2 decomposition rate decreases as chelating agents cocentration increases from 10 to 50mM. So, in these two soils, not only SOM, likely metals are also responsible for H_2O_2 consumption. The Citric acid is the most effective H_2O_2 stabilizer in all the experiments. The oxidant conversion is reduced around 50% at 50mM compared with the results obtained without chelating agents. Also, this reduction of the H_2O_2 decomposition is in relation to the decrease of pH value. The solution pH with the acid chelating agents increased from the initial acid pH=2~3 to a stable value below to the intial soil pH=5~6 due to its high buffering capacity. This decrease in the pH value respect to the initial is responsible of the H_2O_2 stability. This shows that the H_2O_2 stability is greater under acid conditions.

P115

BCR SEQUENTIAL EXTRACTION OF SELECTED METALS FROM SOIL OF ORGANIC FARMING APPLE ORCHARD

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Nowadays the importance of organic farming and products of it are gaining more and more interest due to the growing awareness of healthy lifestyle. Whereas organic farming excludes or strictly limits the use of synthetic fertilizers and synthetic pesticides, and genetically modified organisms the composition of the soil plays only a minor role. Not only in industrial areas, but also in remote regions there is a not negligible impact of metals released by industry on the environment and arable land.

Thus the amounts of extractable metals, especially heavy metals, from soil of an organic farming apple orchard in middle Croatia were determined in order to see the potential impact on apple trees and further on the collected fruits and their products. The investigated soil has the following mineral composition: quartz, dolomite, illite, chlorite, chlorite-smectite and kaolinite and organic matter ranging between 5 and 9%.

Sequential extraction was used for the fractionation of trace metal content in the studied soils, using acetic acid, hydroxylamine hydrochloride, hydrogen peroxide, and ammonium acetate as extraction reagents.

The obtained extraction solutions were analyzed by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) for Ag, Al, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Na, Ni, Pb, Sr and Zn. The results of the extractable amounts were compared to the total amount of metal in soil determined by XRF to calculate the extractable amount of each element. Furthermore the mobilizability was determined through the extraction yields of the four steps.

P 116

BIOMASS ASHES – DISTRIBUTION OF PLANT NUTRIENTS IN THE DIFFERENT ASH FRACTIONS

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Biomass (e.g. wood pellets or wood chips) is increasingly used as fuel in the generation of heat and electricity. The main reason for this development is the CO_2-neutrality - if transportation and pre-treatment of the biomass is not taken into account. In the incineration process, the organic material gets decomposed to nearly 100%, but the inorganic components remain as ashes.

Biomass ashes contain valuable plant nutrients, especially phosphorus, potassium, calcium and magnesium. As long as heavy metal concentrations are below certain limit values, the best recycling method for these ashes is to use them as soil enhancers on the ground where the biomass was grown,.

For this investigation, different fly ash-fractions from various biomass incineration plants were collected. The ash-fractions were analysed by REM-EDX and XRD. After a microwave digestion the concentrations of K^+, Ca^{2+}, Mg^{2+} and PO_4^{3-} of the ash-fractions were determined by IC. The mass balance for each nutrient was developed using the results of the analyses and the percentage of each ash-fraction on the total amount of ash.

P 117

GEOGENIC SOIL CONTAMINATION BY CHROMIUM AND NICKEL IN EASTERN SLOVAKIAN FLYSH BELT – SOME ENVIRONMENTAL IMPLICATIONS

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The main task of this report is to suggest the presence of diffuse geogenic soil contamination by chromium and nickel, eventually also by arsenic, molybdenum and vanadium in some regions of Eastern Slovakia as well as to the necessity of its implications to environmental study of Flysch.

On some sedimentary lithosequences of Eastern Slovakian Flysh Belt (Paleogene) soils characterized by high content of iron, magnesium, chromium, nickel (Co, V), and low calcium level are present. Chromium and nickel content ranges from 150 - 807 mg.kg^{-1} and 45 - 617 mg.kg^{-1} respectively. Such soils are usually developed on serpentinic rocks. The presence of „serpentine like soils" points to the fact that sedimentary flysh deposits from which soils weathered, were derived from ultrabasic (serpentinic) rocks. The new analytical plant data obtained the fact that geogenic chromium and nickel are at least partially available to the plants. This is reflecting in anomalous content of these elements in foliage and needles of some tree species and in dandelion leveas from contaminated soils.

The results showed that mainly geological factors have an influence on nickel and chromium high contents in soil and by far not come from atmospheric contamination as a saying goes. The plants and mosses are mirrors this geogenic contamination, which cover not only the flysch zone but also adjacent territory of the East Slovakian Lowland and Tisa Lowland in Hungary. These results indicate that these elements have been in the mobile form partly and have transported by rivers as suspension or soluble and have ingested by biota.

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P 118

DIAGENETIC PRODUCTS OF β -CAROTANE IN SEDIMENTS FROM LOPARE BASIN (BOSNIA AND HERZEGOVINA)

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Carotenoid compounds are widely distributed in nature because they are biosynthesized by almost all photosynthetic organisms[1,2]. One of the first carotenoid biomarker to be identified in organic compounds of geosphere is β–carotene. Although highly sensitive to oxidation, the carotenoid structures may be preserved intact in recent or even in immature ancient sediments deposited under strictly anaerobic conditions[2]. Despite they being research in many studies β – carotane diagenetic transformation pathways and their related carotanoids have not been completely investigated.

Total of 46 samples of sedimentary rocks from Lopare basin (Bosnia and Herzegovina) were investigated in this study. This region was selected as an ideally suited model system of anoxic environment. β – carotane and its related carotenoids was analized from its hydrocarbons fraction by gas chromatography–mass spectroscopy (GC–MS) technique.

In most of investigated sedimentary rocks samples, was identified β – carotane in relativy high amounts, and many its diagenetic derivates. These compounds were formed by reduction of the double bonds of β-carotene (i) cyclisation and aromatisation of the polyene isoprenoid chain, (ii) expulsion of toluene and m-xylene from the polyene isoprenoid chain, and (iii) aromatisation of the l,l.S-trimethylcyclohex-5-enyl moieties resulting in l,2-dimethylbenzene end groups.

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P 119

NI AND CO IMMOBILIZATION IN AQUEOUS SOLUTION THROUGH SYNTHETIC HIDROXYAPATITE

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Heavy metals have tendency to accumulate in food-chain causing serious maladies even at low level. Allergy to nickel is a phenomenon which has assumed growing importance in recent years, therefore, Ni-containing alloys should be avoided. This makes indispensable the development of technologies in reducing the "bioavailability" of these elements in the environment.

Many technologies are well known for the remediation of heavy metal contamination which are expensive; on the contrary the in-situ immobilization seems a better way. Many studies indicate phosphates reduce the solubility of heavy metals, in particular hydroxyapatite reacts with heavy metals such as Pb, Cu and Cd precipitating a heavy metal-Ca-phosphate which has low solubility and is more stable under ambient environmental conditions than the corresponding oxide, hydroxide, carbonate and sulphate phases.

Nickel and Cobalt batch tests were carried out using synthetic hydroxyapatite (HA) in the supergenic environment. The first step is based on the interaction of Ni and Co vs. HA (0.2 g), heavy metal concentration is: 100; 500 and 1000 mg/L; interaction time is: 2h, 4h, 24h, 48h, 1 week, 2 weeks and 3 weeks. All the solution have been analyzed at ICP-AES.

From ICP-AES results it is inferred that HA is a good amendment for the immobilization of Ni and Co, both are well immobilized even though HA concentration is the same for the three metal concentrations.

P 120

THE ROLE OF GYPSUM KARST IN CONTAMINANT TRANSPORT FROM AGH DARREH TAILING DAM IN IRAN

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The Agh Darreh tailings dam located in 23 km north of Takab in West Azarbayjan province in northwest Iran.This tailings dam is used for disposal of mine tailings. Gypsiferous portion of Qom formation has conduit karst characteristics and present in some portions of reservoir and foundation of tailings dam. The role of gypsiferous portion of Qom formation on cyanide contaminat transport from tailings dam is discussed using the environmental monitoring data, hydrogeological and hydrogeochemical measurements and geophysical investigations. Study area is tectonically active and karstic solutional springs and conduits has aligned along the structural fractures in Qom formation. This conduits has a controlling role on groundwater flow direction and provide a hydraulic connection between southwest area of tailing dam reservoir and karstic springs at downward of the dam.

P 121

TOXIC METALS LEACHING FROM COLUMNS OF MINE TAILINGS AMENDED WITH COMPOST

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Mobilization of toxic metals should be a primary concern in the implementation of mine tailings reclamation with compost or other organic amendments. In fact, dissolved organic carbon (DOC) is a key component involved in metals solubilisation and mobility.

In this study we investigated the effect of compost addition to a mine tailing from washing deposits of a sphalerite (ZnS) and galena (PbS) dismissed mine site in repacked columns. The native mine tailings were collected from the Raibl mine (Cave del Predil, Italy) and contained 373 µg As g^{-1}, 1935 µg Pb g^{-1}, 521 µg g^{-1} Tl and 7180 µg Zn g^{-1} . They were compared with a single profile of compost amended tailings and with a two layer profile: the 10 cm top layer made by compost amended tailings and the 10 cm bottom layer made of native tailings. Columns were irrigated with deionized water simulating average local precipitation events for 100 days and leachates collected by gravity. Leacheates were analyzed for pH, for As, Tl, Pb and Zn by ICP-OES and for DOC by dry oxidation (Shimadzu TOC). Microbial respiration in compost amended tailing was measured in closed jars by CO_2 absorption to 0.5 M NaOH solution. Monitored trace elements showed different leaching patterns: significantly more Zn and Tl leached from the composite profile (amended tailings + native tailings) while Pb and As showed a much larger mobility in the amended tailings (single profile). The lower horizon of native tailings was able to drastically reduce metals leaching from the top horizon. This different behaviour is coherent with the fundamental role of DOC in the mobilization of Pb and As and with its much lower influence on that Zn and Tl. Mobilization of Zn and Tl was governed by S oxidation and to a lesser extent by carbonates.

These results highlight the need of an appropriate assessment of metals mobilization risks before performing any amendment application to highly contaminated tailings.

P 122

ASSESSING AND MAPPING INCREASED DROUGHT RISKS IN AGRICULTURAL SYSTEMS AS A RESULT OF CLIMATE CHANGE

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Drought is a recurrent meteorological phenomenon with a considerable ecological, economic and social impact on the environment. During recent years there is a rising concern about the increasing frequency of draughts, especially because of the possible correlations between droughts and climate change. In the past decade there were four severe agricultural droughts in Slovenia, resulting in the damage of most of non-irrigated crops and considerable economic loss. To minimize the impact of drought occurrences it is necessary to conduct drought vulnerability and risk assessment, which could help developing mitigation and adaptation strategies.

As a pilot case we started drought vulnerability assessment for Goriška region in 2008 with the objective to identify principal impacts of drought and to develop a methodology for drought vulnerability assessment in agriculture. In 2009, we extended the vulnerability assessment area to the entire area of Slovenia. This contribution will in addition present drought risk assessment, which is another key point of the drought analysis. In our case we applied quantitative risk assessment as a function of hazard and vulnerability, $R = pE\ pL$, where risk (R) is taken as a product of the probability for a drought (pE) and the probability of a specific consequence of that event, e.g. economic loss (pL). The results of the risk calculation will be presented in a graphical form using GIS tools. Risk maps will show areas in Slovenia where droughts pose a major threat to the agricultural systems and will improve drought management with regard to facilitating appropriate mitigation and response actions. It is expected that the developed methodology could be applied to the entire region of South-Eastern Europe.

P 123

EVALUATION OF THE ADSORPTION CAPACITY OF THE HEAVY METALS Cd AND Pb BY SYNTHESIZED Fe OXIDES AND HYDROTALCITE

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Heavy metals constitute only a minor part of the Earth's crust composition, however the pollution of soils and waters caused by these elements is a continuous growing problem that can affect everyone. Among the main pollutant sources, the agricultural practices, the combustion of coal and oil and the incineration of urban and industrial residues are of major concern. Additionally, wastewater from industrial discharge can become a major environmental issue when it contains high levels of heavy metals. Among the heavy metals, cadmium and lead are of increasing concern because of their elevated toxicity for humans and animals. To decrease the environmental hazardous imposed by these two metals, they have to be removed or kept to low levels in agricultural soils and potable waters. The removal of these cations is difficult and one of the alternatives is the adsorption by different materials, especially natural or synthetic minerals, specially the Fe oxides. In this work, adsorption experiments with cadmium and lead were conducted, using as adsorbing materials synthesized Fe oxides - ferrihydrite, goethite and hematite - and hydrotalcite, a Al and Mg layered double hydroxide. The synthetic minerals were obtained and analyzed by X-Ray Diffraction. The X-ray diffractograms showed the absence of other mineral phases, demonstrating the efficiency of the methods used in the synthesis of all minerals. The adsorption experiment was carried out using 20 mL of solutions of increasing concentrations of the heavy metals under study and 0.100 g of the synthesized minerals, in centrifuge tubes. The tubes were shaken at 30 rpm in vertical shaker for 12 hours. After this equilibrium time the suspensions were centrifuged at 2500 rpm for 10 minutes. Then the supernatant was filtered, the filtrate collected and stored in plastic flasks at low temperature. The determination of Cd^{2+} and Pb^{2+} was made by atomic absorption espectrophotometry (AAS) and the data were adjusted to Langmuir and Freundlich isotherms with the main objective of comparing the maximum adsorption capacity (MAC) for cadmium and lead for the different materials. The results for Cd showed that the values of MAC were larger for the hydrotalcite, that stood out adsorbing higher amounts as compared to the other synthesized minerals. For the lead adsorption the same trend was observed, even in a larger scale, i.e., hydrotalcite adsorbed the highest amount of Pb followed more closely by the ferrihydrite and, in level below, goethite and hematite. For all the minerals, hematite presented the smallest values of adsorption for Cd and Pb. The Fe oxides, in general, are well known for their ability to adsorb heavy metals. Interestingly, hydrotalcite also showed to be a very good adsorbent although it is a layered double hydroxide (LDH), or the so-called anionic clay, which constitute a class of lamellar ionic compounds containing a positively charged layer.

P 124

ENVIRONMENTAL BIOGEOCHEMISTRY OF EUTROPHIC SEDIMENT REMEDIATED WITH CALCIUM NITRATE AND PHOSLOCK™ IN LABORATORY MICROCOSMS

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The Ibirité reservoir (SE Brazil) is a eutrophic water body because of high load of raw urban sewage that is discharged into it via the Ibirité creek. This contribution corresponds to about 88% of the ammonium and 77% of the orthophosphate relative the total external load. Internal loadings are, respectively, about 2.5 and 1% of the external loadings of those nutrients. Although the reservoir receives treated effluents from an oil refinery (REGAP-Petrobras) no severe contamination with hydrocarbons (PAH's and *n*-alkanes) was detected, except in a few samples, but absolute concentrations are lower than those of contaminated sites around the world. Foreseeing that external sources would be abated in the future microcosm experiments were run to understand how the important internal load of P may be controlled through the addition of calcium nitrate and Phoslock^{TM}. The added nitrate caused strong sediment oxidation. The redox potential increased from values very negative values like -197 mV to high values as +83 mV. The acid volatile sulfide decreased by 99% and dissolved organic carbon increased by 55% respect to control. The nitrate concentrations of pore water were very high at t=0, but underwent a 98% reduction at t=145 days; the orthophosphate concentration reduced by 81±10% in the water column. The addition of Phoslock^{TM} yielded a 97% reduction of turbidity in water column and an 82±3% reduction in orthophosphate concentration in the water at t=41 d of incubation, while no changes in pH and redox potential were detected. The potential application of both technologies and the major biogeochemical processes associated to the sediment chemistry will be discussed.

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P 125

TEBUCONAZOLE SORPTION ON SELECTED SOIL MINERALS

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The aim of the presented study is to investigate tebuconazole sorption on four selected common soil minerals (birnessite, calcite, ferrihydrite and goethite) at different pH values (4, 5.5 and 7). Tebuconazole was used in commercial form Horizon 250 EW and as analytical grade tebuconazole with a purity of 99.9 ± 0.1% (m/m). The experiment was performed using the batch equilibrium approach. In the experiment with the commercially available tebuconazole, a significant pH-dependent sorption onto ferrihydrite, goethite and birnessite was observed (decreasing sorption with increasing pH). The highest sorption was found for ferrihydrite (0.137 mmol g^{-1}) due to its high specific surface area, followed by birnessite (0.027 mmol g^{-1}) and goethite (0.012 mmol g^{-1}). Furthermore, the sorption onto goethite occurred only at pH 4. No detectable sorption was found for calcite. It is probably caused by its small specific surface area and the predominant occurrence of neutral sites at pH 7. The sorption of analytical grade tebuconazole on ferrihydrite, goethite and birnessite was significantly lower compared to the commercial product. The sorption was the highest for ferrihydrite 0.019 (mmol g^{-1}) and almost negligible for goethite and birnessite without any pH dependence. No sorption was observed for calcite. The differences in sorption of the commercially available and analytical grade tebuconazole can be attributed to the additives (e.g., N, N-dimethyldecanamide) present in the commercial product that support fungicide effectiveness and simplify its application. Tebuconazole has a high affinity to organic compounds and the additives are mainly of organic origin. It is needed to point out that these additives in pesticide formulations can significantly influence the sorption mechanisms, behavior in soils and increase their sorption ability. This work proved the importance of soil mineralogy and composition of the commercially available pesticides on the behavior and degradability of tebuconazole in soils.

P 126

BUILDING A HUMIC-METAL BINDING CONSTANTS DATABASE

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The fraction of natural organic matter more refractory to degradation, often known as fulvic and humic compounds, plays a decisive role in trace element behaviour in environmental systems. For this reason, a lot of research has been devoted to its characterization as well as to the determination of binding constants to quantify its interaction with trace elements. However, in spite of the effort deployed, the difficulties encountered when trying to compare complexation constants reported in the literature or to find constant values for less studied elements remain well-known problems. The reason is that our ability to measure and interpret the complexation equilibria of humic substances is severely constrained by their ill-defined nature that hinder the application of the experimental and interpretation methods usually applied in the field of stability constant determination. Moreover, no systematic compilation of published data exists. For this reason, we have undertaken the gathering of all data published on the complexation of trace elements with humic substances over the past 50 years. Our ultimate goal is the critical analysis and the interpretation of all existing data with the objective of providing a robust framework for further research as well as a useful tool for practical applications. The project started in January 2009 with the collection of publications in electronic form for subsequent information extraction by members of the project. Currently this collection comprises some 900 articles. So far, a first spin-off of the project has been the elaboration of recommendations concerning quality assurance issues.

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O 11

BIOCONCENTRATION AND IMMUNOTOXICITY IN SEA BASS (*DICENTRARCHUS LABRAX* L.) AFTER A CHRONIC EXPOSURE TO HYDROCARBONS

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After the development of an experimental system to expose adult fish to low and stable concentration of pollutant over a prolonged period, the *in vivo* effects of Polycyclic Aromatic Hydrocarbons (PAHs) were evaluated on sea bass, *Dicentrarchus labrax*. A total of 90 fish were acclimated for 15 days, 45 fish were exposed to water soluble fraction (WSF) of reference crude oil, similar to a complex pollution by hydrocarbons chronically observed *in situ* in the Brittany rivers, while 45 others control fish sustained the same experimental conditions in clean seawater. After 21 days exposure, 30 contaminated and control fish were sampled, then others were collected after 15 days recovery period in clean sea water. PAHs concentration in WSF was monitored using stir bar sorptive extraction (SBSE) and an analysis with gas chromatography coupled with a mass spectrometer (GC/MS). PAHs concentrations in crude oil and muscles were measured by GC/MS analysis too. White blood cells counts and differential leucocyte counts were determined by classical hematology methods. Mortality and phagocytosis activity of leucocytes were analyzed by flow cytometry.

After 21 days of contamination (78 ± 19 ng.L^{-1}), a leucopenia due to a lymphopenia was noted and phagocytosis activity was decreased suggesting an attack of both innate and specific immune systems. Effects seem reversible because the decontaminated fish presented similar parameters to control fish. The bioconcentration of PAHs in flesh of contaminated fish was in process of analysis.

The effects of chronic exposure to PAHs were evaluated on the health status of sea bass and will be put in prospect with environmental quality thresholds and a potential risk to human consumers.

Key words: PAH, SBSE, GC/M, bioconcentration, leucocytes, Dicentrarchus labrax

O 12

STUDYING THE EFFECTS OF CHRONIC FLUORIDE EXPOSITION TO THE ZEBRAFISH (DANIO RERIO) CARDIAC FUNCTIONS USING ELECTROCARDYOGRAPHY

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Fluoride is known as an enzyme inhibitor of which genotoxic and teratogenic impacts have been well studied in the last few decades. They started to study its toxic effects on the cardiovascular system in the last decade. It was found that long-term fluoride exposure causes changes in the ECG, prolongation of P-Q and Q-T intervals was detected. A few years ago ECG measurement and analysis became possible in the well-known model organism, the zebrafish (*Danio rerio*) too. Our aim was to study the effects of chronic fluoride exposure on the zebrafish ECG and to find out if these effects were similar to those in mammalian models.

Zebrafish were treated with 50 ppm, 100 ppm and 200 ppm NaF. Solutions were changed twice a week during the 3 months study. 9-9 zebrafish in 3 paralell tanks were exposed to each concentration. ECG was measured monthly according to the EXPERIMETRIA Ltd. Zebrafish ECG measurement system and ADVANCE HAEMOSYS haemodynamic software for data acquisition and analysis.

Following the evaluation of data of the first two months, significant Q-T prolongations ($p<0,05$) were found between the 1st month control (181,17±19,23 ms) and 1st month 200 ppm (205,20±45,85 ms), 2nd month 100 ppm (207,74±42,23 ms), 200 ppm groups (202,63±27,68 ms).

O 13

BIOCHEMICAL AND FUNCTIONAL RESPONSES OF ARABIDOPSIS THALIANA SEEDLINGS EXPOSED TO CADMIUM, COPPER AND ZINC

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Arabidopsis thaliana L. is considered a model plant for many studies as its genomic sequence was completely identified and its mechanisms in genomic, transcriptomic and proteomic regulation are often similar to other plant species. Seedlings of *A. thaliana* were exposed to cadmium, copper and zinc at two different concentrations, chosen on the basis of the levels of heavy metals realistically found in contaminated soils. After 7 and 12 days of exposure to metals, applied separately or in different combinations, plant shoots and roots were sampled and analyzed. Microscopic analysis revealed that root morphology was strongly affected by metal exposure, both alone or in combination, if compared to control plants. The different growth patterns observed for shoots and roots were likely due to a different production and proportion of auxins and cytokinins, the two most important classes of phyto-hormones affecting cell expansion and proliferation, respectively. The levels of trans-zeatin, dehydrozeatin and indolacetic acid, as well as the ratio auxins/cytokinins, were different among the plants treated with the metals above, and the perturbation given by cadmium appeared to be significant. Preliminary data on phytochelatins, thiol peptide compounds mainly produced by plants and algae, indicate that they can play an important role in metal homeostasis and detoxification of *A. thaliana*.

P 127

A STUDY ON ECOTOXICITY OF ARSENIC AND THE SEARCH FOR POTENTIAL AMELIORATIVE AGENTS

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Arsenic (As) is a toxic element widely distributed in the environment and humans are exposed to it from soil, water, air and food. In natural systems As occurs mainly as As(V), As(III) and their methylated derivatives (MMA, DMA, TMAO). Generally, inorganic As presents a higher acute toxicity, and As(III) species exhibit more toxicity than As(V) species. Therefore, a comprehensive knowledge of As toxicity and the search for potential ameliorative agents is needed. In this work, the acute toxicity of As(V), As(III) and DMA (dimethylarsinic acid) was investigated using the Microtox® bioassay based on change in light emission by the luminescent bacteria *Vibrio fischeri*. The effect of several potential inhibitors of As toxicity was evaluated establishing dose-response curves for these As compounds both in absence and in presence of phosphate (1:1, 1:10 and 1:100 As:P molar ratios), 0.1M ascorbic acid, and for As(III), also 0.1M citrate or 0.1M cysteine. The results obtained showed the following sequence of acute toxicity: As(III)>As(V)>>DMA. The acute toxicity of As(V) was almost suppressed in the presence of phosphate within all the dose range studied (0–225 mg/l), and the toxic effect did not reached the EC20 value (As concentration at which a 20% loss of light emission is significantly observed and which represent a measurable threshold of toxicity), probably due to the saturation of phosphate–As(V) transporters. However, phosphate reduced only slightly the As(III) toxicity, even at 1:100 As:P molar ratios. The toxicity of DMA was also diminished in the presence of phosphate. The addition of 0.1M ascorbic acid or 0.1M citrate did not diminish the acute toxicity of neither As(V) nor As(III). However, in the presence of 0.1M cysteine, the toxicity of As(III) was inhibited by the complexation of As(III) species in solution, and the EC50 was not reached even for an initial As(III) concentration of 450 mg/l.

P 128

EFFECTS OF HEAVY METALS (Cu, Zn) TO THE SAPROTROPHIC FUNGI

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The growth of twenty litter-decomposing saprotrophic fungi and their production of extracellular enzymes, laccases and peroxidases, were tested with different Cu^{2+} (0, 100, 200, 400 mg dm^{-3}) and Zn^{2+} (0, 100, 200, 400 mg dm^{-3}) concentrations. Bioluminescent *Saccharomyces cerevisiae* yeast and *Escherichia coli* bacteria were used to test bioavailability and toxicity of Cu^{2+} and Zn^{2+}. The best growing ascomycete fungus was *Coniothyrium sp*. both in the Cu and Zn containing ABTS plates. The most sensitive ascomycete was *Sordaria sp*. in the Zn and Cu containing ABTS plates. Cu (200 mg dm^{-3}) inhibited (22-100 %) the growth of all eight basidiomycete fungi in the ABTS plates compared to the control plates. The growth of *Agrocybe praecox*, *Gymnopus peronatus, Gymnopilus sapineus, Mycena galecurilata, Stropharia aeruginosa* and *Stropharia rugosoannulata* was higher (2 – 272 %) with the content of 100 mg Zn dm^{-3} compared to the control plates. Zn was 2-20 times less toxic than Cu to *S. cerevisiae* yeast. Tested ascomycete, zygomycete and basidiomycete fungi showed that Cu was more toxic than Zn.

P 129

PHOTOLYTIC/PHOTOCATALYTIC OXIDATION OF BISPHENOL A: ESTROGENICITY AND TOXICITY

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Bisphenol is a generic name of a group of diphenylalkanes commonly used in the production of plastics. Incomplete polymerization or depolymerization of plastics may result in the release of bisphenol A (BPA) into the environment. BPA is considered as toxic to aquatic organisms and estrogenic active, which has been demonstrated by several studies. Therefore, BPA should be removed from waters before they are discharged in the environment. Photolytic/photocatalytic oxidation is one of advanced oxidation processes, mainly used for the removal of organic pollutants from waters.

The aim of our study was to evaluate the efficiency of photolytic/photocatalytic oxidation of BPA in regard to toxicity and estrogenicity. For those purposes, acute toxicity tests with water fleas *Daphnia magna* and zebrafish embryos *Danio rerio* as well as YES bioassay were performed. HPLC and TOC methods were used for the quantification of BPA and TOC removal in aqueous solutions during oxidation processes. Photolytic/photocatalytic oxidation of an aqueous solution of BPA (20 mg/l) was performed by using a commercially available TiO_2 catalyst Degussa P-25 under UV and visible light for 6 hours. After the end of experiments treated solutions were examined for toxicity and estrogenicity. The results show that despite of high conversion of BPA (up to 84 %) during the photolytic oxidation, treated samples were still toxic to *D. magna* (up to 30 % of immobility) and zebrafish embryos (up to 80 % of lethal effects), but not estrogenic active. In the presence of TiO_2 catalyst, complete conversion of BPA was obtained. However, due to the presence of by-products, all exposed water fleas were immobile and high levels of lethal effects on zebrafish embryos were still observed. Also, estrogenic activity of end-product solutions was still detectable when samples treated with catalyst. To conclude, despite of high BPA conversions obtained during the photolytic/photocatalytic oxidation, remarkable toxicity and estrogenicity were measured in the liquid phase after the treatment.

P130

FATE AND EFFECTS OF CYTOSTATIC PHARMACEUTICALS IN THE ENVIRONMENT AND IDENTIFICATION OF BIOMARKERS FOR AN IMPROVED RISK ASSESSMENT ON ENVIRONMENTAL EXPOSURE (CytoThreat)

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The FP7 project CytoThreat addresses the needs of the European society for assessing the risks associated with the release of pharmaceuticals into environment. It focuses on cytostatics that are due to their genotoxic mechanism of action, highly hazardous compounds, but the data that would allow for adequate risk assessment is insufficient. The research will address occurrence, distribution and fate of selected cytostatics in aquatic matrices, and their chronic toxicity and genotoxicity to aquatic organisms. A combination of state-of-the art analytical chemistry, *in vivo* and *in vitro* systems, cell biology, and "OMICS" technologies will be applied. The *in vivo* studies with zebrafish models in combination with transcripotmic and bioinformatics are aimed to identify linkages between the genomic profiles, exposure conditions and adverse outcomes, to identify molecular biomarkers of exposure and effects of specific groups of cytostatics that will serve as diagnostic markers for these types of pharmaceutical exposure, and to predict synergistic effects at combined exposures. Comparative *in vitro* genotoxicity and transcriptomic studies with zebrafish and human cells are aimed to provide basis for more reliable extrapolation of toxicological data from zebrafish models to humans. CytoThreat is expected to generate new knowledge on potential environmental and health risk of cytostatics in the environment, providing objective arguments for recommendations and regulations.

P 131

EVALUATION OF IODOSULFURON TOXICITY TO AQUATIC ORGANISMS AFTER PHOTOCATALYTIC OXIDATION

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Advanced oxidation processes based on chemical oxidation represent a good choice for removal of biologically recalcitrant pollutants such as pesticides, pharmaceuticals and endocrine disrupting compounds present in wastewaters. Experiences have shown that during the oxidative treatment and transformation towards CO_2, intermediates and end products could occur exhibiting similar or even higher toxicity to aquatic organisms than parent chemicals. For this reason, treated solutions should be checked not only for their physico-chemical properties, but also for possible adverse biological effects before discharging them to the aquatic environment. The main purpose of this study was to assess the effectiveness of heterogeneous photocatalytic oxidation of herbicide iodosulfuron in regard to its potential toxicity to aquatic organisms. Photocatalytic activity of various TiO_2 based catalysts was examined for the degradation of iodosulfuron-methyl-sodium dissolved in either ultrapure or tap water under both UV- and visible-light irradiation. Toxicity of iodosulfuron and photocatalitically treated solutions was studied by means of determination of bacterial luminescence *Vibrio fischeri*, immobility of water fleas *Daphnia magna* and growth of green algae *Desmodesmus subspicatus*. The obtained results demonstrate that the toxicity of iodosulfuron and treated solutions is species - specific. In many cases the toxicity of treated iodosulfuron solutions was higher than the toxicity of initial solutions, indicating that higher toxicity of the former is related to different partially oxidized products. We conclude that high removal efficiency of pollutants from aqueous samples by means of photocatalytic oxidation could not be always a reliable indicator of decreased toxicity potential to aquatic organisms.

P 132

STRUCTURE - ECOTOXICITY RELATIONSHIPS OF CHEMICAL POLLUTANTS SEDIMENT DATA

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Effective sediment risk assessment requires finding a relationship between sediment chemistry and toxicity endpoints. In the present state of art one common approach is linking chemical concentrations to toxicity data. This is a typical univariate strategy which produces traditional Sediment Quality Guidelines (SQG). The problems of the SQG estimation procedure are connected with the bioavailability of sediment contaminants and the effects of covarying chemicals and chemical mixtures. Chemometric and other methods of intelligent data analysis could be a suitable tool to achieve this goal.

The aim of the present study is to get a deeper insight into the relationships between the sediment toxicity and polluting chemicals (PCB congeners, PAH and organochlorine pesticides) in the Turawa lake sediment dataset previously analysed by SOM classification [1]. In particular, QSAR and chemometric approaches are used to clarify the importance of the three different groups of chemicals. For each category the "aquatic" toxicological profile is predicted using the ECOSAR models of ECOWIN program for acute and chronic toxicity. Within the obtained new SOM patterns the chemical categories as formed by the QSAR analysis are identified and their influence on the toxicity of the pattern is discussed.

The proposed multistep approach is an example for intelligent data treatment of complex sediment data, starting with more general SOM based classification approach to more detailed QSAR approach. The general purpose is to help identification of major sources of threats caused by mixtures of numerous pollutants present in the sediments.

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P 133

INTAKE OF FLUORIDE WITH TEA AND DIET

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Fluorine is considered as a beneficial nutrient and is presented it trace amounts in human body. The adequate intake (AI) of fluoride from all sources is set at 0.05 mg/day/kg body weight for all ages above six months, because it confers a high level of protection against dental caries and is not associated with any known unwanted health effects[1].

Due to the natural sources of fluorine, its levels in soil can be relatively high. Due to the use of fertilizers, the discharge of industrial waste into streams and deposition of airborne fluorides these levels can be even increased. This can result in increased levels of fluorine in the tea plant, for which it is known that it selectively absorbs fluoride from the soil and accumulates it in higher levels in tea leaves, from where it is released during the tea preparation[2]. The intake of tea can significantly contribute to fluoride exposure, therefore fluoride levels in some of the best sold black, green and oolong teas, available in Slovenian markets were determined. The results showed in average 2-fold difference in fluoride content between teas prepared in tea bags and stick-shaped teas. The type of tea plays an important role in releasing of fluorine; the highest % of total fluorine is released from black tea (67–90 %), lower from green tea (55–84 %) and the lowest from oolong tea (21–68 %). Considering an average consumption of five cups per day (1000 ml) 9–101 % of AI (for an adult person with 70 kg) is reached. If taking into account also data of fluoride content in 2500 kcal diet from earlier investigations[3], the estimated % of AI ranges between 30–173 %, therefore the consumption of high quality tea low on fluoride is recommended.

Reference:

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P 134

EFFECT OF 6-CHLORONICOTINIC ACID ON TERRESTRIAL ISOPOD *Porcellio scaber* (ISOPODA, CRUSTACEA)

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Following the legislation for the food safety in vegetables, fruits and for the water safety, only parent insecticides are monitored, but there is no control of the presence of transformation products (TPs) which can be formed after the application of insecticides under various environmental conditions. Lately, neonicotinoid insecticides are gaining in application and therefore not so many data is known about the toxicity of their common transformation product; 6-chloronicotinic acid. In our study, we tried to assess the physiological and biochemical parameters of non-target organisms terrestrial isopods as a sensitive indicators of a stress due to exposure of different xenobiotics. The animals, both males and females, were exposed for 14 days to dry hazelnut tree leaves dosed with different concentrations of 6CNA, expressed as μg of 6CNA per g of dry food in concentrations 1, 10, 50 and 100 μg/g. Humidity was maintained with regular spraying of water on the inside lids of Petri dish. The measured endpoints were survival, weight change, faecal pellets production, feeding parameter expressed as consumption rate as well as assimilation efficiency. After two weeks of exposure, the biomarker of oxidative stress, malonaldehyde (MDA), was determined with thiobutiric acid (TBA) procedure as it was described in the literature and expressed as rate of lipid peroxidation (LPO) per each animal. The results of experiments showed significant difference at higher concentrations in rate of LPO between exposed and non exposed groups, while on the other hand physiological parameters were not significantly affected.

P 135

ECOTOXICITY OF PROCESS METALLIC MICRO AND NANO PM

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Micronic and sub-micronic particulate matters (PM) are emitted in the environment by industrial activities. Carried from the air to the soils as fine particles, metals could be released easily in the soil solution and became toxic for plant and microorganisms.

This study focuses on a real case of soil contamination by investigating environmental effects of industrial particles from a lead-recycling facility after atmospheric fallouts on soils (Uzu *et al.*, 2009). The impact of PM on lettuce (*Lactuca sativa*) and bacteria was investigated by standardized tests: germination test, growth assays and microtox analysis. The effect of soil properties on environmental effects was studied by using 3 types of PM-amended soils with different characteristics. Ageing effect was investigated too with spiked soils with primary particles; 3 months aged spiked soils and a historically polluted soil.

The results showed that metallic particles have a toxic effect on seedling growth (roots and shoots were shorter and thinner) and on *Vibrio fisheri* suggested by bioluminescence inhibition (EC50 = 68.7 mg.L^{-1} after 5 min in Microtox test). However, lettuce germination was not affected by metal soil pollution, suggesting that this indicator was not sensitive enough. Soil properties modify the amplitude of toxic effects. Toxicity is also more acute after 3 months ageing period of spiked soils. However, the long-term exposed soil (for thirty years) was less toxic than the spiked soils. This could be explained by stabilisation processes accelerated by climate effect, grass-cover and root uptake.

Reference :

Uzu et al., 2009. Environmental Pollution 157, 1178-1185.

Thanks to ADEME and CNRS for their financial support in this study.

P 136

DETERMINATION OF CELL-SIZE VARIATION UNDER THE ENVIRONMENTAL STRESS BY FLUORESCENCE CORRELATION SPECTROSCOPY WITHOUT IMAGE MAGNIFICATION

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Ever since Gösch et al.(2000) applied fluorescence correlation spectroscopy (FCS) to a microchannel flow system, this technique has attracted attention in various fields.

In most of the works related to FCS, a con-focal optical configuration has been adopted because the observation volume should be less than a few fL (10^{-15} L) for observing molecules, where the size determination of the fluorescent particles is based on the Brownian rocomotion. On the other hand, we have previously shown that a regular optical configuration in fluorescence spectrometry without the image magnification tools are adequate to determine the size less than 0.1 µm. We have proved the size determination of algae which we made move in the present system by simply stirring the plaktonic suspension (sample solution). In the present paper, we would like to prove the feasibility of our system to observe the variation of cell-size under the environmental stresses.

A 20 mW Ar^+ laser (488 nm) was used as the light source of which output diameter was controlled by a 50 µm-pin hole. The fluorescent signal through a pinhole (10µm) was detected by a photon counter with 500-nm low-cut filter. E. coli DH5α (100 µL) was contacted with a GFP plasmid. This E. coli was incubated in the LB medium with the different concentrations of MitomycinC (MMC). When the concentration of MMC is increased from 0 to 0.4 fg/L in the incubation media, the diffusion time increases 7-hold (0.2 to 1.4 ms), which means more than 10 times increase in the E. coli cell volume.

The present result shows that our system is simple but is convenient to observe the cell-size variation induced by the environmental stresses of chemical and physical factors.

P 137

GENE EXPRESSION ANALYSES OF PUTATIVE CHROMATE TRANSPORTERS AND STRESS RESPONSE FACTORS UNDER CHROMATE EXPOSURE CONDITION IN A CYANOBACTERIA

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Technologies of molecular biology have been applied for analyzing mechanisms of heavy metal toxicity and for bioremediation of their environmental contamination. For example, the screening of genetic markers under the heavy metal stress is essential for finding targets of gene manipulation. Hexavalent chromium is one of the toxic metal species for almost all organisms, due to the strong oxidative capacity. On the other hand, some bacteria have shown resistance to chromate ion by discharging it from cytoplasm to extracellular space. Some chromate transporters were found in *Pseudomonas aeruginosa* which had a capacity of chromate excretion (Cervantes et al. *J.Bacteriol.*, 1990, **172**, 287-91). These transporters were named as ChrA proteins and were could by *chrA* genes. A fresh water cyanobacterium *Synechocystis* sp. PCC6803, possesses two open reading frames (ORFs; *slr1457* and *slr5038*) which are homologous to *chrA* genes. In this study, the expression levels of the ORFs were investigated in *Synechocystis* sp. PCC6803 under the chromate exposing condition. We also searched the specific genes responding to chromate stress and identified them. Total RNA was extracted from the cells of logarithmic growing phase after 30 min exposure to the different chromate concentrations. And then, Gene expression levels were examined by quantitative real-time PCR. The gene expression patterns were analyzed using the differential display method described in Bhaya *et al.* (*J. Bacteriol.*, 2000, 182, 5692–9). Four-induced and four-reduced transcripts fragments were found out in the cells exposed to chromate. In this presentation, it will be reported that the results of genes expression levels in *chrA* homologs and the genes responded for the chromate exposure in *Synechocystis* sp. PCC6803.

P 138a

EFFECTS OF IMIDACLOPRID ON F11 CELLULAR MODEL

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Neuronal excitability is a parameter related to neuron potential to generate signals of novel stimuli. Long-term exposure to environmental chemicals is believed to be a predisposing factor for further establishment of altered neuronal functions that often can be translated into chronic neuronal diseases. The molecular irreversible events leading chemical exposure to become risk factors for neuronal sensitisation, however are not yet completely understood. Imidacloprid is an insecticide of the neo-nicotinoid family, that operate preferentially via nicotinic neuronal receptors expressed on both invertebrates and mammalian cells. In this work, we explored the effects of imidacloprid (0.1 - 4 mM) on F11 neuronal cell cultures. At first we performed immunofluorescence to characterise expression of nicotinic ACh receptors in F11 cells, in control and after imidacloprid treatment. Cells were first than analysed for survival, total protein content and reactivity of enzymes involved in stress reactions. At low doses imidacloprid induced, as nicotine, higher extention of neurite processes and consequent stress-induced tubulin acetylation. Finally, imidacloprid exposure activates MAP kinase p38 and increase stability of Nrf2. Imidacloprid induced also reorganisation of a3 –containing nicotinic ACh receptors, an effect partly prevented by the antagonist mecamylamine (1mM, 1h). These results contribute to new assessment of imidacloprid effects on mammalian tissue.

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P 138b

LIPID PEROXIDATION AFTER IMIDACLOPRID INCUBATION ON F11 CELLULAR MODEL

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Neuronal excitability is a parameter related to neuron potential to generate signals of novel stimuli. Long-term exposure to environmental chemicals is believed to be a predisposing factor for further establishment of altered neuronal functions that often can be translated into chronic neuronal diseases. The molecular irreversible events leading chemical exposure to become risk factors for neuronal sensitisation, however are not yet completely understood. Imidacloprid is an insecticide of the neo-nicotinoid family, that operate preferentially via nicotinic neuronal receptors expressed on both invertebrates and mammalian cells. In this work, we explored the effects of imidacloprid (0.1 - 4 mM) on F11 neuronal cell cultures. Cells were analysed for mitochondrial activity with MTT assay, in vivo mitochondrial staining and reactivity of lipid peroxidation enzymes involved in stress reactions. These results contribute to new assessment of imidacloprid effects on mammalian tissue.

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P 139

NEONICOTINOIDS - EVALUATION OF PHYSIOLOGICAL AND BIOCHEMICAL RESPONSES OF GAMMARUS FOSSARUM KOCH

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Imidacloprid is a nicotine-derived widely used insecticide of neonicotinoid chemical family, with a preferred insect neurotoxic action. Since a still limited number of studies referring to this compound and its persistence in the environment, it presents a potential important hazard for the contamination of soil and freshwater ecosystems with additive/cumulative effects on biota and human health. Therefore, we have chosen to explore baseline of imidacloprid biological effects on non-target aquatic bioindicator species such as Gammarus fossarum (Amphipoda, Crustacea). We tested the effect of different doses of imidacloprid on animal survival, behaviour, changes of total protein content and general biochemical biomarkers (e.g. enzymatic activities). Our data demonstrated an overall lower toxicity of imidacloprid after 24 h incubation, with no loss in live mass, nor significant changes in the mortality rate with respect to control. We found that low concentrations of imidacloprid (0.4 μM) resulted in increased lipid peroxidation levels, while no effects were observed on achetylcholinesterase and catalase activities. Interestingly, intermediate 0.6 and 0.8 μM concentration of imidacloprid resulted in a significant depression of acetylcholinesterase activity. Our results provide the basis for further development of new protocols useful for the risk assessment of chronic exposure of complex pesticides mixtures in the aquatic environment.

O 14

Rh-CeO$_2$ AS AN EFFICIENT AND STABLE CATALYST FOR METHANE REFORMING WITH CO$_2$

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Catalytic reforming of CH_4 with CO_2 enables simultaneous elimination of two green-house gasses: (i) CO_2, produced in enormous quantities when burning fossil fuels and (ii) CH_4, an abundant fossil fuel. The gas mixture of CH_4 and CO_2 (biogas) can be obtained independently from fossil fuels, namely by anaerobic degradation of organic wastes and household waste waters.[1] The examined reaction yields syngas with the H_2/CO ratio of unity, which is suitable for production of added value chemicals, such as methanol.[2]

2 % Rh-CeO$_2$ catalyst was synthesized using the hard template method[3] with subsequent impregnation of aqueous $Rh(NO_3)_3$ solution and calcination at 550° C. The prepared catalyst was characterized by N_2 adsorption/desorption, XRD and H_2-TPR/TPD methods.

Conversion of CH_4 and CO_2 increased with rising temperature during activity tests (Figure 1), which were performed in a tubular fixed-bed reactor and reached 87 and 93 % at 800° C, respectively, with the H_2/CO ratio being equal to 0,96. Besides H_2 and CO, H_2O was identified as the only side product, revealing the occurrence of reverse water-gas shift reaction. During the 21-h stability test carried out at 650° C, negligible catalyst deactivation was observed.

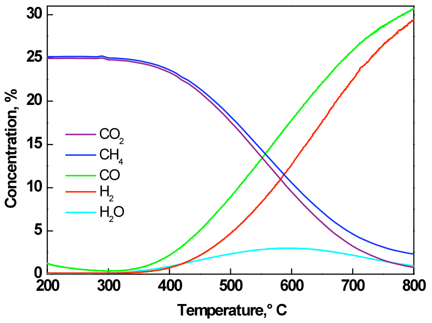

Figure 1. Performance of 2 % Rh-CeO$_2$ catalyst in methane dry reforming reaction.

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O 15

SIC-DOPED PPY-LIFEPO$_4$: NEW CATHODE MATERIAL FOR GREEN ENERGY BATTERIES

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SiC-doped PPy-LiFePO$_4$ cathode material was prepared by precipitation polymerization of pyrrole in presence of SiC. The average size of SiC particles was 50-60 nm. The surface morphology and thermal stability of SiC- doped PPy-LiFePO$_4$ composite materials were investigated by scanning electron microscopy (SEM) and pyrolysis capillary gas chromatography (Py-cGC). The electronic and ionic conductivities were determined using electrochemical impedance spectroscopy (EIS). Si-doping exerts a donor effect and hence increases ionic conductivity. SEM images showed that particles of SiC are distributed homogeneously between the PPy-LiFePO$_4$ particles. Pyrolysis capillary gas chromatography measurements at 500 °C showed minimal thermal decomposition of organic species contained in cathode material, compare to undoped samples. Our results proved that SiC-dopping was an effective way to increase ionic conductivity and thermal stability of SiC-PPy-LiFePO$_4$ cathode material used in Li-ion battery technology.

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O 16

PERTURBATIVE MODULATION OF THE VISIBLE LIGHT RESPONSE OF SILVER HALIDES FOR ENVIRONMENTAL APPLICATIONS: A FIRST PRINCIPLE STUDY

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Harvesting of solar energy for different photocatalytic applications have got wide spread interest for the last few decades. Several inorganic semiconductors can be used for the solar hydrogen production by photocatalytic water splitting; however, the efficiency of the overall reaction is still too low. Hence, the quest for a new semiconductor with the ideal band gap has started long ago and its realization is still far from finished. Computer simulations, especially density functional theory (DFT) based calculations play a key role in the development of a new photocatalyst and/or the modulation of the electronic properties of the existing ones. Among the modulation techniques, the application of an external static electric field on wide band gap semiconductors seems to be promising. Due to widespread popularity of silver halides as a photo-active and photocatalytic material we conducted a series of studies on the modulation of the electronic properties of AgCl and AgBr within the framework of DFT using B3LYP hybrid functional. We have applied a static electric field along three crystallographic directions, i.e., [001], [011] and [111], and studied the variation of electronic properties with respect to external field. We focused on the variation of the photocatalytic characteristics such as optical band gap, band width, relative band positions and the band dispersion of these materials, which all strongly influence the overall photocatalytic activity. We will also discuss the directional dependence of the band gap variation of these semiconductors under the applied field.

P 140

REMOVAL OF URANIUM (VI) FROM AQUEOUS SOLUTIONS USING CHEMICALLY MODIFIED MALT SPENT ROOTLETS AS BIOSORBENTS

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Non-biodegradable heavy metals or radionuclides can contaminate the environment, because they have been released due to rapid industrialization or diverse applications of nuclear technology. Adsorption is a physico-chemical method found to be effective in removing heavy metals or radionuclides from aqueous solutions. Recently, the research is focusing on the production of cheaper adsorbents. Wastes or by-products from agro-industrial activities have no or very low price and therefore could be considered as low cost adsorbents.

The objective of this project is to assess the potential utilization of malt spent rootlets (MSR), brewery by-products, as pre-concentration means of uranium.

Preliminary sorption experiments revealed that NaOH treated MSR exhibit higher metal capacity than untreated ones. NaOH treatment of lignocellulosic materials is widely considered in the literature as a way to enhance metal uptake. The optimum pH for the removal of uranium was found to be at 4.5 and the procedure was found to be rapid (equilibrium was reached within 1 h). Isotherm data can be described by Langmuir isotherm model ($K_L = 0.031$, $q_{max} = 176$ mg U(VI) / g). Dubinin – Radushkevich isotherm model implies that ion exchange is involved in the mechanism of sorption of uranium onto the biomass. Finally, salinity experiments indicated that uranium uptake is strongly dependent on the concentration of $NaNO_3$ in the aqueous solution. More specifically, taking into consideration uranium speciation, a linear correlation between uranium removal and the concentration of $UO_2NO_3{}^+$ species was revealed, indicating that this species is favorably sorbed against $UO_2{}^{2+}$.

P 141

PLATINUM DEPOSITION ON PET-ITO SUBSTRATE

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A dye sensitized solar cells (DSSC) consists of three main components: dye-covered nanoporous TiO_2 layer on a glass substrate coated with a transparent conductive oxide (TCO), an iodide contained electrolyte and the platinised conductive substrate.[1] Glass covered with TCO, which is usually used as a substrate, is heavy and fragile. For that reason the polyethylene foil covered with indium oxide (PET-ITO) was also used.

In the present work the platinum deposition on a PET-ITO substrate was studied. Sol-gel synthesis using $H_2PtCl_6{\cdot}xH_2O$ as a platinum precursor was applied. Thin films were deposited on conductive foil with dip-coating technique and heat-treated at various temperatures to improve adhesion of platinum film to the substrate. Thin films were characterized by thermogravimetric (TG) analysis, differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and cyclic voltametry (CV).

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P 142

INHIBITED BIOGAS PRODUCTION FROM BREWERY SPENT GRAIN BY p-CRESOL

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Brewery spent grain (brewery by- product) as a substrate in the process of methanogenic anaerobic digestion has not been understood well yet. Despite its high biomethane potential, brewery spent grains (BSG) is a problematic substrate for biogas production, because of high lignin content and inhibitory biodegradation products (aromatic compounds), which arise during the process of anaerobic digestion. Slow degradation and presence of inhibitory components are the main reason that BSG should be pretreated before biogas production. As a substrate a combination of brewery wastewater and brewery spent grain was used in this study. The substrate was mechanically, thermally and chemically pretreated. In the experiment we used pilot-scale semi-continuous bioreactors (CSTR) which have operated under mesophilic conditions (37°C). The performance of the reactors was monitored once a week by determining the following parameters: volatile fatty acids (VFA), chemical oxygen demand (COD), ammonia-N. Biogas production and pH were followed daily. In addition to these parameters we also followed the lignin degradation products during anaerobic digestion, especially the group of aromatic compounds. Inhibition of biogas production and the accumulation of the incompletely degraded lignocellulosic substrate and *p*-cresol were detected in the methanogenic reactor in all experiments. Presumably this was attributed to the inhibitory effects of lignin and/or its degradation products on certain functional groups of anaerobic bacteria and archaea. Paralelly to increasing concentration of *p*-cresol (over 200 mg/L) we detected the increased levels of VFAs and decreased biogas production. Based on the given results it may be concluded that the mechanical and thermal pretreatment of BSG could offer the best conditions for further microbial biogas production from BSG. Biogas production from chemically pretreated or raw BSG is notably less efficient.

Key words: anaerobic digestion, biodegradation, biogas production, brewery spent grain, inhibition, lignocellulose, methanogenic activity, p-cresol

P 143

SIMPLE, SAFE, AND CLEAN PROTOCOLS FOR MANNICH REACTION IN WATER

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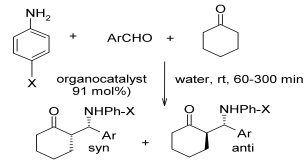
Contrary to the general image that chemistry has in public opinion, chemists are great observers, admirers, and lovers of Nature. Chemists have a relationship with Nature at a molecular level, learn from it, and attempt to copy its perfection and harmony. In their activities, chemists work to find solutions for human health; to widen the range of sustainable processes and materials; to prevent pollution and maintain the quality of climate; to devise clean, renewable energy sources; to preserve and restore the cultural heritage; and to develop new technologies for improving everyday life. Using synthetic processes and discovering and manipulating molecules, chemists are increasingly establishing a primary role within prominent interdisciplinary scientific and technological fields such as those of nanoscience, nanotechnology, and biotechnology.

In this context, in this presentation, a mild and practically-convenient one-pot procedure for the direct Mannich reaction has been developed by condensation of amines, aldehydes and unmodified ketones in water in the presence organocatalyst in good to excellent yields. The present methodology offers several advantages such as excellent yields, simple procedure, short reaction times and milder conditions with very small amount of catalyst.



P 144

PROPERTIES OF BIOFILMS FROM KERATIN BASED MATERIALS

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The keratin-based materials have shown promise for revolutionizing the biomaterial world due to their intrinsic biocompatibility, biodegradability, mechanical durability and natural abundance [1]. Possible applications are compostable packaging and agricultural films. The research goal of this work was to evaluate the viability of using a solids waste containing keratin – chicken feathers, sheep wool, human hair, goat and bovine hair – as a sustainable source for the production of biodegradable films by thermo-compression.

The preparation of materials was carried out according to their type and source. The chicken feathers and sheep wool were washed with hot water containing detergent, then thoroughly rinsed with water and dried at room temperature. The human, goat and bovine hair were washed with water at room temperature and dried at 60 ºC. Films were made by thermo-compression, using solids waste containing keratin mixed with 30% of glycerol. The process parameters were fixed at 160 ºC, 89 N and 4 min and mechanical properties were evaluated in a Texture Analyser.

With these conditions, human hair was not able to produce films. It was verified that films made with sheep wool and made with chicken feathers had similar properties. However, films prepared with sheep wool had higher stress at break and Young Modulus (21.17 MPa and 32.69 MPa, respectively). Films produced from goat hair had higher strain at break, around 1.96 %. On the other hand, the worst results were obtained with films produced from bovine hair (0.4 MPa, 0.33 MPa and 0.33 % for Stress at Break, Young Modulus and Stain at Break, respectively).

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P 145

METAL-ORGANIC FRAMEWORK MATERIALS FOR HYDROGEN STORAGE APPLICATIONS

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Hydrogen storage is still a technological challenge, especially in transport applications. Hydrogen has very low density at normal conditions and its storage, for example in transport applications, requires too large and too heavy containers. Adsorption of molecular hydrogen on high-surface-area porous materials has raised huge interest of hydrogen storage community in recent years, especially after the discovery of crystalline metal-organic framework materials (MOF) [1, 2]. MOFs have porous structures formed from covalently bonded metal atoms and organic ligands that can store up to 10 wt. % or 53 kg/m^3 of hydrogen, which is related to their large surface areas up to 6000 m^2/g and low densities < 1g/cm^3. The sorption process is quick and reversible, which is crucial for on-board applications, the disadvantage is that the process requires T ~77 K and pressure ~70 bar, because of too weak interactions of the nonpolarizable hydrogen molecule with the materials surface (van der Waals interactions up to 5 kJ/mol).

We have studied the potential of iron carboxylates for their use in safe and effective hydrogen storage. We have concentrated on the synthesis of MOFs, i.e. on the control of the type, number, distribution and accessibility of metal sites in the framework or in the pores, which represent primary sites for hydrogen loading and which could enable better interactions of the surface with hydrogen. The prerequisite goal was also the high crystallinity of the structure that assured materials' homogeneity.

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P 146

BIOCONTROL AND OZONE TREATMENTS AS POSSIBLE ALTERNATIVES TO FUNGICIDES

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Synthetic fungicides are the primary means to control pre- and postharvest diseases of fruits. However, several reasons, such as the public's growing concern for the human health conditions and the environmental pollution, the development of fungicide-resistant strains of phytopathogens and the lack of continued approval of some of the most effective fungicides have motivated the research for alternative approaches. Biocontrol using antagonistic yeasts has emerged as one of the most promising alternatives due to their antifungal effects and in particular competition (e.g. antagonistic interactions against phytopathogens). Siderophores, a low molecular weight iron-chelating ligands, that sequester iron and thereby inhibit phytopathogen growth or metabolic activity may have a role in biocontrol applications. The other possibility to control phytopathogens is the usage of ozone, a powerful oxidant, which is effective against various kinds of microorganisms on fruits. In our study we evaluated siderophore and ozone treatments to control *Botrytis cinerea*, which causes grey mold, one of important fruit diseases. In biocontrol study we performed screening of several yeasts for siderophore production by using ferric perchlorate assay and further on selected siderophore-producing strains tested for antagonistic activity upon *B. cinerea* with biocontrol assay. Grape berries and cherries, without and with *B. cinerea* inoculation, were also treated with gaseous ozone and ozonated water. Our results show reduction in *B. cinerea* growth on the observed fruits in both cases: when treated with siderophores or ozone.

P 147

SYNTHESIS OF BIODIESEL FROM WASTE VEGETABLE OIL IN NORTHERN CYPRUS

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Experts suggest that fuel oil reserves in the world will be limited by the near future around 2040. Therefore, it is vital to look for alternative energies. Biodiesel is an alternative to diesel that is produced from petroleum. The main difference between diesel and biodiesel is that while diesel is a fossil fuel which is finishing, biodiesel is renewable and reproducible since it is produced from agricultural activities and recycling oil wastes. Biodiesel has been mixed into diesel fuel at 2% in European Union (EU) countries. According to the "White Book", which is shaped by the EU Energy politics, the amount of biodiesel in diesel fuel is aimed to be increased to a level of 5.75% in 2010 and to a level of 20% in 2020. In this sense, it is important to recycle the oil wastes for biodiesel production, since it will decrease the high costs of biodiesel and protect the environment. In this study, examination of the potential use of waste frying oils (WFOs) for production of biodiesel was investigated in Northern Cyprus. The sample oil wastes were collected locally from restaurants for the feasibility tests. Firstly the capacity of oil wastes was measured. After determining the characteristics of the waste, such as its water content, acid amount and viscosity, and production of biodiesel from the WFO was carried out at the laboratory on low scales. The production of biodiesel from used frying oils is feasible by basic catalyzed transesterification and the biodiesel produced has the quality required to be a diesel substitute. The results show that after 1 h of reaction, a methanol/waste frying oil molar ratio of 7:1 and a catalyst/waste frying oil weight ratio of 1.0% give the highest yield of methyl esters and allow an efficient separation/purification of the methyl esters phase, as shown by the viscosity reduction (4.4 mm^2/s, 40^0C) and increased purity (97 %) of this layer.

P 148

SWELLING PROCESS OF POLYACRILIC ACID HYDROGEL AND ABSORPTION OF COPPER IONS IN MILK PROTEIN SOLUTIONS

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Hydrogels are three-dimensional crosslinked polymeric structures that are able to swell in an aqueous environment. They have been utilized in a wide range of medicine and pharmacy, agrochemistry and environmental chemistry (purification of waste water by removing heavy metal ions and other pollutants). Swelling of hydrogel in distilled water leads to multiple increasing of mass of dried xerogel. Swelling of hydrogel in investigated protein solutions (whole milk proteins, whey proteins and serum albumine protein) causes penetration of water molecules in hydrogel's structure. Both swelling process can be determinated by measuring equilibrium swelling degree (SD_{eq}). Hydrogel completely collapsed in whole milk proteins solution which can be caused by high ionic force in this solution. On the other hand hydrogel swelled in whey proteins solution and serum albumin solution but swelling degree was significantly less than in the distilled water. Thus, it is possible to concentrate milk proteins solutions by removing inorganic components which can be adsorbed on hydrogel. It is particularly important for removing of heavy metal's ions that can be present in milk proteins solutions. One of them is copper (II) ion, Cu^{2+}. Presence of this metal's ion in milk protein solutions was determinated by atomic absorption spectroscopy. Results have shown that amount of bind Cu^{2+} ions on hydrogel was biger in whey proteins and serum albumin protein solutions than in whole milk proteins solution.

P 149

ON THE REMOVAL OF AQUEOUS MANGANESE, NICKEL AND ZINC IONS USING THE NATURAL CLINOPTILOLITE

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The natural zeolitic tuff from the Zlatokop mine (Vranjska Banja, Serbia) has been studied as sorbent for Mn(II), Ni(II) and Zn(II) ions from aqueous solutions. The zeolite sample containing mainly clinoptilolite (more than 70%) removes the metal ions by ion-exchange process, which was confirmed by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDXS). XPS showed that there is no surface accumulation of the metal ions but an almost uniform distribution inside the sorbent; EDXS confirmed that aqueous Mn(II), Ni(II) and Zn(II) ions replaced the clinoptilolite Na^+ counter ions. The sorption isotherms were studied at 298-338 K by batch experiments showing that the Mn and Ni removal is best described by the Sips model whereas the Zn sorption isotherm is best represented by the Langmuir model. The kinetics followed the pseudo-second-order model for all three metal ions, the activation energy being strongly influenced by the metal type. Thermodynamic data suggest spontaneity of the endothermic ion-exchange process. Thermal treatment of the metal-loaded clinoptilolite samples at about 500 ºC results in the formation of spherical nano-oxide particles of approx. 5 nm in diameter which are randomly dispersed in the clinoptilolite lattice. Moreover, the zinc-containing sorbent exhibits ability to remove phosphate ions and shows also an excellent antibacterial activity towards *Acinetobacter junii*. This indicates that the exhausted clinoptilolite sludge could find various applications as a novel material.

P 150

ECONOMICAL AND ENVIROMENTALLY FRIENDLY SYNTHESIS AND EVALUATION OF IMIDAZOLE DRUG

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The rapid growth in energy production, industrialization and urbanization and a significant increase in agricultural production in the world have caused a remarkable increase in pollutant (SO2, heavy metals, persistent organic compounds, etc) emissions during the past several decades. The consequences of these growing emissions have been closely connected with enforced pollution loading on human and ecosystems health, which results in actual and potential risk for many sensitive individuals and receptors.

Many environmental problems in the world are closely connected with increasing energy demand and production. Another large set of environmental problems is related to waste production and utilization. All Asian countries are touched by these consequences of urbanization, industrialization and agricultural development, and there are many specific regional peculiarities in how this problem is solved regarding the air, soil, fresh and marine water pollution, human and ecosystem health.

On the other hands, development of strategically important processes which are environmentally clean, more efficient, and lead to greater structural variation, with very simple work up procedure and high purity that minimize the formation of waste, and high yields are currently receiving considerable attention. In this context, herein we reported a very mild, easy, and one-pot procedure for imidazoles based drug such as Trifenagrel from aldehyde, benzyl and ammonium acetate in water under environmentally friendly condition and evolution the impact of new method with the old methods based on economic and environmental program.

P 151

THERMOCHROMIC COBALT (II) HALIDE COMPLEXES AND NEW MATERIALS FOR AUTO-REGULATED SHADING PROTECTION

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A large number of passive solar agricultural greenhouses use latent heat storage materials undergoing solid/liquid phase change [1]. They have been extensively used in the past three decades in order to increase plant quality, productivity and to decrease consumption of fossil fuels for heating. Research work in this area involves studies of new materials and their optical properties upon addition of some thermochromic complex compounds. The thermochromic substance is usually transition metal complex with mixed ligands undergoing reversible changes of optical properties in response to a change of temperature, acting thus, as a self-regulating shading [2].

Well known fact that cobalt(II) halide complexes in various media undergo the changes of the coordination, absorbance and colour with the increase of temperature was combined with the high latent heat of fusion of new phase change materials (PCM) giving new materials suitable for heat storage and simultaneous control of temperature and light intensity.

Several binary mixtures of ammonium nitrate – formamide with the melting points near the ambient temperature were studied as suitable PCM-s and solvents for the formation of cobalt(II) halide complexes. Absorption spectra have been investigated in the visible spectral range 400-800 nm. Stability constants and thermodynamic parameters for the complexation reactions were determined.

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P 152

ALTERNATIVE AND RENEWABLE ENERGY STORAGE SYSTEMS

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There is a growing interest of utilization of so-called alternative energy sources, such as solar radiation, wind, cooling water, exhaust gases, off-peak electric energy, etc. So far, the solar energy is mainly used in residential field and in agriculture, but there are also several pilot solar electric power plants. To achieve demands of alternative and renewable energy sources, solar energy should be stored and available at night and on cloudy days. For that reasons, all solar heating systems require a thermal energy storage device suitable for passive solar applications. The development of such "smart materials" is mostly oriented towards the area of latent heat storage in phase change material (PCM). Most of the studies have been concentrated on the solid – liquid phase change transition in inorganic salts or mixtures of inorganic salt with organic compound. The high latent heat of fusion, high density, low cost and suitable melting temperature of inorganic salt hydrates is particularly suitable for thermal energy storage on the low-temperature level. The main disadvantages of salt hydrates are: supercooling of the liquid phase, incongruent melting and slow crystallization. Paraffins, polyhydroxilic alcohols, fatty acid esters, mixture of dimethylsulfoxide or formamide with inorganic salts etc. have been considered as phase change materials suitable for solar heating in order to avoid supercooling and incongruent melting, inherent with salt hydrates. Some disadvantages of organics are the low density, wide temperature range of phase transition and poor thermal conductivity.

In this work, ammonium nitrate – formamide and ammonium nitrate – dimethylsulfoxide mixtures were studied. Conductivity, viscosity and density measurements were performed in order to characterize these mixtures. In the combination with cobalt(II) halide complexes, mixtures show thermochromic effect which make them suitable for protection of agricultural greenhouses from solar overheating.

P 153

TRIGENERATION BASED ON LANDFILL GAS AND SOLAR ENERGY

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Currently at least half of total energy consumption is derived from imported fossil fuels in Europe. In addition, the production and use of energy from fossil fuels is responsible for most greenhouse gas emissions. The energy situations as well as the climate change, therefore, encourage the research of new and renewable sources of energy. This contribution presents an integration of innovative technologies to the development of a competitive and efficient trigeneration system (6 FP project "SOLBIOPOLYSY"), based on the use of landfill gas and its conversion into syngas by reforming using steam generated by exploitation of solar energy. Advantage of this technology is reducing of CO_2 emissions, while preventing emissions of methane as a 21-times more powerful greenhouse gas. On the basis of energy, heat and mass balance of the pilot process, we studied the economics of the investment and operating costs of a trigeneration system.

Modeling approaches enabled us to study different scenarios of the operating system, its efficiency and economic analysis. Research was upgraded with emergency analysis, which is based on inputs of renewable and/or nonrenewable energy into the system in order to estimate its energy yield and level of environment impact caused by the system. The results enable to assess the level of sustainability of the SOLBIOPOLYSY technology and comparison with other systems for the exploitation of landfill gas.

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P 154

THE ROADMAPS FOR NANOTECHNOLOGIES: RUSSIAN EXPERIENCE IN CARBON FIBERS AND WATER PURIFICATION

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The Roadmap for Nanotechnologies is a document describing the multi-layer system of strategic development for the sphere of nanotechnologies in Russia within a common timescale. The project is aimed at identification of prospective demand for new high-technology products of nanoindustry competitive on the world markets. The launched Roadmaps reflect current status of R&D, manufacturing capabilities in the selected segments of the Russian science and industry and also show the parameters that reflect economic efficiency of leading-edge technologies and products characterized by a high potential demand and attractive consumer properties. The Roadmaps help to find potential market niches and choose technologies enabling to develop competitive products for emerging markets. This project is implemented by the Institute for Statistical Studies and Economics of Knowledge (ISSEK), the State University-Higher School of Economics, for the Russian Corporation of Nanotechnologies (Rusnano). The research embraces several directions among them are Roadmaps for carbon fibers and water purification.

The Roadmap for Nanotechnologies in Carbon Fibers (CF) explains the structure of demand for CF and outlines the most prospective markets for CF-products. The Roadmap provides an assessment of technical capabilities required for manufacturing of CF with the most preferable consumer properties which would allow generating the significant competitive advantages for goods produced involving CF. The Roadmap visualization illustrates the correlations between the key technologies which the CF-industry development relies on, the properties of existing and advanced CF and their composites, and the most promising products and their respective market shares whose sizes and growth rates, in turn, would determine the demand for CF.

The Roadmap for Nanotechnologies in Water Purification shows the main technological trends, innovations and alternative directions of development in the field of water purification. The research allows identifying the most prospective products in the considered area and highlighting applications and market prospects of innovation products in the sphere of nanotechnology in water treatment. The Roadmap gives an opportunity to develop a strategy for the sphere of water treatment in Russia and therefore provide clean water for citizens. The launched Roadmaps give an opportunity to make middle- and long-term forecast the certain sphere or industry and to launch a strategy and R&D program for the certain sphere or industry.

O 17

EFFECT OF GLYCOLYZED PRODUCTS COMPOSITION ON THERMAL PROPERTIES OF NANOCOMPOSITES BASED ON CHEMICAL RECYCLING OF POST-CONSUMER PET BOTTLES

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Post-consumer PET bottles were depolymerized by glycolysis using ethylene glycol at 196°C. Three fractions of glycolyzed products were obtained after separation by cold and hot waters. While the fraction soluble in cold water mainly consisted of bis-(2-hydroxyethyl)terephthalate (BHET) monomer, the fraction soluble in hot water had higher amount of its dimer. On the other hand, the fraction not soluble in water composed of trimer and oligomer of BHET.

Each fraction of the glycolyzed products and the mixture of all fractions were polymerized into poly(ethylene terephthalate)s (PET) at 280°C for 2 hours. Their nanocomposites were prepared using the same condition via *in situ* polymerization with various amounts of titanium dioxide (TiO_2). Due to its highest molecular weight confirmed by melt flow index, PET based on insoluble fraction exhibited highest decomposition temperature than PET synthesized from other fractions. On the other hand, their nanocomposites exhibited higher decomposition temperature due to good thermal barrier of TiO_2. However, %crystallinity and melting temperature of all nanocomposites were lower than those of their PET counterparts due to the agglomeration of TiO_2 nanoparticles which can obstruct the chain orientation of the polymer as was revealed by SEM. These properties decreased with increasing TiO_2 content. It was also found that the nanocomposite based on the fraction soluble in hot water had higher %crystallinity and melting temperature than those prepared from other fractions. When considering the ease of processing and the applications where high heat is required, the suitable fraction of the glycolyzed products used for preparation of this nanocomposite is the insoluble fraction.

O 18

SORPTIVE REMOVAL OF Cr(VI) AND Cu(II) FROM BINARY MIXTURES BY GRAPE STALKS

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The industry of electroplating and metal finishing is one of the major sources of heavy metal pollutants (Cr, Cu, Ni, Cd, Pb) and their negative effects can be avoided by treatment of their wastewater. Recent studies demonstrated that grape stalks, olive stones could be used effectively as sorbents of these metals from single metal aqueous solutions.

In this work, the use of grape stalks for Cr(VI) and Cu(II) elimination from aqueous solution in binary mixtures has been investigated. The influence of solution pH, the effect of contact time, the initial metal concentration and the competence between chromium and copper has been studied.

Batch sorption experiments with single metal and binary mixtures solutions were carried out at 20±0.1ºC. After sorption, pH of solution was measured and total chromium and copper concentration in solution were analysed by FAAS.

Results showed that optimum pH for chromium and copper sorption in binary mixtures are pH 3 and within the pH range 3-6, respectively. Therefore, pH 3 was chosen for further kinetics and equilibrium experiments.

In a previous study, an initial pH 3 was found to be the optimum for chromium removal in single metal solutions; nevertheless, a pH 5 was necessary to remove copper in single solutions. According to the obtained results, the presence of Cr (VI) in solution allows to eliminate copper from binary solutions at pH 3. The explanation must be found in the mechanism of Cr(VI) sorption that involves its reduction to Cr(III). The reduction reaction of Cr(VI) to Cr(III) which is proton consuming provokes the increase of the pH that favours copper sorption.

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O 19

EXTRACTION AND DETERMINATION OF HEAVY METALS ON INDUSTRIAL SLUDGES. PROPOSAL OF AN ENVIRONMENTAL FRIENDLY WASTE TREATMENT PROCEDURE

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The metal finishing industry produces a high amount of toxic sludge as a result of i ndustrialeffluent treatment. In Europe, nearly than 150000 Tn/year of galvanic sludge are produced by more than 400 industries in this sector. These sludges are managed by authorized companies, being stored at controlled landfills, which is very expensive and environmentally hazardous. In terms of environment, impact is due to the need of a landfill for sludge store, producing at the same time, a metal loss as raw material at the industrial processes. Usually, the management sludge companies have no options for the treatment and recovery of heavy metals in sludge. Therefore, the development of effective, economical and specific waste treatment procedures has become a priority nowadays. In this sense, it has been optimized a method for the extraction of the heavy metals Zn2+ and Cu2+, from metal finishing industrial sludge, based on the use of biodegradable surfactants (SDS, Triton X- 100) as extractants and the use of EDTA as chelating agent. The 'Microwave Assisted Micellar Extraction' (MAME) method optimized combines the advantages of the micellar media and the microwaves, resulting in a fast, easy, safety, low cost and environmental friendly procedure.

Results show satisfactory recovery percentages, up to 90% in both metals Zn2+ and Cu2+ in the case of synthetic sludge samples. The method has been applied to metal finishing industrial sludge with satisfactory results as well. Finally, a proposal for the separation and recovery of both, metal and surfactants, under a 'Micellar Enhaced Ultrafiltration' (MEUF) method, is presented.

O 20

TRANSFORMATION OF THE ANTIEPILEPTIC DRUG OXCARBAZEPINE UPON DIFFERENT WATER DISINFECTION PROCESSES

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Transformation of the pharmaceutical oxcarbazepine (OXC), the keto analogue of carbamazepine (CBZ) was investigated under different water disinfection processes (ozonation, chlorination and UV irradiation) and biological treatments to compare its persistence, toxicity and degradation pathways with those of CBZ. Analysis by LC–ion trap–MS^n allowed for the identification of up to thrirteen transformation products (TPs). Surprisingly, the major abundant and persistent TPs (10,11-dihydro-10,11-*trans*-dihydroxy-carbamazepine (DiOH-CBZ), acridine (ACIN) and 1-(2-benzaldehyde)-(1H, 3H)-quinazoline-2,4-dione (BQD)) were identical to those previously reported during water treatment of CBZ. Only one new compound arising from an intramolecular cyclisation reaction was identified during UV irradiation. OXC reacted quickly with hydroxyl radical and relatively rapidly with free chlorine while slow reaction rates were recorded in presence of either ozone or upon UV irradiation. An increase of the acute toxicity of UV irradiated solutions, monitored by a *Daphnia magna* bioassay, was recorded, probably due to the accumulation of ACIN. The formation of ACIN is of concern due to the carcinogenic properties of this chemical. ACIN was also generated during the direct UV phototransformation of DiOH-CBZ and 10-hydroxy-10,11-dihydro-carbamazepine (OH-CBZ), two metabolites of OXC and CBZ widely detected in water resources. Analysis of tap water samples revealed the occurrence at ngL^{-1} levels of the major TPs detected under laboratory scale experiments, except ACIN.

O 21

TEXTIL WASTEWATER TREATMENT BY SOLAR-DRIVEN AOP$_s$

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Textile wastewaters, which are generated in textile dyeing processes, are a complex mixture of colorants (dyes and pigments), various organic compounds used as cleaning solvents and plasticizers, and different inorganic compounds, as chlorides, sulphates and heavy metals that constitute a serious environmental problem. In this work, different heterogeneous (TiO_2/UV, TiO_2/H_2O_2/UV) and homogenous (H_2O_2/UV, Fe^{2+}/H_2O_2/UV) photocatalytic processes were studied as an alternative approach for the treatment of a real textile wastewater. The textile wastewater presents a lilac color, with a maximum absorbance peak at 516 nm, high pH (pH = 11), moderate organic content (DOC = 440 mg C/L, COD = 1700 mg O_2/L) and high conductivity (13.6 mS/cm), associated with a high concentration of chlorine ions (4.7 g Cl^-/L). The DOC abatement is similar for the H_2O_2/UV and TiO_2/UV processes, achieving only 30% and 36% mineralization after 190 kJ_{UV}/L. The addition of H_2O_2 to TiO_2/UV system increased the initial degradation rate more than seven times, leading to 90% mineralization after exposure to 100 kJ_{UV}/L (following an initial pH correction to 4.5 for both systems).

The optimal initial iron dose for the photo-Fenton treatment of this leachate is 100 mg Fe^{2+} L^{-1}. Spectrum in the visible wavelength range shows that cleavage of the organic colorant molecules occurs in the first moments after the start of the foto-Fenton Reaction. The degradation curve follows a first-order reaction, with a kinetic constant, k = 0.04 L/kJ_{UV} and an initial reaction rate, r_o = 9.8 mgC/kJ_{UV}. The photo-Fenton process is much more efficient than heterogeneous (TiO_2, TiO_2/H_2O_2/UV) or homogeneous (H_2O_2/UV) photocatalysis, showing an initial reaction rate more than 2 times faster when compared with TiO_2/H_2O_2/UV, consuming 4.2 mM H_2O_2/kJ_{UV}.

P 155

IN-SITU ELECTRO GENERATED H_2O_2 AND ITS USAGE FOR DECOLOURIZATION OF REACTIVE DYES WITH H_2O_2/UV PROCESS

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The main pollution in wastewater from the textile industry originates from the dying and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs. Dyestuffs are generally organic compounds of complex structure. Among textile dyes, azo dyes constitute the largest and the most important class of commercial dyes. Anthraquinone dyes present the second most important class after azo dyes. The disposal of coloured textile wastewaters poses a major problem for the textile industry. For efficient removal of pollutants, like dyes, advanced oxidation processes (AOPs) can be used. AOPs are able to decolourize and mineralize hydrolyzed dyes in textile wastewaters. Among AOPs, chemical oxidation using UV irradiation in the presence of H_2O_2 is a very promising technique. In H_2O_2/UV processes the photolysis of hydrogen peroxide generates effectively hydroxyl radical species which can also destroy hydrolyzed dyes present in textile wastewater. Hydrogen peroxide can be electro-synthesized by reduction of oxygen and protons at a gas-diffusion electrode (GDE). The produced hydrogen peroxide can then be used for the treatment of effluents.

The aim of this study was to asses the feasibility of in-situ generation of hydrogen peroxide in combination with UV irradiation for the decolourization and mineralization of four different commercially important reactive dyes. One anthraquinone and three azo dyes were selected as model dyes.

P 156

ISOLATION AND CHARACTERISATION OF POTENTIALLY PATHOGENIC ANTIBIOTIC-RESISTANT BACTERIAL STRAINS FROM SEWAGE SLUDGE SAMPLES IN HUNGARY

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The objective of our work was to identify and characterise potentially pathogenic and antibiotic-resistant bacterial strains from sewage sludge samples and other industrial wastes in Hungary. Sewage sludge from four domestic wastewater treatment plants and waste from a biogas plant were analysed. Media used included Mueller-Hinton agar and Cetrimide agar plates +/- antibiotics. Selected strains were characterised by antibiotic susceptibility testing, phenotypic traits and/or molecular methods. Integrase genes for class 1 to 3 integrons and the variable region of class 1 integrons were detected by PCR. Overall, bacterial colony forming units growing on screen plates containing gentamicin or ceftazidime were in the range of 0-10^4 cfu/g of the various samples. In sewage sludge from the South Pest treatment plant Flavobacteria with high-level resistance against aminoglycosides were abundant, but did not harbour integrons. However, from the same sample a gentamicin-resistant *Aeromonas* spp. isolate carrying a class 1 integron was identified. A *Pseudomonas* spp. strain with high-level resistance against gentamicin and ciprofloxacin that also harbours an integrase gene was cultured from the biogas plant waste, and another integrase-gene carrying strain was identified from sewage sludge from Salgótarján. These findings are in contrast to earlier data obtained with 41 *Pseudomonas* spp. isolates recovered in Hungary from healthy animals, groundwater and Lake Balaton, where clinically relevant antibiotic resistance and integrase genes could not be demonstrated. Our observations underscore the importance of monitoring antibiotic-resistant microorganism contamination in sewage sludge and other industrial wastes in order to identify potential environmental, food safety and public health risks.

P 157

COMPETITIVE ADSORPTION OF Pb^{2+}, Cu^{2+}, Zn^{2+} AND Ni^{2+} IONS FROM AQUEOUS SYSTEM ONTO ACTIVATED ALGERIAN BENTONITE CLAY: APPLICATION IN WASTEWATER TREATMENT

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A sample of bentonite from Mostaganem (N.W. Algeria) was characterized by powder X-ray diffraction, FT-IR spectroscopy and elemental analysis. The acid-activated bentonite was employed as adsorbent for four heavy metal ions from aqueous solutions by mean of batch experiments. The effect of shaking time, pH of aqueous solution, metal concentration and adsorbent amount was studied. The effective pH range was from 4 to 6 for these metals. It was found that Algerian bentonite had significant removing potential for Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} ions from aqueous solutions.

Keywords: Algerian bentonite Clay, Removal, Kinetic, Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+}

P 158

EFFECT OF TEMPERATURE AND USE OF DIFFERENT COAGULANTS ON PARTICLES FORMATION IN WATER TREATMENT

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The paper presents results of coagulation experiments dealing with the influence of temperature upon particles aggregation in treatment of humic water. Different aluminium coagulants and biopolymer chitosan were used as coagulant.

Biopolymer chitosan is an emerging coagulant, applicable in water treatment. Most of amine groups of chitosan in acetic solution are protonated and they can attract particles with negative surface charge (e.g. humic substances, bacteria, macromolecules). The results show that coagulation efficiency and optimal dose of chitosan are dependent on pH.

Coagulation with aluminium sulphate was negatively influenced by low water temperature, but results with chitosan and prepolymerised aluminium coagulants were hardly affected by low temperature. This is very important for drinking water treatment as alternative coagulants to aluminium sulphate could assist to overcome problems in cold water treatment with aluminium sulphate in existing waterworks.

P 159

REMOVAL OF PBDE AND ALKYLPHENOLS IN A TRICKLING FILTER WASTEWATER TREATMENT PLANT DURING DRY AND WET WEATHER PERIODS

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The European Water Framework Directive (2000/60/CE) requires a good chemical status of all water bodies for a list of substances of concern, including polybromodiphenylethers (PBDE - brominated flame retardants) and alkylphenols (AP - surfactants). Although AP and PBDE’s fate in conventional activated sludge wastewater treatment plant (WWTP) has been extensively studied, few data refer to tricking filter WWTP and no study examines the treatment of stormwater within such facilities. Therefore, the aim of this work is to evaluate the removal of AP and PBDE in a trickling filter WWTP during dry and wet weather periods. The Seine-Centre plant located near Paris (France) was considered. Its treatment consists of a lamella clarifier and a 3-stage submerged trickling filter unit (stage 1: treatment of carbonaceous pollution; stage 2: nitrification; stage 3: denitrification). Under wet weather conditions, this WWTP changes its operating mode: the biological treatment becomes less extensive since 30 % of the flow is treated through stage 3 only, while 70 % is successively treated through stages 1 and 2. To follow PBDE and AP along the WWTP, three sampling points were considered: raw effluent, before, and after the biological step. A total of 5 campaigns were carried out during dry weather periods; 4 campaigns were performed during wet weather events. Additionally to conventional wastewater parameters, PBDE were analyzed by gas chromatography coupled with mass spectrometry and AP by liquid chromatography coupled with tandem mass spectrometry. Dissolved and particulate phases were analysed separately in order to calculate the repartition of PBDE and AP in each phase. This presentation discusses in detail the results of PBDE and AP concentrations along the process under dry and wet weather conditions.

P 160

TREATMENT OF WASTE WATER USING ALKYLPHENOLS

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Nowadays large quantities of untreated effluent or indirectly from sewage treatment plants are generally discharged in to aquatic environments. These compounds are known to be persistent toxic chemicals.

The aim of this work consisted in studying the extraction of salts of cobalt, cadmium, zinc and copper from aqueous solutions using an ammonia solution of some alkylphenols synthesized (ter-butyl and ter-amylphenol). The study focused on the distribution of these ions according to the concentration of hydrogen ions, the composition of the aqueous solution and the nature of solvents used for this purpose. 10^{-3} M aqueous solutions of Zn^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+} were prepared from their salts (chlorides, sulfates) purchased from Prolabo or Merck. The extraction was carried out in flasks at 22 + 0.5°C by contact with an aqueous solution of these ions containing 0.02M NH_4Cl and various volumes of 0.5N NH_4OH with a 0.1M organic solution of alkylphenol. The mixture is stirred for 5 minutes to reach equilibrium. The phases were then separated and the pH measured.

The concentration of these ions in the organic phase at equilibrium, was determined after a second extraction using a dilute solution of HCl 2%. The Zn^{2+}, Cd^{2+}, Co^{2+} and Cu^{2+} were extracted with a coefficient D maximum in the pH range = 9.5- 0.0. When pH = 8.0-9.5, the curve has a linearity (log D-pH) and slope (tgα) is equal to 2. To confirm that the extraction of those ions is an exchange reaction, an IR spectroscopy study by was performed as for solutions of alkylphenols as those of the sample.

The isothermal nature of the extraction of these ions shows that they are extracted in the form of bivalent ions. Taking into account that these metals can exist as cations Me^{2+} and $[Me(NH_3)_4]^{2+}$ in ammonia solutions, we can exclude the probability of equal extraction (same probability).

P 161

SOLAR PHOTOCHEMICAL PRETREATMENT FOR SULPHUROUS GROUND WATER PURIFICATION PROCESS

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The sulfurous water deposit exploitation in volcanic, swamp, or wetland regions, represent an alternative option for potable water supply in cities and communities around the world. However before its consumption it must be treated by the application of physicochemical or biological methods with the ability to separate high contents in sulfates, sulphites and sulphides wich have a laxative, allergic and toxic properties in humans. Coventional methods require the supply of chemical compounds or the adequate control of different parameters such as pH, temperature, etc., within their reactors. Fo these reasons these systems could have elevated operating costs and require additional steps to enable the treatment of separated products and the final disposal of its residual waste generated.

In this research, compound parabolic collectors are implemented for the use of solar energy, UV-B type, in Advanced Oxidation Processes in $H_2O_2/O_3/UV$ homogeneous phase. Its application during the pretreatment of four sulfur water wells from the region of Puebla, México, demonstrated its ability to transform their sulfur compounds in sulfates of easy removal by a later stage of reverse osmosis. The photochemical pretreatment process eliminates the residual waste generation and can be automated to promote the general reduction in operating costs of the treatment plant.

P 162

THE EFFECTS OF SEWAGE SLUDGE ON THE PLANT NUTRIENTS AND HEAVY METAL CONTENTS OF PEACH (*PRUNUS PERSİCA* VULGARİS MİLL.) PLANT

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This research was carried out to determine the effects of urban sewage sludge that is applied to soil, on the plant nutrients and heavy metal contents in the fruits and the leaves in peach. Peach plants were grown in grower orchad containing different amounts of sewage sludge (corresponding to 0, 20, 40 and 80 T/ha, as dry weight basis). Sewage sludge applications have important effects on N, P, K, Ca, Mg, Fe, Zn, Mn, Cu, Pb, Ni, Cd and Cr contents in the leaf. It is observed that when the application level is increased, mineral contents and heavy metal accumulation are also increased. For the fruit; N, P, K, Mg, Fe, Zn, Cu, Pb, and Cd contents were increased importantly by increasing levels of sewage sludge application; Ca, Mn, Ni, and Cr contents have not shown an important change. The quantity of the accumulation in the leaf is high than in the fruit for all nutrients and heavy metals.

Key words: Heavy metals, plant nutrients, sewage sludge, peach

P 163

PURIFICATION OF ZINC PLATING WASTEWATER USING ALKALINE RESIDUE OF ELECTRIC ARC FURNACE DUST

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The purpose of this work was development of an appropriate procedure for the purification of zinc plating wastewater (ZPW) with alkaline solid residue (ASR) by-product of the alkaline extraction of zinc and lead from various types of electric arc furnace dust (EAFD). Removal efficiency of alkaline solid residue at optimum purification conditions (pH 8 and mixing time; 20 minutes) for the elements Pb, Cr (VI), Cr (III), Fe, Ni, Cu and Zn were 99.17 %, 100 %, 100 %, 99.88 %, 100 %, 99.69 % and 99.95 %, respectively. The concentrations of all elements in the purified wastewater were significantly lower in relation to the upper permissible limit. The remaining waste mud was regenerated in the strong alkaline medium and successfully applied once again for the purification of zinc plating wastewater. Removal efficiencies of heavy metals accomplished with regenerated waste mud were comparable to these achieved by original alkaline solid residue. Elemental concentrations in the eluates of the waste mud were in accordance with regulated values. There was no progressive increase in toxicity of waste mud after its regeneration and repeated usage for zinc plating effluent purification which justified closed cycle of: EAFD alkaline extraction - usage of remaining alkaline solid residue for zinc plating effluent purification - regeneration of waste mud by alkaline extraction - usage of solid residue of waste mud for zinc plating effluent purification. Conducted research confirmed successful application of toxic waste from one industry for the treatment of waste from other industrial processes.

P 164

EFFECT OF REACTION TIME AND ACIDS IN CHEMICAL LEACHING OF HEAVY METALS IN SEWAGE SLUDGE

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The present study present values of concentration (mg/l) of HM following solubilization with nitric and acetic acids at various contact times. The concentration of HM was found to be highest when solubilization was performed at a contact time of 1 hr using both acids except for Mn in both acids and Cu in nitric acid. It was observed that there was no trend in HM extraction as the contact times was ascended. It was also noted that solubilization at 6 hrs extracted much less HM using both acids. Cu (3.3416 mg/l) was the overall highest metal extracted using acetic acid, while Cd (0.0012 mg/l) was the overall lowest metal extracted using acetic acid at 1 hr contact time.

P 165

GREAT POTENTIAL OF NANOFIBERS FOR WATER PURIFICATION

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With increasing the world population, the demand of high quality of water is one of the most important global concerns. The separation of micron and nano particles contaminants has gained increasing importance in water purification. These particles tend to clog and foul the filter elements and will significantly decrease the efficiency of the treatment. Traditional filter media are wet laid, melt blown and spun- bonded nonwoven with micron size fibers, but recently electrospun fibers with diameter 10 to 100 times smaller than those article have shown better efficiency. Electrospun nanofibers are produced using electrical force, from polymer solution. Nanofibers have a large surface to volume ratio and small pore size in comparision with commercial filter media, thus they could effectively be used in water purification and improve water quality. Due to great surface area of nanofibers, they could use as an effective antibacterial element for removing pathogens such as bacteria and viruses from water. The problem of elevated level of heavy metals in ground water and its risk to local users and natural environment is solved with using Nanofibrous filter media. Nanofiber filter media has great potential to improve water quality for different applications. In this article the potential of applying nanofibrous filter media, to improve water quality is investigated, and a comprehensive review would be presented on the research and development's related to apply nanofibers for water treatments.

P 166

RECOVERY OF SILVER FROM AQUEOUS SOLUTION BY ENHANCED ULTRA FILTRATION AFTER PRECONCENTRATION ON ALUMINA MODIFIED WITH DITHIZONE

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Environment contamination from heavy metals in general and precious metal in particular has become a great concern by environmentalists and analysts for long period of time because of their chronic or instant toxicity. Industrialization is a major source of initializes increasing contamination of our environment with heavy metals. Moreover Industrial waste streams such as mine effluents remain a serious problem. Despite significant advances in the treatment of such streams in recent years, it is still significant amounts of these elements may in some instances be discharged as soluble ions into mine effluent streams. There is still no satisfactory method for removal of these metals such that environmental regulations and industrial companies are completely satisfied.

The aim of this project is to investigate recovery methods for silver at low concentration (less than 5ppm). Rrecovery of silver ions in the trace amounts is very difficult and it is essential to apply a preconcentration process to recovery of the metal ion. Methods include liquid – liquid extraction, ion exchanger, evaporation and Polymer Enhanced Ultra Filtration (PEUF). None of these processes are ideal and all have some drawbacks which include: of using large volumes of organic solvent; high energy consumption or poor selectivity.

In this study metal recovery by solid phase absorption onto coated micro particles has been investigated. Using surface coated alumina with dithizone, the absorption dilute silver solution concentration range 1-5 ppm has been investigated. The process was found to work well over wide range of pH (1-9) giving efficient absorption of low concentration. The collected silver could be desorbed as a concentrated solution using thiourea.

P 167

BIOLOGICAL AND CHEMICAL OXYGEN DEMAND OF LEACHATE AND PIEZOMETRIC WATER FROM SEMI CONTROLLED, NON SANITARY LANDFILL IN NOVI SAD, SERBIA

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Landfill leachate is one of the most complex problems of municipal solid waste landfills. Leachate is generated as a result of the percolation of water through landfill body and the squeezing of the waste due to its weight, and it is contaminated with dissolved and suspended organic and inorganic compounds with different characteristics. Since all natural waterways contain nutrients and bacteria, their enzymes will initiate biochemical reactions of almost any waste compounds that are introduced into such waterways. Any oxidizable material present in a leachate will be oxidized both by biochemical (enzymatic) or chemical processes. The result is that the oxygen content of the water will be decreased. Both the BOD_5 and COD tests are a measure of the relative oxygen-depletion effect of a waste contaminant. In August and September of 2008. research campaign was conducted to determine composition and quantity of waste that is disposed at landfill in Novi Sad. The landfill in Novi Sad is semi controlled non sanitary, municipal waste landfill without impermeable bottom liner to prevent impact contamination of soil and groundwater with leachate. The biggest part of waste from households and commercial sector is biodegradable organic waste that is decomposed by microbiological and chemical mechanisms in landfill body.

The leachate samples and samples from piezometers were collected from collecting channel and 6 piezometers in municipal solid waste landfill in Novi Sad in January and May of 2010. Biological oxygen demand (BOD_5) was determined using HACH BOD TRAK device. Chemical oxygen demand was determined using reagent test tubes in HACH DR5000 UV visible spectrophotometer.

Keywords: BOD, COD, landfill, leachate, waste, Serbia

P 168

SELECTION OF ADSORBENTS TO REMOVE ARSENAT IN DOMESTIC WATER

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Development of techniques for the removal of arsenic from aqueous matrixes is an important issue due to the high toxicity of this element[1-3]. In this study the adsorption of arsenate from aqueous solution on amorphous hydrous iron oxide incorporated highly porous diatomite is assessed in a batch mode. The procedures of preparing materials are environmentally acceptable, cost effective and simple. These sorbents are characterized by various methods: XRD, FTIR, BET, SEM, TEM, EDX and H_2-TPR. Effects of various experimental parameters such as initial As concentration (C_o), contact time (t), Fe contents, pH of the solution and the presence of interfering silicate, phosphate on the adsorption process have been studied. The arsenate adsorption capacities of 10%Fe-diatomite are 28mg/g which are comparable to or higher than those of the reference hydrous ferric oxide (HFO). The optimum pH value is found to be 6.0.

The Freundlich and Langmuir adsorption models are used for mathematical description of the adsorption equilibrium and it is reported that experimental data fitted very well to Langmuir model, although they could be modeled by Freundlich equation. Bath adsorption models, based on the assumption of the pseudo-first order and pseudo-second order mechanism, are applied to examine the kinetics of the adsorption. The results show that the pseudo-second order equation is successfully used to represent the adsorption data. Finally, small-scale column experiments are conducted to determine arsenate removal efficiencies for materials.

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P 169

TREATMENT OF ELECTROPLATING SLUDGE BY CALCIUM OXIDE, ACTIVATED CARBON AND PHOSPHORIC ACID

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Three methods for the treatment of electroplating sludge highly loaded with zinc and iron were presented and compared: (1) Calcium oxide based solidification/stabilization; (2) Conversion into inert material by adsorption of organic and inorganic pollutants onto activated carbon; (3) Conversion of mobile components of the waste into insoluble phosphates. All three methods proved to be highly efficient in the conversion of hazardous waste into inert material. Under optimum treatment conditions concentration of zinc in the leachate of solidified waste was reduced by 99.7% compared to untreated sludge. Zinc retention efficiency in the waste treated with activated carbon and phosphoric acid was 99.9% and 98.7%, respectively. Advantages of the treatment of electroplating sludge with activated carbon compared to the other two methods are as follows: high sorption capacity, insignificant pH and volume changes of the sludges, as well as simplicity of the application.

P 170

NITRATES REMOVAL FROM DRINKING WATERS WITH PUROLITE A520 E AND A100 ION EXCHANGE RESINS

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The wastewater from fertilizer production has a significant quantity of nitrogen in the ammonium and nitrate form. There are many different processes and methods which are used for industrial wastewater treatment (1). Several well known methods for nitrogen removal can be used satisfactorily (2) especially denitrification and physicochemical processes. The excessive concentrations of nitrate-nitrogen or nitrite-nitrogen in drinking water can be hazardous to health, especially for infants and pregnant women. In this study, removal of nitrate from aqueous solutions was investigated by using nitrate selective anion exchange resin, Purolite A 520E and Purolite A 100. The adsorption process obeys the Langmuir isotherm. From the analysis of experimental results, it has been observed that the ion exchanger A100 has kinetic values of ion exchange relatively high, but lower than those of ion exchanger A520 E. Comparative kinetic data reveal that the ion exchange kinetics is still differentiated for the two samples: under similar conditions, ion exchange rate is higher for strong basic anion exchanger (Purolite A520 E) although both have a macro-porous morphology. The temperature influences the nitrate sorption kinetics. The temperature involves the decreasing the time necessary for equilibrium attain.

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P 171

IDENTIFICATION OF THE MAIN VARAIBLES BY PRINCIPAL COMPONENT ANALYSIS DURING THE ADSORPTION OF NATURAL ORGANIC MATTER BY MODIFIED COCONUT-SHELL BASED ACTIVATED CARBONS

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Some fractions of NOM are hardly removed from drinking water when using conventional coagulation-flocculation processes. These difficulties in removing sufficient NOM make difficult to meet some quality criteria. Adsorption onto activated carbon beds is an alternative treatment. In the last decade a vast amount of characterisation and adsorption data have been reported with a large variety in the variables used to characterise an activated carbon. In the present study the multivariate statistical tool principal component analysis (PCA) was applied in order to highlight patterns, groups and trends in the characterisation data of coconut shell based activated carbons. Activated carbon was chemically and physically modified. The produced changes in the carbon structure were used to identify main properties affecting carbon performance.

Results indicate that total and/or fractional pore volume, iron and oxygen content were sensitive enough to detect good adsorption potential even for “a priori” non optimal overall properties. For example, low values of pHpzc not always correlated with poor adsorption performance. Additionally, the sum of N and O content may be also a good indicator to select a carbon with good adsorption performance. Based on PCA results, a prediction equation was developed to estimate values for the equilibrium uptake capacity. The model provided reasonable predictions even for activated carbons made of different source material.

P 172

KINETIC AND THERMODINAMIC STUDY OF THE ADSORPTION OF CATIONIC AND ANIONIC DYES ONTO ACTIVATED CARBONS

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In last few decades there has been a high increase in production and utilization of dyes resulting in a big threat of water pollution. It is difficult to treat dye effluents because of the hardly biodegradable nature of these compounds. In order to gain knowledge about the main factors involved it is important also to report exhaustive characterisation data of the sorbent textural and chemical properties. The present paper is an attempt to remove a well-known dye, the methylene blue (MB) and compare its adsorption behaviour with the anionic dye alizarin red S (ARS). Two activated carbons, Filtrasorb 400 and picahydro L27, were investigated as a function of several operating parameters such as initial dye concentration, contact time, pH and temperature.

Results obtained suggest that low basicity is a key factor since it allows favourable adsorption of both acid and basic dyes. Langmuir isotherms best represent adsorption system. Reported maximum adsorption capacities were 765.6 mg/g and 855.45 mg/g for MB and ARS, respectively. The adsorption processes of cationic and anionic dyes on ACs studied obey the pseudo first–order model. Hydrophobic interaction played a dominant role in the adsorption of cationic dye whereas anionic dye was bound through electrostatic interaction. This coincided with the lower activation energy values reported for MB (9.58 – 18.68 kJ/mol) in comparison to ARS (23.79 – 27.67 kJ/mol). It is likely that the nature of the bonds between dyes and AC depends on the solution concentration of the dye what affects the formation of poly nuclear species. Finally, for adequate desorption it is more important to enhance interaction between dye and surfactant rather than the repulsion between micelles and adsorbent surface.

P 173

COMBINED TREATMENT OF LANDFILL LEACHATE USING CALCIUM OXIDE, FERRIC CHLORIDE AND CLINOPTILOLITE

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Landfill leachate was formed by complex physico-chemical and biochemical transformations of solid waste deposited at sanitary landfill as well as by percolation of atmospheric water thorough the waste body of sanitary landfill. It is characterized by dark color, unpleasant odor, high conductivity, high concentration of organic biorefractory compounds and ammonia as well as increased to high concentration of heavy metals. Due to the complex nature of the effluent a combined treatment approach should be applied. The leachate was taken from Piškornica old sanitary landfill, Koprivnica. Samples were treated by calcium oxide followed by ferric chloride and finally by clinoptilolite. The optimum amount of treating agents and contact time were determined. Application of calcium oxide (25 g/L, 20 min. contact time) resulted in the reduction of color, turbidity, suspended solids and ammonia for 94.5, 96.55, 95.66 and 21.6 % respectively while total amount and of heavy metals decreased 91.56 %. After addition of ferric chloride (570 mg Fe^{3+}/L, 20 min. contact time) removal efficiency of color, turbidity, suspended solids, ammonia and total amount of heavy metals increased to 96.04, 99.27, 98.61, 43.2 and 93.45 % respectively. Removal of ammonia (81.6 %) increased significantly after final adsorption onto clinoptilolite (2.5 g/L, 4 h contact time). Slight increase was also found for the removal of total amount of heavy metals (96.94 %). Removal of COD after successive treatment by calcium oxide, ferric chloride and clinoptilolite was 64.7, 77.4 and 81 % respectively.

P 174

SPECIFIC FEATURES OF CHEMICAL DEGRADATION OF PHARMACEUTICALS IN THE PRESENCE OF SURFACTANTS

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During last decade pharmaceutical fate in the environment is in a focus of many studies because of low biodegradability and expressed negative effect of some drugs. Different ways of pharmaceutical detoxification in wastewater are suggested, chemical oxidative degradation being among of them.

In the previous study we researched oxidative degradation of some medicines, in particular widespread analgesic analginum (sodium 1-phenyl-2,3-dimethyl-4- methylamino-pyrazolone-5-N-methansulphonate) [1]. A solution of hydrogen peroxide and an iron salt (Fenton reagent) have been used for degradation. We recommended oxidative degradation of analginum with iron-catalysed hydrogen peroxide for deactivation of the pharmaceutical.

However the results described have been obtained for idealized analginum solution in distilled water. Real wastewater always contains many other organic pollutants. In the present study an experimental simulation of analginum oxidative degradation in a presence of surfactant has been carried out. Alkylphenylethoxylate, non-ionic surfactant was used for this purpose.

The mixture of analginum and surfactants with molar ratio 3:1 was subjected to degradation by Fenton reagent. Initial rate of oxidative degradation of analginum was shown to be 30 % lower in a presence of surfactant. Thus both analginum and surfactant are degraded though the rates of their degradation are different.

Acknowledgement: The study has been financially supported by Russian Foundation for Basic Research and Government of Belgorod region (grant № 09-03-97538).

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P 175

REMOVAL OF HEAVY METAL BY NANOMAGNETICALLY RECOVERABLE DITHIOCARBAMTE

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Heavy metals such as copper, cadmium, mercury, and lead are found in waters from a number of industrial processes. Because of the toxicity of many heavy metals, their concentrations must be reduced to very low levels prior to release of the wastewater. A number of approaches are used in heavy metals removal. Different treatment Techniques have been developed to remove either or both ddissolved and suspended heavy metal ions from industrial waters and wastewaters.

Recently, functionalized magnetic nanoparticles have emerged as viable alternatives to conventional materials, as robust, readily available, high-surface-area. They have been used in organic synthesis as catalyst and they offer an added advantage of being magnetically separable, Thereby eliminating the requirement of catalyst filtration after ccompletion of the reaction.

In this study, dithiocarbamate-incorporated magnetically recoverable nanoiron was used for selective removal of heavy metal from aqueous solutions. The resulting dithiocarbamate is highly active and is capable of removing heavy metal such as mercury efficiently. The magnetic dithiocarbamte is simple to prepare, insensitive to air/moisture and easily recoverable by exposure of the reaction vessel to an external magnetic field.

P 176

EFFECTS OF Al,Fe-PILLARED CLAY CATALYST IN THE PURIFICATION OF DYE CONTAINING WASTEWATER

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In order to perform purification of textile dye (Everdirect black) containing wastewater by means of catalytic wet peroxide oxidation (CWPO), Al,Fe-pillared clay (PILC) was synthesized, characterized and tested as catalyst in the oxidative removal of present organic pollutants.

The PILC was obtained using a common procedure consisting of the following steps: grinding, sieving, Na exchange, intercalation, drying and calcination. Fe^{3+} to Al^{3+} molar ratio in the pillaring solution was 1:9. Phase composition, textural and morphological properties of the starting clay and synthesized PILC were determined using X-ray diffraction, physisorption of nitrogen, UV-Vis diffuse reflectance spectrometry and scanning electron microscopy. Chemical composition of the PILC was determined using ICP-OES. X-ray diffraction analysis confirmed that the pillaring was successful. Chemical analysis confirmed the incorporation of Al^{3+} and Fe^{3+} species in the PILC.

Catalytic test was carried out in a semibatch reactor at 35°C under stirring. Catalytic performance of the catalyst was examined using UV-Vis spectrophotometry and total organic carbon (TOC) measurements (Shimadzu TOC 5050). The catalytic tests showed good performance of the obtained Al,Fe-PILC in the degradation of dye. Obtained UV-Vis spectra indicated simultaneous dye removal and occurrence of new species – probably reaction products – which disappeared in proceeded reaction. TOC measurements showed that approximately 75% of the initial amount of organic carbon remained adsorbed on the PILC material. It was, however, concluded, in comparison with corresponding UV-Vis spectrum, that the remaining carbon was not in the form of initially present dye molecules, since the absorption at dye related wavelengths was small.

Here investigated method was proven to be efficient in the removal of the dye from wastewater, thus reducing sunlight cut-off effects, and have prospects as a first step in a two stage water purification method, where the second one could be biodegradation.

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INVESTIGATION OF NITRATE SOURCES FOR JUST WASTEWATER TREATMENT PLANT: A CASE STUDY

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Eutrophication occurred at JUST constructed pond. Since it is affected by human made effluents, an algal bloom is expected to happen resulting from excessive load of nutrients, calm conditions and less water inflow. The influent to the pond is the effluent from the university campus and Wadi-Hassan wastewater treatment plants (WWTP) as well as rainfall. JUST WWTP receives wastewater from different activities in the campus. It is expected that the increase in ammonium would increase nitrate content of the water effluent. The objective of this project is to determine whether the reason for eutrophication in the JUST constructed pond is the nutrient content in the effluent of JUST WWTP; and then to determine the source of this increase in nutrient concentration that led to eutrophication.

Samples were collected from major manholes located at different locations in the campus. These samples were analyzed for ammonium and phosphate. The first set of samples were collected from major manholes from engineering buildings, medical buildings, service buildings, King Abdullah Hospital and residential buildings. After collecting samples from these locations over different periods of time, specific samples were collected. Results showed that the two locations containing the highest ammonium and phosphate concentrations were the engineering and medical buildings. The ratio between nitrogen and phosphorous was high enough for eutrophication to occur, which means that the nutrient content in the effluent of JUST WWTP is the reason for eutrophication in the pond. Highest ammonium content was detected in manholes located close to the Civil and Architecture buildings.

P 178

INFORMATION SYSTEMS SUPPORTING SUSTAINABLE LABORATORIES

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The concept of “sustainable development” and the term “sustainability” proposed by the World Commission on Environment and Development [1] have been increasing recognition in recent years. Concerning a Chemical Laboratory, a set of sustainability principles are required considering the exploration of new design approaches, the incorporation of new technologies and mainly the modification of user behaviours [2]. Researchers, teachers, students and technicians should take an attitude that contributes to the laboratories themselves become safe places where environmental concerns are a part of the whole management of the laboratory. Reagents and products are usually toxics and hazardous products but the search of new trends in the concept of Green Chemistry must be investigated. A proper management of reagents and laboratory waste is also essential in a sustainable laboratory [3].

The outlook of nowadays laboratories must change the usually operating mode. To contribute for the success of sustainable laboratories a good organization cannot be forgotten. The contribution of various acknowledgements in an interdisciplinary framework is essential. Information technology and systems are powerful and valuable tools that can bring important benefits for a sustainable laboratory.

The aim of this project is the development of an information system able to support a laboratorial wastes management system created in 1999. This system is a set of interrelated components that collect, process, store and transfer information/knowledge to support the laboratory team management in controlling, analysing and decision making. Its main purpose is to contribute for the sustainability of the laboratories of an Engineering Polytechnic Institute in Portugal, with Chemical Engineering courses using information systems. This work presents how the laboratorial wastes management system works, where the information system acted and the main results obtained.

P 179

OPERATIONAL PARAMETERS EFFECT ON THE TREATMENT OF OIL-IN-WATER EMULSION BY ELECTROCOAGULATION PROCESS

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The cutting fluids are used in particular during mechanical operations of cutting and shaping metals. With the use, these fluids lose their properties and effectiveness and need to be replaced periodically. The oily wastewaters generated contain stable oil-in-water emulsions and are very charged in surface-active agents and organic pollutants. In order to reduce the impact of their discharge, an appropriate treatment of these wastewaters is necessary. Electrocoagulation (EC) has the potential to be competitive with respect to both economical and environmental criteria for treatment of wastewater and other related water management issues.

This study is mainly focused on the EC treatment of cutting oil emulsions (1% in v/v) for investigation of the effect of the main operating parameters e.g. initial pH, current density, supporting electrolyte concentration and electrolysis time. Turbidity and COD values were used to evaluate the EC progress and the removal efficiency. For all cases, two phases were observed during the discontinuous treatment: (i) reactive phase for which the treatment efficiency increases regularly with time, (ii) a steady phase for which further Al dissolution has no effect on the treatment efficiency. Also, the optimum current density, initial pH and electrolysis time were 100 mA/cm^2, 7 and 45 min respectively. For these conditions the treatment efficiency and the energy consumption were respectively 90%, and 0.057 KWh/Kg of COD removal.

P 180

WATER QUALITY MODELLING OF MINHO/MIÑO RIVER (PORTUGAL/SPAIN)

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Minho, also called Miño (in Spain), is an international river with an extension of about 300 km. Its source is in Spain (Serra de Meira, Lugo) but in the last 75 km the river defines Portugal and Spain border before reaching Atlantic Ocean near Caminha (Portugal) or La Guardia (Spain). Under the scope of the Cooperation Project North Portugal – Galicia region of Spain (POCTEP_NATURA_MIÑO_MINHO 2009-2010), “Valorization of the natural resources of the Minho/Miño drainage basin”, several water and sediments monitoring campaigns were carried out during the two last years in Minho river basin. Seven sampling sites were selected along the international stretch of the river, and five were chosen in its main tributaries: Coura, Mouro and Manco (Portuguese), Tea and Louro (Spanish). Water samples were analyzed in terms of physicochemical and microbiological parameters. Results so far have indicated a reasonably good water quality in the international section of Minho River, according to Portuguese legislation for surface waters. Valença/Tui has showed to present the most polluted water considering all samples collected in Minho River. Louro has shown to be the most polluted tributary. QUAL2Kw model was used to describe water quality along the international stretch of Minho River. Calibration of this model was performed, using real values determined in field surveys. This model has also allowed evaluating the impact of Portuguese and Spanish discharges and tributaries. Louro and Tea Rivers have shown to produce the most negative effects on the water quality of the studied stretch.

P 181

MASS SPECTROMETRIC APPROACHES TO IDENTIFYING PHARMACEUTICAL TRANSFORMATION PRODUCTS IN THE ENVIRONMENT

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In natural and in engineered systems such as water treatment plants pharmaceuticals undergo various physical or chemical processes, which result in their elimination and/or chemical transformation. Transformation products may be more persistent or hazardous than the parent pharmaceutical. The identity, the fate and the effects of these compounds are the subjects of an increasing number of studies, in which the development of mass spectrometry-based methods has resulted in increased analytical sensitivity and selectivity.

This work deals with the identification and trace-level analysis of unknown transformation products, where complementary mass spectrometric approaches play a crucial role. For this, gas chromatography hyphenated with a single quadrupole or ion trap mass spectrometer and liquid chromatography coupled to a quadrupole – time-of-flight mass detector, were utilized. The chromatographic techniques complement one another and can account for a wide-range of polarities, acido-basic characteristics and functional groups, while the applied mass spectrometric methods enable multiple and tandem mass fragmentation, as well as accurate mass determination.

A nonsteroidal anti-inflammatory drug ketoprofen [2-(3-benzoylphenyl)propanoic acid] was used as a model compound. Transformation products were generated using photolysis and photocatalysis. The identification process yielded more than 20 transformation products, the majority of which were previously unknown, and were included into a ketoprofen breakdown scheme.

P 182

RECYCLING OF ORGANIC SOLID WASTE TO LIQUID FERTILIZER CONCENTRATE, A WASTE TO RESOURCE INITIATIVE FOR ENVIRONMENTAL SUSTAINABILITY IN NIGERIA

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Improper solid waste management is a panacea of the developing nations, which threatens environmental sustainability. For Public-Private-Partnership that facilitates sustained waste management, it is expedient to improve the waste management technology and market value of waste derived organic fertilizers. Study thus aimed at the transformation of agricultural solid waste to liquid fertilizer concentrate (HUM-SOL09). The humic fraction of HUM-SOL09 was subjected to spectroscopic studies (infrared and Uv-visible) and Ca-acetate titration for qualitative and quantitative estimation of chemical functional groups present in the molecular fragment. Heavy metal (Cd, Pb, Cu, Zn and Cr) contents of raw materials and HUM-SOL09 were analyzed using atomic absorption spectrophotometer after acid digestion. A 20 week long randomized screen house experiment was carried out with the HUM-SOL09. Being a concentrate (100%), the latter was subjected to serial dilutions (2, 2.25, 3.35, 5.0 and 10%: for each, n = 3) and the indicator crops were Okro (*Abelmoschus esculentus*) and maize (*Zea mays L.*). Indices of HUM-SOL09 efficacy were: leaf number, plant height, seed number and seed weight; fruit number and fruit weight. Data were subjected to relevant statistical analyses. Results showed that the humic fraction was basically characterized by oxygenated functional groups [hydroxyl {OH) and carboxyl {COOH}] in addition to hydrocarbon skeleton and displayed some degree of molecular condensation, established by E_4/E_6 ratio less than 5.0. The serial dilutions of HUM-SOL09 sustained plant growth and gave enhanced productivity relative to the concentrate and the heavy metal levels were below toxic levels. Study showed for enhanced environmental management and protection, solid waste management in the developing countries could be improved on by transformation of the organic fraction to liquid fertilizer concentrate.

Keywords: developing region, waste management, environment, sustainability

P 183

SELECTIVE REMOVAL OF Hg (II) IONS FROM WATER BY CHITOSAN BASED HYDROGEL

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Waste waters containing heavy metals pollutants come from different industrial activities such as mining, power plants, plating facilities and electrical equipment manufacturing. Mercury (Hg) is one of the most toxic heavy metals commonly found in the global environment. In this study, Polyacrylamide was grafted onto chitosan, in high yields (260%), using UV-induced radical polymerization methodology. The polyacryamide grafted chitosan hydrogels have been observed to exhibit as much as 790 % swelling. Polyacrylamide grafted onto chitosan has been demonstrated to be a very efficient selective sorbent for removal of mercuric ions (Hg(II)) from aqueous solutions. The mercury sorption capacity under nonbuffered conditions is around 5.29 mmol g^{-1} (i.e., 1.061kg of mercury/kg) and mostly occurs with the formation of diamido–mercury linkages, which result in the crosslinking of polyacrylamide brushes outside the chitosan hydrogels. The crosslinks can be destroyed by treatment with hot acetic acid, without hydrolysis of the amide groups. This regeneration process allows a complete elution of the mercury as mercury acetate, and the overall result is reversible crosslinking of the outer shell by mercuric ions. Thus, regeneration of the loaded polymer without losing its original activity can be achieved using hot acetic acid. The polyacryamide grafted chitosan hydrogel presented is efficient in the removal of mercury at concentrations measured in parts per million, and the mercury sorption is extremely selective over some foreign ions, such as Fe(III), Ni(II) , and Zn(II) ions in 0.1 M concentrations. The graft copolymer described seems very suitable for removal of large amounts of mercury in hydrometallurgical applications and may also be useful for other water treatments.

P 184

EXPLORATION OF THE ABILITY OF A PROBIOTIC BACTERIUM TO BIND U(VI). THE CASE OF *Lactobacillus casei*

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During the last decades, the scientific community investigates economical and environmentally friendly methods to decontaminate waters from heavy metals. The use of microorganisms for this purpose is well known [1]. Furthermore, it is known that probiotic microorganisms affect in a beneficial manner humans' health. In contrast to numerous reports, that have studied the binding of U(VI) onto microorganisms, only few studies have focused on the possible detoxification effect of probiotic microorganisms [2, 3, 4]. This kind of studies, may be proved very advantageous, as they provide the basic knowledge, so as these microorganisms to be classified, according to their selectivity against the diverse contaminant species, which could probably invade the food chain.

The objective of the present study is to explore the binding of U(VI) by the probiotic bacterium *Lactobacillus casei*. The effects of key parameters, such as pH of the sorbate solution and the dependence of metal uptake upon initial concentration, were studied at constant ionic strength (0.1 M $NaNO_3$). Sorption experiments were carried out at 37 ^{0}C and at pH 4, which represent an average of the pH in human gastrointestinal system. Cell surface was characterised by using potentiometric titration.

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P 185

ADSORPTION OF BASIC FUCHSIN AND METHYLENE BLUE ON VEGETABLE WASTE

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Many industries such textile, printing or food companies use dyes to colour their products and, as a result, generate considerable amount of coloured wastewater. Adsorption onto activated carbon is established to be a very efficient treatment to remove dyes from wastewater but the high cost and the regeneration problems of this treatment encourage researches to find an alternative low cost adsorbent.

In this work, two vegetable wastes cork bark and grape stalk have been investigated for the removal of two dyes, basic fuchsin and methylene blue. The effect of several parameters such us contact time, dye concentration, pH and temperature on sorption has been investigated. For the comparison sake same experiments were performed by using a commercial activated carbon.

The optimum initial pH values resulted to be: pH 5.8 and 6.6 for basic fuchsin and methylene blue sorption onto activated carbon and grape stalks, respectively and pH 8-9 for both dyes removal by using cork bark. Sorption by activated carbon resulted to be quite faster (4 hours) while 8 hours were necessary for equilibrium achievement in the case of grape stalks and cork bark. Langmuir maximum capacities for activated carbon, grape stalks and cork for basic fuchsin were 80 mg/g, 60 mg/g and 30 mg/g for, and for methylene blue 160 mg/g, 120 mg/g and 20 mg/g, respectively.

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P 186

ELECTROXIDATION TREATMENT FOR TEXTILE WASTEWATER DECOLORATION USING DIMENSIONALLY STABLE ANODES

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Textile effluents have high concentrations of organic and inorganic compounds and strong color, caused by residual dyes that were not fixed to the fibers in the dyeing process, and present as main characteristic high variations of flow and composition, large amount of non-biodegradable compounds, presence of toxic substances, high temperature and high pH value [1]. Electrochemical treatment is a power tool for the purification of this kind of wastewater. This study deals with the treatment in two textile wastewaters, containing disperse dyes by electrochemical oxidation at dimensionally stable anodes (ADS). Two anodic compositions were used: Ti/PtPb(1%)Ox and Ti/PtPd(10%)Ox. The characteristics of the textile wastewater were: pH=6.9, color=24.8 m-1, COD=198 mg/L for wastewater yellow color (YC) and pH=4.1, color= 40.6 m-1, COD=1276 mg/L for wastewater grape color (GC). The values of wavelength that corresponded to the maximum absorbance of textile wastewaters in the visible region, A431 nm= 0.270 and A442 nm= 0.468 in wastewater YC and GC, respectively. Experiments were carried out at applied different potential difference 4, 6, 7, 9 V, type and concentration of electrolyte (NaCl, KCl) and pH values at various electrolysis times. UV-VIS spectra of the electrolysed solutions were recorded and color removal efficiency was determined. For anodic compositions of Ti/PtPd(10%)Ox in the wastewater YC, color removal efficiency was 94% and 97 % COD removal at 7V, 4.0 g/L of KCl and pH of crude wastewater. For anodic compositions of Ti/PtPb(1%)Ox in the wastewater GC, color removal efficiency was 93.5% and 70 % COD removal at 9V, 3.0 g/L of NaCl and acid pH of crude wastewater.

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P 187

SORPTION CAPACITY OF FOUNDRY SANDS FOR Cr (VI): pH EFFECT ON SORPTION COEFFICIENTS

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Large quantities of chromium are discharged into the environment as a consequence of its wide use in modern industries. The sorption capacity of foundry sands, industrial waste of the iron foundry industry, was evaluated for the removal of Cr (VI) from aqueous solutions by using sorption batch equilibrium tests. These chemical foundry sands are composed of fine silica sand, furanic resins as binder, chemical catalyst and residual iron particles.

Cr sorption in a specific material depends heavily on experimental conditions such as pH, metal concentration, material composition, competing ions, and particle size. In this study, discontinuous sorption tests were performed in duplicate, using 100 mL polypropylene bottles at 20º C containing 2 g dry mass of foundry sands and initial Cr concentrations between 10 and 100 mg/L as $K_2Cr_2O_7$. The initial pH value was adjusted to 2.5, 4.0 and 6.0. Test time was set at 72 h, which was found to be enough to ensure equilibrium. Control tests without sands were used as blanks to estimate losses of Cr during the test procedure. Sorption coefficients were obtained by fitting the sorption data with Langmuir isotherm models.

High removal capacities for Cr (VI) of foundry sands (70%) were achieved at pH 2.5. Decreasing pH results in the formation of more polymerised Cr oxide species. The sorption active sites of the adsorbent becomes highly protonated, as can be silanol ($SiOH_2^+$), aluminol ($AlOH_2^+$) and phenol ($C_6H_5OH_2^+$) groups, and favours the uptake of Cr (VI) in the anionic form, under acidic conditions. Langmuir sorption coefficients of foundry sands were 1.18, 0.97, 0.90 mg/g at pH 2.5, 4 and 6, respectively, which are similar to other waste and by-products which could be used in permeable reactive barriers (PRBs) as an alternative treatment for polluted groundwater.

P 188

WATER SAVING POSSIBILITIES AND REUSE IN SLOVENE TEXTILE COMPANIES

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Sustainable water use becomes one of the most important issues in European water policy. Textile finishing industry is very water intensive. For development of strategies for water treatment and reuse, complete characterization of water related textile process effluent streams is needed. This paper presents the systematic analysis of all relevant water related processes in two textile finishing companies. All individual discharges connected to textile processes relevant on yearly basis were collected and characterized by physical-chemical parameters. The diversity of waste discharges characteristics vary significantly. Some streams were very polluted what was expressed in high conductivity, absorbance, COD and total suspended solids. Other streams were not so concentrated and after proper treatment the quality of recycled water could be good enough for reuse purposes. Selected waste streams from different textile processes (like dyeing, washing, rinsing) were treated by membrane techniques and AOP separately or with different combinations of both techniques. Reclaimed water was used in laboratory dyeing experiments on cotton, simulating real textile production process. Dyed cotton material with reclaimed water was checked by colour matching studies and compared to the quality of the material dyed with softened process water. On the basis of such methodology several reuse options could be proposed for both companies.

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P 189

EXPERIMENTAL STUDY OF OILY WASTEWATER TREATMENT BY NOVEL HYBRID BAFFLED BIOREACTOR

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Oil refineries, petrochemical factories and oil platforms produce a large amount of oily wastewater every day. If these wastewaters are released in environmental, it can damage soil and water seriously. Although, Biological treatment of oily wastewaters is a well-established method for remediation of these wastes, efficiency of conventional systems such as Activated Sludge, aren't very high. We have designed a new bioreactor system to increase the efficiency of treatment by (1) allowing greater organic loads, (2) increasing microbial concentration by using attached and suspended bacteria, and (3) increasing stability and resistance to hydraulic and organic shocks. Novel media used in this Fixed-Film bioreactor provides a high surface area-to-volume ratio (600 m^2/m^3) which increases MLSS in the reactor. Reactor Biodegradability for COD *(Chemical Oxygen Demand)* and TPH *(Total Petroleum Hydrocarbon)* is evaluated for different Hydraulic Retention Time and oil pollution concentration. The best COD and TPH removal is reported in TPH= 300 $mg.L^{-1}$ in HRT= 48 hr, but optimized performance is reported in HRT= 24 hr and TPH= 300 $mg.L^{-1}$. Existing CAS (Conventional Activate Sludge) plants can be upgraded by changing the reactor configuration and introducing support media into aeration tank.

Key words: Oily wastewater, Hybrid baffled reactor, Biofilm, COD and TPH removal

P 190

ASSESSMENT OF CONTAMINATION OF SEWAGE SLUDGE AND WASTEWATER FROM WASTEWATER TREATMENT PLANT BY DRUG RESIDUALS

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A method for determination of drug residuals in wastewater and sewage sludge from wastewater treatment plant has been developed. Selected sulfonamide and diaminopyrimidine antibiotics, which are used in human and veterinary medicine, were selected as target compounds. They are discharged to the sewer systems together with the urine and faeces and enter the sewage treatment plant, where they are not completely removed. They can be found in treated wastewater or in sewage sludge. They can enter to the environment, where they can induce negative effects on organisms in soil and water ecosystem. An optimized method was used for identification and determination of these antibiotics in real samples from the large-scale wastewater treatment plant in Brno-Modřice and from the wastewater treatment plant situated in the area of Veterinary and Pharmaceutical University Brno. Antibiotics were extracted from sewage sludge by ultrasonic and by pressure solvent extraction (PSE). Wastewater and sewage sludge real samples were concentrated and cleaned by solid phase extraction (SPE). For determination these antibiotics high performance liquid chromatography with diode array detector (HPLC–DAD) was used.

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P 191

BORON REMOVAL FROM AQUEOUS SOLUTIONS BY CALCIUM ALGINATE GEL BEADS AND AMBERLITE IRA-743

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Boron is extensively used in industrial applications. The discharge of boron containing wastewater to the environment causes several pollution problems. In this work the removal of boron from aqueous solutions was carried out in batch system. At the same time is proposed the bioadsorption technical for the elimination of boron from polluted waters using adsorbents manufactured with naturals polymers. Calcium alginate gel beads were used as adsorbent in different alginate concentrations (1.6%, 2.4%, 3.2%). It was demonstrated that this biopolymer can be used effectively for boron removal. In addition, it was used the commercial resin Amberlite IRA 743 to compare with our biopolymers proposed. The parameters studied affecting the process performance were pH [3, 11], initial boron concentration and concentration of alginate in the beads (1.6%, 2.4%, 3.2%). Maximum boron removal obtained at pH 11 and 25ºC was 44.43 mg/g using calcium alginate beads and 18.17 mg/g employing Amberlite IRA 743. In the isotherm studies, Langmuir and Freundlich isotherms model were applied and it was determined that the experimental data conformed to Langmuir isotherm model.

Keywords: Boron removal, alginate gel beads, bioadsorption

P 192

BIOSORPTION OF ACID BLACK 1 AND ACID YELLOW 25 FROM AQUEOUS SOLUTIONS BY CHITOSAN. COLUMN STUDIES

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This research analyses a mixture of dyes and the influence of one on other, from aqueous solutions on chitosan column. Acid Black 1(AB1) and Acid Yellow 25 (AY25) were the dyes chosen for this study. First, the individual dynamic adsorption capacity of AB1 and AY25 was determined. The influence of the variation of initial dye concentration and adsorbent mass was studied. Three experiments were carried out for the mix dyes studies at different concentrations: 1) [AB1]=[AY25]= 25 mg/L 2) [AB1]= 50 mg/L; [AY25]= 25 mg/L and 3) [AB1]= 25 mg/L; [AY25]= 50 mg/L. In all cases the pH solutions and flow velocity were 2 and 1.5 m/h, respectively. Column data obtained at different conditions were described using Adams-Bohart and Thomas models. The breakthrough curve prediction by the Adams-Bohart and Thomas models were found to be very satisfactory for the individual experiments. In the case of the mixture of the dyes the breakthrough curve prediction by the models notably diverted from the experimental results. The experimental results show that AY25 has an inhibiting effect on AB1's capacity of adsorption on chitosan, proving AY25's greater affinity with chitosan.

O 22

THE FORMATION AND STABILITY OF N-NTIROSAMINES AND N-NITRIAMINES IN THE ATMOSPHERE: A THEORETICAL STUDY

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Aliphatic amines emitted to the atmosphere will react with OH rapidly to form alkylamino radicals, which may take place subsequent reaction with NO and NO_2 to produce nitrosamines and nitroamines. It is known that nitrosamines and nitroamines are extremely carcinogenic class of compounds. Nitrosamines have been found in food, tobacco smoke, and even drinking water. EPA has placed a limit of $(CH_3)_2NNO$ (NDMA) in drinking water of 3 ng/L. Therefore, it is necessary to understand the formation of these compounds, and the possibility of their photolysis loss in atmosphere condition.

The reactions of the CH_3NH and $(CH_3)_2N$ radicals with NO have been studied by quantum chemistry methods. The results show that the formations of CH_3NHNO and $(CH_3)_2NNO$ are similar, and that the isolated molecules are both thermally very stable, and the formation process takes place via a barrierless addition of the initial reactant. Because of high barrier surpass, other products such as imines, HNO and HON could be neglected. The reactions of the CH_3NH and $(CH_3)_2N$ radicals with and NO_2 have been studied at the same time, and nitroamines are the dominant product similarly.

The calculated excitation energy for the first excited state of these nitrosamines and nitroamines indicates that nitrosamines are easily to photolyse, while nitroamines are difficult to undergo photolysis under sunshine.

O 23

HETEROGENEOUS OZONOLYSIS OF TRIFLURALIN AND ISOPROTURON

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Early studies have shown that during agricultural treatments 30 to 50% of the pesticides applied is lost into the atmosphere. Therefore, a comprehensive knowledge of the atmospheric behaviour of these compounds is required in order to understand their environmental fate. Due to their low volatility, a significant fraction of these pesticides will integrate into the atmospheric particulate phase and undergo heterogeneous degradation. However, only gas phase reactivity is currently taken into account in atmospheric lifetime estimations since heterogeneous degradation mechanisms are very complex and only little is known about them. As a result, disagreement is often observed between the predicted (hours to days) and the observed (several weeks) atmospheric residence times.

In this study, the heterogeneous reactivity of trifluralin and isoproturon to ozone was investigated in order to better understand their atmospheric fate. An experimental setup for determination of absolute kinetic rate constants for ozonolysis was optimized for both high and low reactive compounds. The pesticides were first adsorbed on silica particles surface by liquid/solid adsorption technique. The coated particles were then placed in a 500 mL round flask reactor connected to a rotating evaporator (specifically modified) and continuously exposed to a constant flow of ozone. The kinetics of ozonolysis was studied as a function of exposure time and/or ozone concentration (in the dark, at 25°C and under dry atmosphere) by analysing remaining pesticides on particle surface by HPLC-UV.

The trifluralin degradation constant seen under the conditons used is consistent within a factor 3 to our previous data (Pflieger and al., Atmospheric Environment 43 (2009) 5597–5603) in flow through reactor, which validates our experimental setup. The atmospheric lifetime of isoproturon regarding ozonolysis was found to be in the order of few days while trifluralin's was more than one month. Product identification studies are being performed in order to elucidate the degradation mechanisms.

O 24

SOURCE APPORTIONMENT OF VOLATILE ORGANIC COMPOUNDS IN BELGRADE SEMI-URBAN AREA

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Volatile organic compounds (VOCs) are very important local and regional atmospheric pollutants. They play a significant role in tropospheric chemistry by affecting OH radical concentrations and the production of secondary air pollutants: tropospheric ozone and secondary organic aerosols.

In order to assess the ambient levels and possible origin, concentrations of thirty one compounds were measured on-line using Proton Transfer Reaction Mass Spectrometer (PTR-MS), in February, 2010. PTR-MS allows real-time measurements of VOCs in the air, with a high sensitivity and a fast time response. One-hour mean values have been calculated and used for further analyze.

The most abundant compound was propanol followed by methanol, propene, and acetaldehyde with mean concentrations of 58.6, 27.7, 23.4 and 20.9 μg m^{-3} respectively. Average concentrations were high for benzene, 10.5 μg m^{-3}, and very high for 1,3-butadiene, 5.1 μg m^{-3} , with 1-h maximums of 212.1 and 76.6 μg m^{-3} respectively - well above the regulatory limit (for benzene regulatory limit settled by European air quality standards is 5 μg m^{-3}, annually). High concentrations of benzene and 1,3-butadiene in the ambient air are worrisome and pose a threat to human health, especially knowing that they may cause cancer and leukaemia during a long, chronic exposure.

Positive Matrix Factorization (PMF) receptor model was used for source apportionment purpose and four main source profiles were identified. Biomass burning was the most significant source with average contribution of 40% followed by sources associated with solvent use (25%), traffic (23%) and various local productions (12%).

P 193

IDENTIFICATION OF CITY AREAS WITH SIMILAR AIR POLLUTION BEHAVIOURS: PM_{10} IN LONDON

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The aim of this study was to apply principal component analysis (PCA) to identify city areas with similar air pollution behaviour. PCA was applied to hourly average PM_{10} mass concentrations measured at 27 monitoring sites of the London air quality monitoring network during the period from January 2000 to December 2009. The monitoring sites were selected according their efficiency in the study period.

It was observed that the hourly average PM_{10} mass concentrations were decreasing along the selected period, having the maximum in 2003 for all monitoring sites. The number of principal components was selected to have 95% of the original data variance. Analysing the frequency that the monitoring sites are grouped in the same principal component, nine city areas with specific PM_{10} behaviour were identified. Some monitoring sites presented redundant measurements during all studied period, being possible to remove them to decrease the costs relative to their maintenance.

P 194

MASS AND ELEMENTAL CONCENTRATIONS OF AIRBORNE PARTICULATE MATTER COLLECTED IN THE CITY OF MEGALOPOLIS (SOUTHERN GREECE)

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Particulate matter measurements are of great interest due to the fact that epidemiological studies have linked the inhalation of urban aerosol with adverse health effects on human, which depend not only on their diameter, but on their chemical composition as well. In this study, daily aerosol samples for PM10 were collected at one site in the centre of the city of Megalopolis (southern Greece) located in the vicinity of 2 lignite-fired power plants. The sampling was conducted from March 2009 to August 2009 by a low volume air sampler on PTFE filters. The mass concentration of the PM10 samples was measured gravimetrically and ranged between 4,0 and 53,3 μg m^{-3} with an average value of 24,6 μg m^{-3}. The elemental composition of the particles was analysed using XRF spectroscopy and the concentrations of K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and As were determined. The concentration of the Black Carbon on the filters was also measured. The Pearson correlation coefficients of the measured parameters were calculated in order to examine the possibility of a common source.

P 195

MODELLING OF GAS-PARTICLE PARTITIONING OF PCB AND PAH ACCORDING TO AB/ADSORPTION APPROACH

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The objective of the study was to assess the consistency between the gas-particle partition coefficient of selected PCBs and PAHs predicted by the ab/adsorption Dachs-Eisenreich model and the experimental results gained within the field measurements. A total number of 129 air samples was obtained from 24 urban, industrial and background monitoring stations in three countries of Former Yugoslavia. Conventional high volume sampling method was applied, with quartz filters for collecting the atmospheric particles and polyurethane foam filters (PUF) for retaining the free gas molecules of PCBs and PAHs.

The gap between the predicted and measured K_P values was less than one order of magnitude for the most of selected PCBs congeners. Particle bound fractions of the lower chlorinated PCBs (PCB 28, PCB 52 and PCB 101) predicted using the ab/adsorption model was significantly lower in comparison with values obtained during the sampling campaign (ϕ measured/ϕ predicted>1). The results on modelling of the atmospheric distribution of PAHs using the Dachs-Eisenreich model showed deviation between the measured and predicted ϕ values less than one order of magnitude for Flo, Phe, Ant, Flu, Pyr, B(a)A and Chr. For the PAHs of high molecular weight, B(b)F, B(k)F, B(a)P, I(1,2,3-cd)P, D(ah)A and B(ghi)P, very good agreement was confirmed.

P 196

THE IMPACT OF HEAVY METALS FROM AIRBONE PARTICLES IN AN URBAN AREA

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Trace elements are part of the atmospheric pollutants and their determination in the total air particulate, as well as in the corresponding inhalable fraction, represents an important parameter in the evaluation of the possible implications in the public health. The analysis of the elemental composition plays an important role in the chemical characterization of particulate matter (PM) and provides interesting data, not only for the evaluation of its impact on human health, but also for the identification of emission sources. The sampling station used in this work is located in the urban area of Bilbao, north of Spain. PM sampling was performed by using low volume samplers (2.3 m^3h^{-1}) equipped with IND PM_{10} and $PM_{2.5}$ inlets and Whatman quartz microfibre filters (QMA 1851-047). The sampling was carried out daily for PM_{10} and $PM_{2.5}$, respectively, during the study period (January 2006 – December 2008) fractions of each filter were bulk acid digested for the analysis for trace elements (Cr, Ni, Cd, Cu, Mn, Fe, Pb y As) using ICP-MS Agilent 7500a. The highest average annual PM_{10} and $PM_{2.5}$ concentrations were registered in 2007 with 32 and 21 $\mu g \cdot m^{-3}$, respectively. The correlation of particulate pollutants with the wind direction allowed us to identify the origin of polluted air masses. It was concluded by rose wind plot that the direction of PM source was south-east, from A-8 highway. The time series of Cd, Mn y Pb show a clear decrease (18, 13 and 23 %) during the study period, instead As increases 16%. The source identification was carried out by principal component analysis. Factors with high eigenvalues were considered. Four metal sources were identified: Vehicular emissions, Industrial I, Industrial II and crustal material.

P 197

CONTINUOUS MEASUREMENTS OF ULTRAFINE PARTICLES AT URBAN BACKGROUND SITE OF LJUBLJANA

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Concentrations and size distributions of atmospheric particles were measured continuously over a period of one month at an urban background sampling site in Ljubljana, Slovenia. The sampling site is located on the bank of the Ljubljanica River at the eastern part of Ljubljana, and was selected because of its proximity to the city centre (10 km) and its partially rural setting. A long-term data set of aerosol particle size distributions (10–1100 nm) was utilized in the urban background air of Ljubljana in May 2010 using a Grimm Scanning Mobility Particle Sizer (SMPS+C). The meteorological and air quality parameters were obtained from the nearest meteorological and air quality monitoring station Ljubljana Bežigrad.

An average total particle concentration of 7900 cm–3 and an average particle size of 56 nm were obtained. Further, the total particle concentrations (diameter 10–1100 nm), the ultra-fine particle concentrations (diameter 10–100 nm) and the fine particle concentrations (diameter 100–1100 nm) have been analyzed and their correlations with the relevant meteorological and air quality parameters – temperature, atmospheric pressure, relative air humidity, wind speed and direction, precipitations, particulate matter concentration (PM10) and concentration of air pollutants O3, SO2, NOx – sought. Precipitation appears to have a major influence on particle concentration. However, strong correlations were also found with relative air humidity, temperature, and wind speed and direction. For further data evaluation, classic induction algorithms in machine learning tool, including regression trees, linear regression, k-nearest neighbours and bagging are foreseen.

Keywords: ultrafine particles, meteorological parameters, particle size distribution, correlation

P 198

FOLIAR METALLIC MICRO AND NANOPARTICLES UPTAKE BY PLANTS EXPOSED TO INDUSTRIAL ATMOSPHERIC FALLOUTS

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During the last decade, the proportion of fine and ultra fine particulate matters (PM) have increased in the atmosphere with recycling activities and the use of more effective filters in industry. Metal uptake by plants occurs by direct transfer of contaminants from the atmosphere to shoots, especially in kitchen gardens near industrial plants (Uzu *et al.*, 2010).

This study is therefore focused on lead-rich micro- and nanoparticles particles emitted by a lead battery recycling facility and on their fate after foliar absorption by plants. Several contrasted plants (lettuce, parsley, vine and ray-grass) were exposed 1 month in the courtyard of a secondary lead smelter under atmospheric contamination. A geotextile membrane avoided root transfers. Five plants of each species were harvested every 2 weeks. Their shoots and roots were cut, washed and dried; metal concentrations were determined by ICP-OES or ICP-MS. Shoots were characterized by microscopic observations with Environmental SEM-EDS and TEM-EDS.

First results showed that Pb concentrations raised: 122 ± 5.5 $mg.kg^{-1}$ dry weight (DW) of lettuce shoots (above the UE limit concentration in leave vegetables), 299 ± 33 $mg.kg^{-1}$ DW of parsley shoots and 700 ± 28 $mg.kg^{-1}$ DW of ray-grass shoots (not washed). Microscopic observations had shown a Pb accumulation in leaves and more specifically in necroses zones and in the base of the central vein due to rainfall and watering. Moreover obstruction of stomata was observed. Additional spectroscopic (EXAFS), microscopic analysis (SEM-EDS, Raman) and isotopic (Pb) studies are planned to better understanding foliar pathways.

Reference: Uzu et al., 2010. Environmental Science and Technology 44, 1036-1042.

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O 25

IMPORTANCE OF NATURAL ORGANIC FRACTIONS IN THE PHYTOREMEDIATION OF THE ENDOCRINE DISRUPTOR 4-NONYLPHENOL IN AQUEOUS MEDIA

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The endocrine disruptor 4-nonylphenol (NP) is able to interfere with the hormonal system of animals and humans by imitating the female hormone 17β-estradiol. NP derives principally from the anaerobic degradation of nonylphenol ethoxylates, industrial surfactants commonly used in cleaning products and pesticides. NP enters the environment mostly by the disposal, application and discharge of effluents and sludges produced by sewage treatment plants. Humic acids (HA) and dissolved natural organic matter (NOM) are ubiquitous in soil and water systems and play an important role in the bioavailability and environmental fate of xenobiotic compounds. In this work, we studied the effects of a soil HA and a river NOM separately at concentrations of 10 and 200 ppm (HA_{10}, HA_{200}, NOM_{10} and NOM_{200}) on the capacity of germinating seeds of perennial ryegrass (RY, *Lolium perenne*) and radish (RA, *Raphanus sativus*) to remove NP at concentrations of 1 (NP_1) and 2 ppm (NP_2) from aqueous media. After 7 days (RY) and 5 days (RA) of germination, biometric measurements of seedlings were obtained and the residual NP in the aqueous media was determined by using HPLC analysis and fluorescence detection. The NP_1 and NP_2 alone were not toxic to germinating seeds of both species examined, whereas most of NP combinations with HA and NOM inhibited the germination process. No significant NP degradation occurred in 7 days in all aqueous media in the absence of plants. In the case of RY, the residual NP in NP_1 (63%) was almost halved averagely in the combinations of NP_1 and HA_{10}, HA_{200} and NOM_{200}. The residual NP varied from 54 to 60% in NP_2 and its combinations with HA and NOM, with the only exception of NP_2+NOM_{200} (81%). In the case of RA, the residual NP in NP_1 (about 50%) decreased significantly (16%) in the combination NP_1+HA_{200} and increased (72%) in the combination NP_1+NOM_{200}. The residual NP resulted about 50% in NP_2 and its combinations with HA at both doses and much higher in the combinations with NOM at the two concentrations.

O 26

MERCURY SEQUESTRATION IN SALT MARSHES SEDIMENTS: THE CASE STUDY OF TWO HALOPHYTES WITH DIFFERENT LIFE CYCLES

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Mercury contaminated sediments resulting from "*historical contamination*" are still cause for concern due to its potential release into other environmental matrices. In this study special attention is given to Hg sequestration in the belowground biomass of *Juncus maritimus* and *Scirpus maritimus* colonizing, respectively, 50% and 30% of Ria de Aveiro (Portugal) Hg-contaminated salt marsh area. Both halophytes are annual plants widely distributed in Europe. However, they have different life cycles, i.e, *J. maritimus* has a continuous and slow growth, whilst *S. maritimus* photosynthetic shoots are active for a single growing season and only belowground parts persist into the next year. It has been shown that aboveground senescent plant tissues should not be a significant source of metals to marshes, thus, the main objective of this study is to evaluate how the belowground decomposition rates may affect the sequestration of Hg by these two halophytes. The Hg concentration in *S. maritimus* belowground biomass was 2.3 times higher, respectively 0.54 and 1.25 ng Hg mg^{-1}. After 180 days of decomposition the relatively remaining percentage of Hgin belowground biomass, i.e., Hg bound to cellular structural compounds, was much higher in *J. maritimus* (94%) comparatively to *S maritimus* (49%). This study highlights that the Hg-sequestration capacity of halophytes is species specific. In addition, it is very important to evaluate the ability of salt marsh halophytes to auto-remediate systems, phytoremediation, by reducing mercury availability.

P 199

STUDIES ON THE BIODEGRADATION OF FLUOROANILINES BY A SINGLE MICROORGANISM

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Aromatic amines are considered important environmental pollutants due to their toxic and recalcitrant properties. The widespread use of these compounds in the industry and agriculture has led to their release to soils and waters. Microbial degradation has been found to be the major mechanism to avoid the accumulation of these pollutants in the environment.

Literature studies on the biodegradation of halogenated anilines have mostly focused on chlorinated anilines and very little is known about utilization of fluorinated derivatives. This study focuses on the biodegradation of 2-, 3- and 4-fluoroaniline by a microbial strain (strain F11) identified as *Labrys portucalensis.* This microorganism has the capacity to degrade aerobically fluorobenzene as sole carbon and energy source. Non-induced cells and cells induced in fluorobenzene were used to examine the capacity of the degrading strain to metabolize the target compounds. Co-metabolic studies with fluorobenzene were also conducted. The experiments were run in batch mode at 25ºC with constant shaking. Growth, depletion of the target compounds and fluoride release were monitored.

Strain F11 was capable to completely degrade 2-fluoroaniline. 3- and 4-fluoroaniline were degraded nearly to completion by F11 cultures induced with fluorobenzene and by cultures fed simultaneously with fluorobenzene. The fluoride liberation for those two fluorinated anilines occurred at different extents.

P 200

ECODYNAMICS OF FUNGAL COMMUNITIES IN SOILS CONTAMINATED WITH PAHs

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The polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic compounds of particular concern because of their toxic, mutagenic, and carcinogenic properties. Volatile and particulate PAHs were added (30 and 300 ppm) to microcosms of an agricultural soil already contaminated (0,5 ppm). Phenanthrene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, most present in the initial soil, were added as a mix. At each stage of experimentation (days: 0, 8, 35, 60) fungi and PAHs were quantified. The characterization of the fungal communities was done by determination of ergosterol and the quantification of 18S rDNA by real time PCR. PAHs were extracted by microwave (CEM Mars X) and quantified by GC-MS (Varian).

At low concentrations, we observe the degradation of 93% of PAHs added to soil, especially for benzo(a)pyrene indicating the presence of a specific flora. The degradation is much less effective at 300ppm, but the benzo(a)pyrene is the most degraded to 79%. The fungal community is impacted transiently at day 8, but found a good level at the end of the experiment. Correlations between fungal contents, fungal activities and HAP contents are presented.

The main objective of this multidisciplinary study is to better understand

(i) the dynamics of PAHs in a highly anthropized agricultural soil,

(ii) the ability of endogenous fungi to degrade PAHs,

(iii) the dose effect on communities (from what concentration? At what time? Is there impact on communities?)

(iiii) impact on diversity and community activity

P 201

BACTERIAL DEGRADATION OF THE PHARMACEUTICAL DIAZEPAM, AND RELATED PRODUCTS, IN FRESHWATERS

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Diazepam is a commonly-prescribed pharmaceutical that has been detected in surface waters. Such pharmaceuticals may pose toxicological risks to aquatic environments because of their chemical stability and continuous input to surface waters.

The environmental fate of pharmaceuticals may be biotically- or abiotically-controlled. A recent photo-degradation study of diazepam in water showed that it yielded soluble products, including 2-amino-5-chloro-benzophenone (ACB).

This study investigated the *bacterial degradation* of diazepam and ACB in two contrasting estuaries (the Tamar and Mersey), under environmentally relevant conditions.

Biodegradation was determined in laboratory incubations containing cleaned water (low SPM, DOM and nitrate) collected at the river-estuary interface, with indigenous riverine bacteria added. Substrate concentration changes and potential degradation products were determined using electrospray ionisation-mass spectrometry.

Results to date show that, over a period of 21 days, ca 36% of the diazepam was removed from solution by bacteria, and no metabolic products were detected in solution. Addition of a readily bio-available tri-peptide reduced the bacterial uptake of diazepam to zero. Bacterial removal of ACB from solution was ca 58% after 21 days. However, addition of the tri-peptide increased removal of ACB to ca 84% over the same period. Again, metabolic products were not detected in solution.

It appears that these compounds can be incorporated into bacterial biomass, with the extent of uptake likely depending on the molecular structure of the substrate, and ambient sources of C and/or N. Diazepam uptake was accompanied by a significant reduction in the number of bacterial cells, as determined by DAPI counting.

P 202

TRACE METAL AND METALLOID CONTAMINATION LEVELS IN A FORMER INDUSTRIAL SITE: ACCUMULATION IN SOILS AND NATIVE PLANT SPECIES, EVALUATION OF THEIR PHYTOREMEDIAL POTENTIAL

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Abandoned sites of metallurgical industry represent an important source of environmental contamination by trace metals and metalloids. The former silver smelting factory site of Escalette on the littoral zone south-east of Marseille, whose activity was based on silver-bearing lead and ceased in 1920, is a key site to study metal trace elements (MTE) contamination and transfer, because of its important metal concentrations in soils (referred BASOL: Pb, As, Zn and Sb mainly). The study aimed at defining the extent of the soil contamination, and the accumulation of the MTE and arsenic in naturally growing native plant species, in order to evaluate the MTE environmental risks and to investigate the phytoremedial potential of these plants, the latter representing a promising sustainable technology to remediate metal-contaminated sites. Twenty-two soils were sampled according to the site specificities (on slag deposits, near the chimney, in more vegetated area, in valley), and their characteristics were determined (MTE and arsenic concentration, pH, organic matter, major elements). For each soil sample site, roots and aerial parts from Mediterranean naturally growing plants (6 species, 28 individuals) were collected for analysis.

While total Pb, Zn, Cu soil concentrations varied from 0.075 to 130, 0.2 to 52, 0.01 to 8.0 g kg^{-1}, respectively, and for As from 0.01 mg kg^{-1} to 5.7 g kg^{-1}, those in the plant parts ranged from 0.007 to 1.35, 0.002 to 1.02, 0.007 to 0.2 and 0.01 mg kg^{-1} to 0.183 g kg^{-1}, respectively. Soils contamination exhibited a great variability: the highest contaminated site corresponded to the chimney areas for Pb and As, and to slag deposits for Cu and Zn. Among the plant species naturally growing on this former industrial contaminated site, *Rosmarinus officinalis* L. and *Juniperus phoenicea* L. were capable of accumulating Pb and Zn in the roots at concentrations > 0.5 g kg^{-1}. However, they had low BioConcentration (BCF) and Translocation factors (TF), making them bad hyperaccumulators but potential candidates for phytostabilization. Even if for the less Pb-contaminated sites, *Globularia alypum* L. could be considered as a phytostabilizer (BCF ≥ 1 with low TF), on high Pb and Zn contaminated sites, with aerial parts concentrations over 1 g kg^{-1}, *G. alypum* satisfied the criteria of a hyperaccumulator.

P 203

WATER IN PESTICIDE APPLICATION

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During pesticide application in plant protection a number of preparations, depending on the formulation type, is previously diluted in water, which can originate from a various sources (reservoirs, natural and artificial waterflows) and be of a different quality. Composition and quality of water may vary subject to climatic and seasonal changes and/or natural disasters. For pesticide application water pH, hardness and electroconductivity are of significance, and they can affect physicochemical properties and biological effectiveness of the preparation. The aim of the study is to determine the impact of the water quality on pH value of spray liquids of fungicides (azoxystrobin, mancozeb), insecticides (thiamethoxam, cypermethrin), non pesticide substances (complex fertilizer/NPK, surfactant/trisiloxan) and their mixtures. Spray liquids examined were prepared in quantities for practical application. pH value of spray liquids were determined potentiometrically (pH - meter), immediately after preparation, after 24 hours and in following waters: slightly alkaline (pH 7.55), slightly soft (9.2 d^{o}H), with higher nitrite (0.05 mg/l) and iron (0.76 mg/l) content, with extremely high ammonia content (16.9 mg/l); wells – slightly alkaline (pH 7.90), very hard (34.7 d^{o}H) with a high nitrite content (2.5 mg/l); tap – neutral (pH 7.42), slightly hard (15.4 d^{o}H) and surface (river) – slightly alkaline (pH 8.15), slightly hard (11.7 d^{o}H), with higher content of nitrites (0.18 mg/l) and ammonium (0.93 mg/l). Spray liquids of fungicides, insecticides, surfactants and their mixtures expressed slightly alkaline (7.5-8.2) reactions in all waters, immediately after preparation, and 24 hours following the preparation, referring that their pH remained the same as in check variant, regardless pH of pesticide preparations. Complex fertilizer, and mixtures that contain it (regardless of mixture components) expressed slightly acid to neutral (5.7-6.9) reactions, irrespective from the water quality. Based on the above mentioned findings, it is possible to correct pH value of spray liquids, if optimal conditions for pesticide application require so, or the need for specific substances in plant protection exists.

P 204

VERIFY THE EFFICIENCY OF SEWAGE TREATMENT PLANT OPERATE IN A MANNAR ACTIVATED SLUDGE AT LOW TEMPERATURE

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The present study to compare the efficiency of treatment plant, the city of Misurata a city in Libya, which lies on the Mediterranean Sea (station ALSAKT) that work by activated sludge (Biological Treatment of Wastewater), and for the months of February 2 and November 11 and that the temperature ranges between (15-20) degrees Celsius and (25-30) degrees Celsius respectively, during the different time of the day (9-11-13) AM. The flows ranged within the station 140000 m^3/day for the month of February and (15000-19000) m^3/day for the month of November.

The results were analyzed at a laboratory sewage treatment plant to study the VTSS, TSS, COD, BOD as well as determining the value of the PH and tested to determine the quality of sewage as shown in the curves it clear that this station is capable of treating pollutants very efficiently for the outlet flow achieve values less than standard values for water quality, Saluting the percentage of BOD removed more than 90% and the COD upward of 80% and TSS upward of 80% and the VTSS upward of 80% at low temperature around 17 degrees Celsius. The percentage of BOD removed more than 90% and the COD upward of 85% and TSS upward of 85% and the VTSS upward of 85% at a temperature of 29 degrees Celsius.

It is therefore concluded that with a different temperature to 15 degrees Celsius decrease between seasons did not affect the effectiveness of this treatment and this can be concluded that the method of activated sludge is very effective in wastewater treatment in other countries with low temperatures of up to 15 degrees Celsius.

P 205

STUDIES ON THE USE OF BIODEGRADABLE CHELATING LIGANDS FOR IRON AND ARSENIC BIOAVAILABILITY

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The influence of biodegradable chelating ligands on arsenic and iron uptake by hydroponically grown rice seedlings (*Oryza sativa* L.) was investigated. Even though the growth solution contained sufficient Fe, the growth of rice seedlings gradually decreased up to 76% with the increase of pH of the solution from 7 to 11. Iron forms insoluble ferric hydroxide complexes at neutral or alkaline pH in oxic condition. Chelating ligands produce soluble 'Fe-ligand complex' which assist Fe uptake in plants. The biodegradable chelating ligand hydroxyiminodisuccinic acid (HIDS) was more efficient then those of ethylenediaminetetraacetic acid (EDTA), ethylenediaminedisuccinic acid (EDDS), and iminodisuccinic acid (IDS) in the increase of Fe uptake and growth of rice seedling. A total of 79±20, 87±6, 116±15, and 63±18 mg dry biomass of rice seedlings were produced with the addition of 0.5 mM of EDDS, EDTA, HIDS, and IDS in the nutrient solution, respectively. The Fe concentrations in rice tissues were 117±15, 82±8, 167±25, and 118±22 μmol g^{-1} dry weights when 0.25 mM of EDDS, EDTA, HIDS, and IDS were added to the nutrient solution, respectively. Most of the Fe accumulated in rice tissues was stored in roots after the addition of chelating ligands in the solution. The results indicate that the HIDS would be a potential alternative to environmentally persistent EDTA for the increase of Fe uptake and plant growth. The HIDS also increased As uptake in rice root though its translocation from root to shoot was not augmented. This study reports HIDS for the first time as a promising biodegradable chelating ligand for the enhancement of Fe bioavailability and As phytoextraction.

P 206

UPTAKE OF Cu AND Ni FROM REMEDIATED SMELTER-POLLUTED-SOIL BY TREE SEEDLINGS

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The main aim of this remedation study was to determine the effect of adding clean organic mulch on the metal uptake rates of the planted tree seedlings (*Pinus sylvestris* L., *Betula pubescens Ehrh.*). Study area in Harjavalta, southwestern Finland has been subjected to a heavy pollution load since 1945, due to a large Cu-Ni smelter complex. The area was severely damaged and the understorey vegetation almost completely lacking. Pine and birch seedling were planted in soil pockets (2 L, depth about 20 cm) containing mulch. Six plots (5 x 5 m^2) for both species were established. Half of the plots were covered by a mulch layer by spreading it directly on top of the forest floor. The other half was left untreated (control). The mulch consisted of a mixture of household biocompost and woodchips (saw mill waste). After a 10 year period 3 seedlings from each experimental plot were harvested, and their chemical content was analyzed by ICP-IRIS after dry ashing. On the plots covered by mulch, Cu and Ni concentrations in Scots pine were lower in stems, barks and roots compared to control plots. In addition, we recorded the same results for the woody compartments of Downy birch. On the other hand, concentrations of Cu and Ni in needles and leaves were higher in mulch covered plots, than in untreated plots.

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P 207

DIFFERENTIAL MERCURY ACCUMULATION AND PARTITIONING IN SALT MARSH PLANTS: INFLUENCE OF SOME EDAPHIC FACTORS

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The current study intended to understand the influence of seasonal fluctuations and the vegetation of salt marsh plants (*Halimione portulacoides*, *Juncus maritimus*) on sediment's mercury (Hg) and its pH and redox potential (Eh), as well as their cumulative effect on the plant's Hg-accumulation and -partitioning potential. The area selected for the study was Laranjo Basin at Ria de Aveiro lagoon (Portugal) where a known Hg gradient was existed due to Chlor alkali plant discharge. Three sampling sites (L1, L2, L3) were selected along a transect defined by the distance from the main Hg source. Samples were also collected from the Hg-free site (R). Eh of sediments vegetated by *H. portucaloides* exhibited a gradual increase from March 2006 to February 2007. Although, the vegetation of *J. maritimus* led to a differential Eh response but the vegetation of both the plants did not significantly affect the pH of the sediment at all the sites. Irrespective of the plant vegetation, Hg in sediments gradually increased with a decreasing distance towards Hg-point source. As a whole, *J. maritimus* accumulated Hg more than *H. portucaloides* at all the sampling sites, whereas in root, stem and leaf, the concentration was ranked as: L1>L2>L3 in both the plant species. Moreover, root of both plants exhibited highest Hg concentration compared to stem and leaf. In addition, the leaf of *H. portucaloides* exhibited more Hg than leaves of *J. maritimus*. Overall, the seasonal fluctuations, plant vegetation and edaphic factors showed a significant role in the metals bioavailability to the plants.

O 27

PREPARATION AND CHARACTERIZATION OF TITANIA/SILICA PHOTOCATALYSTS FOR PHOTOCATALYTIC DEGRADATION OF VOCs

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The photocatalytic activity of nanocrystalline TiO_2 powders can be significantly suppressed due to the agglomeration of particles to microsized aggregates. Furthermore, for using TiO_2 as a photocatalyst, its poor adsorption characteristics for organic compounds and its relatively low surface area lead to great limitation in exploiting the photocatalyst to the best of its photoefficiency. In this regard, ordered and disordered mesoporous silica as high-surface-area supports were impregnated with different amounts of aqueous TiO_2 sols, which were synthesized using titanium tetrachloride as a precursor via sol-gel method at low-temperature preparation conditions. The physico-chemical properties of photocatalysts were characterized by X-ray diffraction (XRD), nitrogen sorption (BET), UV-vis spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and high resolution transmission electron microscopy (HR-TEM).

The effects of Ti/Si molar ratio and of the mesoporous silica structure were investigated towards measuring the adsorption capacity and photocatalytic degradation of volatile organic compounds. Toluene and isopropanol were chosen as two model VOCs for two different gaseous photoreactor systems, namely fixed-bed and fluidized-bed reactors coupled on-line with FT-IR and GC-MS analyzers, respectively. The results obtained from two different solid-gas photoreactor systems confirm the beneficial influence of the mesoporous support on the low-temperature prepared titania for the removal of an organic contaminant from the gaseous phase in the dark adsorption as well as in the photocatalytic stage of the process.

O 28

PHOTOCATALYTIC HYDROGEN PRODUCTION FROM ETHANOL OVER TiO_2 NANOFIBRE BASED CATALYSTS

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Generation of hydrogen from renewable feedstock, such as ethanol, by photocatalysis in aqueous phase is one possibility for environmentally benign energy production. TiO_2 based catalysts have been studied intensively for their favourable band-gap energy and stability. Especially TiO_2 nanofibre (TiO_2 NF) catalysts provide high active metal surface area and good active metal distribution. Based on the literature, platinum group metals are reported to enhance the photocatalytic activity. [1-3] The aim of this work is to study TiO_2 nanofibre derivatives (doped and/or decorated) for photocatalytic hydrogen production and compare them with traditional TiO_2 nanoparticle based catalysts.

The experiments were done with ethanol-water mixture (molar ratio of 1:3) at room temperature under UV-B irradiation. According to the results, studied TiO_2 NFs are promising materials in photocatalytic hydrogen production from ethanol. Doping and/or decoration were found to enhance the hydrogen production.

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P 208

PHOTOCATALYTIC ACTIVITY OF BiVO$_4$ SYNTHESIZED BY A MODIFIED METAL-ORGANIC DECOMPOSITION METHOD

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Nowadays, a challenge for researchers is to find a new photocatalyst with a higher photocatalytic activity in the visible light of the solar spectrum than the existent ones. Because the *6s* orbitals of Bi^{3+} in mixed oxides form a level above the valence band due to their overlap with the O *2p* orbitals, reducing in this way the band gap for visible light absorption and facilitating the hole mobility, Bi^{3+}-based oxides are good candidates for new visible light driven photocatalyst materials. In the last years, considerable attention was focused on bismuth vanadate, $BiVO_4$, because of its good photocatalytic properties, suitable for water splitting and organic pollutant decomposition under visible light irradiation. The photocatalytic activity of $BiVO_4$ is strongly influenced by the crystal structure. Recently, the monoclinic structure has been recognized to have better photocatalytic activity than the tetragonal $BiVO_4$. We developed a modified metal-organic decomposition method to synthesize polycrystalline bismuth vanadate. This method allows an easy preparation of the single phase monoclinic BiVO4, in an environmental inert solvent, ethanol, and at temperatures below 500°C. Different analysis techniques like X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermal analysis (TG and DTA) were employed to characterize the synthesized BiVO4 photocatalyst. UV-vis spectroscopy was further used to determine the optical properties of the monoclinic BiVO4. The photocatalytic activity of the novel structure was evaluated by the degradation of organic pollutants in aqueous solutions under visible light irradiation.

P 209

MAGNETICALLY RECOVERABLE PHOTOCATALYTIC NANOCOMPOSITE PARTICLES FOR WATER TREATMENT

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Oxidative decomposition using anatase (TiO_2) as the photocatalyst can be effectively used for the purification of polluted water. In the process of photocatalysis a large surface area is required for the photocatalyst. This can easily be achieved when the photocatalyst is prepared in the form of nanoparticles and dispersed in the polluted water. However, there is a problem related to the difficulty in completely eliminating the nanoparticles from the water after the purification, which can result in leaching of the nanoparticles into the environment. One of the possible solutions to this problem involves the immobilization of the photocatalysts on magnetic carriers, which allows them to be eliminated from the water suspension after cleaning using an external magnetic field.

In this study, magnetic carriers in the form of clusters (100–200 nm in size) of superparamagnetic maghemite (γ-Fe_2O_3) nanoparticles (15 nm) were coated with a photocatalytic anatase layer using an original, low-temperature process based on the hydrolysis of aqueous $TiOSO_4$. The magnetically recoverable photocatalytic particles were tested in the photocatalytic decomposition of model organic pollutants in water. The influence of the structural properties of the particles, such as the size, the morphology, the thickness and crystallinity of the anatase layer, the structure of the magnetic clusters, etc., on the photocatalytic activity and the efficiency of the magnetic separation was evaluated and will be discussed.

P 210

COMPARATIVE ASSESSMENT OF THE PHOTOCATALYTIC EFFICIENCY OF TiO_2 WACKHERR IN VARIOUS TYPES OF WATER SUSPENSIONS

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The aim of this work was to assess the photocatalytic activity of TiO_2 Wackherr by applying UV radiation in distilled, tap and river water suspensions on the example of the degradation of 1.0 mM clopyralid. The degradation kinetics was studied by following the changes of clopyralid concentration using HPLC–DAD, and the degree of mineralization with TOC. It was found that the rate of disappearance of clopyralid is significantly higher than the rate of its mineralization. The study encompassed the effects of the initial substrate concentration (0.25−1.0 mM), the amount of the catalyst TiO_2 Wackherr (0.2–2.0 mg/cm^3), pH (3.5−9.8), temperature (25–40 ^{0}C), electron acceptors and $^{\bullet}OH$ scavenger on the photodegradation kinetics in distilled water. The optimum concentration of the catalyst was found to be 1.0 mg/cm^3 under UV light, with the apparent activation energy of the reaction being 37.9 kJ/mol. The photocatalytic degradation of clopyralid followed the first-order kinetics. The most efficient electron acceptor appeared to be $KBrO_3$ along with molecular oxygen. By studying the effect of ethanol as an $^{\bullet}OH$ scavenger it was shown that the heterogeneous catalysis takes place via $^{\bullet}OH$. Besides, it was found that a four times lower content of TiO_2 Wackherr exhibits even somewhat higher efficiency than the widely used TiO_2 Degussa P25. The investigation of the effect of water quality showed that the rate photodegradation of clopyralid in distilled water is about 2 times higher than in tap and Danube waters and that a dominant influence has the presence of HCO_3^-.

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P 211

PHOTOCATALYTIC WATER TREATMENT BY TiO_2 –BASED CATALYSTS

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The photocatalytic performance of different TiO_2 catalysts (anatase and nanofiber) on water purification was studied by photocatalytic degradation of organic model compounds methylene blue, ethanol and butanol. Some preliminary tests were done with oil. The tests were made in a batch photoreactor. Degradation rate of the compounds and the physical properties of the catalysts were determined and compared to each other and to commercial photocatalyst Degussa P25. Some of the catalysts were studied as powders and as granules. The granules were made by binding the powders onto the surface of a support in order to make separable photocatalysts.

The photocatalytic experiments were carried out in an annular type batch reactor at room temperature using air as the oxidizer. Aqueous solutions of organic compounds and desired amounts of titanium dioxide catalysts (dispersed into the solution) were irradiated by Philips Cleo PL-L 36W -UV lamp with the intensity maximum at 350-360 nm placed in the middle of the reactor. After a 30 min dark period the suspensions were irradiated and the samples were taken periodically, filtered, checked for the pH and analyzed by gas chromatograph or UV-Vis spectrofotometer. The mineralization of the samples was followed by TOC (Total Organic Carbon) and COD (Chemical Oxygen Demand) analyses.

The physicochemical properties of the catalysts were determined by different methods e.g. BET surface area and XRD. The results from this research indicate that the studied materials are promising catalysts for photocatalytic water treatment.

P 212

MnO_x NANOPARTICLES AS CATALYSTS FOR THE DECOMPOSITION OF ORGANIC DYE

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One of the major challenges in environmentally-benign catalysis is the search for highly active and stable catalysts for the selective oxidation of organic substrates. Catalytic oxidations in the liquid phase generally employ soluble metal salts or complexes in combination with clean, inexpensive oxidants such as O_2 or H_2O_2. Driven by the industrial advantages of heterogeneous catalysis, particular focus of research is placed on the identification and investigation of cheap, efficient and environmentally friendly solid catalysts. In order to obtain recyclable as well as stable catalysts, it is often preferred to isolate and stabilize the redox-active metal species by incorporating them into inorganic matrices.

Manganese is one of the most intensively used elements for redox catalysis. Recently, we stabilized MnO_x nanoparticles into a new inorganic matrice based on mesoporous silicate with interparticle porosity denoted as KIL-2. Efficient decoloration and deep oxidative destruction of organic dye (*i.e.* methylene blue) using prepared MnO_x/KIL-2 as catalyst and H_2O_2 as an oxidizing agent, which was investigated in a wide range of operating and reaction conditions, proved that the examined material is a promising catalyst in environmentally friendly applications due to its structural characteristics, hydrothermal stability as well as non-toxic and cost-effective nature.

P 213

PHOTOCATALYTIC ACTIVITY AND ANTIBACTERICIDAL EFFECT OF Au–DOPED TiO_2 THIN FILMS UNDER VISIBLE LIGHT

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Au-doped TiO_2 thin films were prepared in order to extend light absorption of the thin film photocatalyst toward the visible light range. Sol-gel method using $TiCl_4$ as a precursor was used. Colloidal gold was added directly into the sol. Thin films were deposited on silica-coated soda-lime glass by a conventional dip-coating technique. Thin films were heat treated for 30 minutes at 500 °C.

The photocatalysts were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), UV-Vis spectroscopy, thermogravimetric (TG) analysis, differential scanning calorimetry (DSC) and contact angle measurements.

Photocatalytic activity under UVA and visible light was estimated by measuring the decomposition rate of aqueous solution of azo dye Plasmocorinth B (40 mg/L).

Decomposition rate of the azo dye was higher under UVA light, whereas decolorisation under visible light occurred after longer exposure time.

Antibactericidal effect under visible light of Au-doped and undoped thin films was tested on *E. coli* cells. Preliminary tests have shown antimicrobial activity on Au-doped TiO_2 thin films under visible light.

P 214

DEVELOPMENT OF TiO_2 PHOTOCATALYTIC FILMS WITH ANTIMICROBIAL PROPERTIES

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The use of aggressive chemicals such as detergents, alcohols and chlorine components for manual disinfection of surfaces is usually rather unfriendly to humans and the environment and has also many others weaknesses. Disinfection with the UVC light is usually not satisfactory, it is associated with increased energy utilization and occupational risk. Concerning water treatment, chlorine reacts with the natural organic matter in water to produce various undesirable chlorinated disinfection by-products (DBPs). In addition, chlorination of water has been associated with taste and odour problems. Free chlorine is also ineffective in controlling all relevant waterborne pathogens. Alternative disinfection processes include ozonation, use of chlorine dioxide, advanced filtration processes, electrolysis and UVC light radiation among others. However, even though they can be effective, many of them require expensive chemicals or costly equipment. Ozone also forms carcinogen bromate and other brominated DBPs in waters with elevated bromide. Immobilized photocatalysts like TiO_2 photocatalytic films, treated in a proper way through their whole lifecycle (i.e. through production, use, disposal, destruction or/and recycling) seems promising alternative to the previous mentioned disinfection techniques. Our TiO_2 photocatalytic films on stainless steel or ceramics, prepared by low-temperature sol-gel process, expressed antimicrobial activity towards model prokaryote and eukaryote *Escherichia coli* and *Saccharomyces cerevisiae*. Antimicrobial activity of different TiO_2 films, developed for self-cleaning ceramic tiles or wastewater cleaning, was evaluated by colony count and by following metabolic activity (XTT assay), concentration of cells (by measuring optical density (O.D.) at 595 nm) or cell viability (LIVE/DEAD® assays, Invitrogene) using microtiter plate reader.

P 215

DIRECT AND INDIRECT PHOTOCHEMICAL REACTIVITY OF PERFLUOROOCTANOIC ACID (PFOA) IN CONDITIONS REPRESENTING SURFACE WATER

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Potential of perfluorooctanoic acid (PFOA) to degrade via indirect photolysis in aquatic solution under conditions representing surface water was studied. PFOA does not absorb solar radiation by itself, but may be potentially transformed by the natural sensitizers present in natural waters such as dissolved organic matter (DOM), nitrate or ferric iron. Reaction solutions containing purified water, fulvic acid (representing DOM), nitrate, ferric iron or sea water from the Baltic Sea were spiked with PFOA with targeted concentration of 150 ng/L and irradiated with an artificial sun (290-800 nm). In comparison similar samples were also irradiated under 245 nm UV-C light in order to study the direct photolysis in a wavelength known to be absorbed directly by PFOA. UV-C radiation decomposed PFOA to perfluoroheptanoic-, perfluorohexanoic- and perfluoropentanoic acids suggesting that PFOA was (sequentially) degraded via decarboxylation. The amount of decomposition products was greatest in the reaction solution containing purified water. In contrary to previous studies ferric ion did not seemingly enhance the defluorination and decomposition of PFOA. The samples irradiated with artificial sun contained no decomposition products and no decrease in PFOA concentration was observed. The photochemical half-life for PFOA in the environment was estimated to be at least 85 years in the surface layer. In the mixing layer of the open ocean the photochemical half life of PFOA was estimated to be 1700 years and in coastal ocean even 8500 years. This study concludes that PFOA is extremely persistent in the nature since there is not known degradation path in environmental conditions. Therefore it is extremely important to further restrict the use of PFOA, avoid its leakage to the nature, develop the decomposition methods in the industry and search for environmentally degradable substitutes for PFOA.

P 216

PHOTODEGRADATION OF ZANAMIVIR AND RIBAVIRIN UNDER SIMULATED AND NATURAL SOLAR IRRADIATION: IDENTIFICATION OF TRANSFORMATION PRODUCTS BY MEANS OF HILIC CHROMATOGRAPHY AND QTOF MS

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Several countries have augmented the stockpiles of zanamivir as an alternative to oseltamivir in the event the 2009 H1N1 swine flu neuraminidase acquired resistance. Ribavirin constitutes the standard treatment of chronic hepatitis C in combination with Interferon. The WHO estimates that about 170 million people is infected with the hepatitis C virus. Therefore, big amounts of these drugs are consumed worldwide and might reach the environment via human excretions or improper disposal. Prasse et al. has identified the antivirals has an emerging pharmaceuticals class of environmental concern.

In this work we have studied their susceptibility to photodegradation. Irradiation experiments have been carried out both under simulated solar irradiation (Suntest CPS) and direct sunlight in Autumn/Winter season. Identification of transformation products and photolysis kinetics were assessed by hydrophilic interaction chromatography (HILIC) coupled to time of flight mass spectrometry (QTOF) or low resolution MS/MS.

Ribavirin is extremely resistant to photodegradation. Under artificial irradiation intensity of 1800 kJ/m^2/h ribavirin degraded negligibly ($t_{1/2}$ ~26 days) and virtually did not degrade under sunlight during 17 days in pure water. Nevertheless, degradation was noticeable in surface water (($t_{1/2}$ ~62 days). Zanamivir degraded much faster with a $t_{1/2}$ ~1.6 h in MilliQ water but the degradation rate was retarded in more complex matrices containing bicarbonate, nitrate or humic acids. Under natural sunlight photodegradtion was negligible in pure water and quite lengthy in surface water ($t_{1/2}$ ~48 days). Three transformation products were tentatively identified and elucidated with $[M+H]^+$ ions: m/z 112, 323 and 333. Nevertheless, only the TP 112 was found in degradation assays at 20 ppb initial concentration of zanamivir but the persistence was considerable reaching a maximum abundance between 30-60 h under artificial irradiation.

P 217

SYNERGY BETWEEN OZONATION AND TiO$_2$ PHOTOCATALYSIS FOR OXIDATION OF ORGANICS IN WATER

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Combination of two different advanced oxidation processes, such as TiO$_2$ photocatalysis (O$_2$/TiO$_2$/UV) with auxiliary oxidants, such as O$_3$, H$_2$O$_2$ etc. often leads to a synergic effect between the two combined processes. In our present work, photocatalytic ozonation process (O$_3$/TiO$_2$/UV), i.e. O$_2$/TiO$_2$/UV coupled with ozonation, was studied in detail. Slightly acidified aqueous solutions of two different organic solutes (thiacloprid and dichloroacetic acid - DCAA) were irradiated by UVA-emitting lamps in the presence of suspended TiO$_2$ in a circulation batch reactor at constant temperature, while the solution was purged by the mixture of O$_3$ and O$_2$. Various commercial TiO$_2$ catalysts (anatase Millenium powders PC10, PC100, PC500; anatase/rutile Degussa P25 and pure rutile Sakai JRC-TIO-6 were tested. The concentration of dissolved O$_3$ was measured by an ozone-sensitive microelectrode and the degradation of organics was followed by HPLC and TOC analysis.

While P25 is the most efficient catalyst in photocatalytic experiments in O$_2$/TiO$_2$/UV, the activity changes with the introduction of ozone. Compared to oxygen, O$_3$ is more efficient acceptor of an electron from the conduction band of titania and therefore even rutile (ineffective catalyst in O$_2$/TiO$_2$/UV) accelerates the mineralization of organics considerably in the presence of O$_3$. Another observation is a remarkable difference in the synergy extent for different catalysts. A good example is PC500, which adsorbs considerable amounts of DCAA, while this is not evident for PC10 or PC100. When ozone is applied to such system, a 6 times higher mineralization rate of DCAA is noticed compared to a system without the ozone, while such increase is lower than 2 for the other catalysts.

P 218

NANOMATERIALS IN THE ENVIRONMENT: SELF-CLEANING SURFACES WITH PHOTOCATALYTIC ACTION

(Group project at Bachelor's programme in Environment)

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The aim of our project was to produce a nanostructured, self-cleaning TiO_2-thin film at low energy for coating glass and ceramic tiles. Our main objective was to discover which of our preparation methods would give us the best thin film. These thin films have a potential photocatalytic activity and they can be used as self-cleaning surfaces.

Aqueous TiO_2 sol was synthesized using titanium tetrachloride as a precursor via sol-gel method at low-temperature preparation conditions. Thereafter, we applied it directly, or as a powder, in many different experimental methods of depositing the solution on a flat surface. Thin films were deposited on glass and ceramic tiles. The characterization of samples was made by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), N_2-physisorption, contact-angle measurements and fluorescent measurements. Out of 13 different samples the sample 1D gave us positive results; we used sol TiO_2, binder (amorphous silica) and ethanol. Contact-angle measurements showed us that all of the fat (methyl-stearate) was degraded after 48 hours of UVA illumination. The surface was hydrophilic, and water on the film spread. The contact angle between the surface of the glass (or a tile) and the water drop fell rapidly from high values of contact angles (~100°) to low values (~10°). SEM photos showed that the film 1D on ceramic tile is homogenous and crack-free. After fluorescent measurements the comparison of our sample 1D with a German commercial self-cleaning ceramic tile was made and results showed us that sample 1D has much stronger activity.

We have found a method to produce TiO_2 film at low energy with good photocatalytic activity. It is constituted only from TiO_2 sol, amorphous SiO_2 and ethanol, therefore it is environmentally friendly and has no corrosive effects on the laboratory instruments during the preparation.

P 219

PHOTODEGRADATION OF α-NAPHTHALENEACETAMIDE USING SODIUM DECATUNSGTATE AS A PHOTOCATALYST

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It is generally known that large-scale use of pesticides in intensive agricultural practises causes miscellaneous negative impacts on environment, providing one of the most common sources of surface and ground water contamination. This leads to serious risks to human health and to aquatic organisms, and it is important to understand their photochemical behaviour in the environment and to find pathways to remove it from water sources.

α-Naphthaleneacetamide (NAD), a phytohormone pesticide, has been employed in agriculture for many years as fruit thinning agent and to prevent fruit drop before harvest[1]. Since its UV/visible absorption is below the solar spectrum, it is not easily photodegraded under environmental conditions. Polyoxametalates (POM´s) are potential photocatalysts in both homogeneous and heterogeneous media[2]. The POM sodium decatungstate (DTA) has been employed for the efficient photodegradation of pesticides, sometimes with total mineralization[3]. DTA presents the advantage of having a maximum absorption around 320-324 nm, which overlaps with solar spectrum providing the possibility of photo-assisted applications.

We report the photophysical properties of NAD as a starting point for a better insight into its photochemical behaviour. The photocatalytic degradation of aqueous NAD solution by DTA (at 365 nm excitation) in the presence and absence of oxygen is also described. Results will be compared with those for the direct degradation of NAD at λ<290 nm. Both kinetics and the identification of the by-products (by LC/MS/MS), will be reported for each case.

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P 220

Mn-MODIFIED ZEOLITES FOR APPLICATIONS IN OXIDATION CATALYSIS

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Zeolites are used as catalytic supports in chemical reactions [1]. Immobilisation of transition metals into their framework via different synthesis procedures generates different types of catalytically active sites. Manganese is one of the most intensively used elements in homogeneous oxidation catalysis. Incorporation of manganese into zeolite silicalite-1 (MnS-1) via direct hydrothermal synthesis generates catalytically active framework redox centres [2]. MnS-1 is an excellent candidate for applications in environmentally friendly heterogeneous oxidation catalysis due to its structural characteristics, hydrothermal stability as well as non-toxic and cost-effective nature.

Recently, we synthesized MnS-1 nanoparticles with Mn redox catalytically active centres via direct hydrothermal synthesis. Efficient oxidative destruction of organic pollutants, using prepared MnS-1 as catalyst and H_2O_2 as an oxidizing agent, was investigated in a wide range of operating and reaction conditions, proved that the examined material is a promising catalyst in environmentally friendly applications.

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P 221

REACTION OF UV-FILTERS BP-3 AND BP-4 BY AQUEOUS CHLORINE - PRODUCT STUDIES

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Organic ultraviolet (UV) filters are widely used in sunscreens, lipsticks, shampoos, and other personal-care products, as well as coatings and plastics, which may cause them to enter the aquatic environment. Particularly exposed to contamination are swimming pools, where a really thorough protection is needed. Although UV filters must be stable under exposure to UV radiation, recent studies showed that several organic UV filters undergo degradation, mainly by photolysis, but also as a consequence of reaction with chlorine in chlorinated media (e.g., the sea or the swimming pool), because the energy absorbed cannot be internally converted quickly enough, resulting in the molecule remains excited long enough to react chemically [1].

In the present study, benzophenone-3 (BP-3) and benzophenone-4 (BP-4) were applied as model compounds for the stability study of selected UV filters under different experimental conditions, such as pH dependence and presence of sunlight and different clorine-based disinfectants (NaOCl, trichloroisocyannuric acid (TCCA)). To simulate the natural sunlight, the set of 6 polychromatic low pressure mercury lamps (355 nm) in special quartz cell were used. HPLC analysis was used for the monitoring of disappearance of parent compound and appearance of products formed during irradiation. The results showed that BP-3 is highly stable within a broad range of pH (4.0−9.0), but may react with NaOCl and TCCA. In both cases two chlorinated products were observed. Preparative chlorination of BP-3 and BP-4 with TCCA or other chlorinating reagents lead to the formation of 3-chloro- and 5-chloro-2-hydroxy-4-methoxybenzophenone. With excess of chlorinating agent the formation of 3,5-dichloro-derivative was also observed. The detailed mechanism of degradation is still under investigation.

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P 222

POLLUTION AND CULTURE HERITAGE CASE STUDY ON THE WORLD HERITAGE SITE OF GALLE FORT

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The old fortified city of Galle was inscribed by UNESCO as a world Heritage Site in 1988. It was so inscribed because it fulfilled the UNESCO requirement of being a site possessing outstanding universal value under Criteria IV which reads as follows:

"An outstanding example of type of building, architectural or technological ensemble or landscape which illustrates significant in human history."

The first fortification in Galle was built by the Portuguese after they arrived in Sri-Lanka in 1505 and took over the maritime provinces of the country. It was a small fort styled as a Fortaleza. It was called the Swart Bastion (the Black Fort).

The control of the city of Galle was taken over by the Dutch from the Portuguese after a fierce battle in the middle of the 17th century.

The considerably expanded and improved the fort which was erected by the Portuguese according to their (Dutch) distinct architectural style. They also constructed a large number of other utility buildings as they used Galle as their defiance and administrative centre.

Towards the end of the 18th century, Galle was taken over by the British from the Dutch without any fighting through an agreement. Though the British did not make any significant change to the fort itself, they added their architectural style to many buildings inside the fort. The British used Galle as an administrative and commercial center. The harbor located adjacent to the fort was the main harbor in Sri-Lanka until the beginning of the 20th century. Therefore, Galle fort also became the hub for harbor related activities.

The Galle Heritage Foundation is making a lot of efforts to control pollution inside the heritage site. The following overall measures are recommended.

1. Make a detailed study of the pollution factors and hoe they are affecting the heritage site and heritage buildings and what preventive and mitigating action should be taken.
2. The Galle Heritage Foundation together with Department of Archaeology, the Galle Municipal Council and the Urban Development Authority (other main stake holders) should formulate a proper Integrated Pollution Management Strategy and implement it effectively.

P 223

PHOTOCATALYSIS IN ARCHITECTIRAL HERITAGE PROTECTION: CASE STUDY – PETROVARADIN FORTRESS IN VOJVODINA REGION

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Photocatalysis is widely used in environmental protection, but only limited number of studies is devoted to its application in architectural heritage. The complex demands concerning the photocatalytic application in built environment protection arise from a spectra of substrates to be considered (porous and non/porous, ceramics, glass, stone, mortars etc), stability of photocatalytic coatings in real conditions. This is even more pronounced when it comes to the cultural heritage protection, being on the edge of material science and technology, architecture, arts and social sciences. The interdisciplinary approach to the problem is necessary, photocatalysis being a promising methodology for sustainable protection. The case study on the TiO_2 based photocatalytic coating application on the selected segments of 17th century Petrovaradin fortress in Novi Sad, important Danube Region cultural heritage, is presented. The detailed characterization of the stone, brick and mortar materials of the main connecting fortress tunnel, still burdened with traffic, was the initial research phase. Based on chemical, structural, textural and microbiological analysis of the bulk and surface specimens, the restoration methodology was proposed. The photocatalytic coating was developed targeting activity, compatibility as well as durability in real conditions [2]. The active TiO_2 suspension was applied to the selected segments of the tunnel interior and exterior, concerning both aesthetics and restoration demands. The effectiveness of the developed photocatalytic coatings in degradation of both organic and microbial deposits was followed by *in situ* and laboratory testing. The obtained results are promising concerning activity and durability of the coating, pointing out the possibilities of further possible improvement of the photocatalyst formulation and application methods.

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P 224

RISK ASSESSMENT ON BUILDINGS AFFECTED BY INDUSTRIAL AND HARBOUR ACTIVITIES

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Buildings can act as repositories of organic compounds (i.e. PAHs), inorganic components (oxides, heavy metals and so on) and biological material. These pollutants accumulate on the facades usually forming grey-to-black crusts mainly composed by gypsum crystals and the mentioned atmospheric depositions. All this chronic pollution on the buildings must be taken into account in order to determine the proper restoration or demolition process of the building.

In this work a multianalytical methodology based on the use of complementary techniques such as Raman spectroscopy, micro x-ray fluorescence, inductively coupled plasma mass spectrometry, ionic chromatography and gas chromatography mass spectrometry, is proposed for the risk assessment of the building materials. The combination of these analytical techniques allowed us to determine the original composition of the materials as well as to characterise the degradation compounds and the atmospheric depositions in order to propose the deterioration mechanisms involved in their formation.

The studied building was constructed in 1918 and it is located in the metropolitan Bilbao (north of Spain) in an area affected by industrial and harbour activities. The facade of the building is made on sandstone, cement and mortar (including rendering mortar). The high impact of acid gases was demonstrated, since the samples showed 5-10% w/w of soluble salts. Although gypsum was in major concentration levels, the presence of other sulphate and nitrate salts as well as PAHs and toxic metals in concentration levels risky for environment and human health was also stated.

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CONTAMINANTS IDENTIFIED IN SEWAGE EFFLUENT USING A TOF SCREENING APPROACH

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A novel QTof instrument coupled with ACQUITY UPLC, along with the Waters Tof Screening Pesticide Database, and POSI±IVE software data processing, was used to rapidly screen treated sewage effluent that had been extracted using SPE Waters' OASIS HLB cartridges. A generic screening UPLC gradient was used, with a total run time of 2 minutes. The mobile phases used were 10 mM ammonium acetate solution in water and 10 mM ammonium acetate in methanol.

Extracted sewage effluent was successfully screened for pesticide contaminants at ultra-trace level. Use of the MS^E functionality of the QTof instrument enabled the acquisition of exact mass data for both precursor and fragment ions in one screening run, with a high level of reproducibility. The RMS variation in acquired exact mass across a peak for thiabendazole was 1.5 ppm. This provides increased confidence in the detection and identification of compounds present, as result of the accurate and precise exact mass data acquired, and also allowed the use of very narrow chromatographic extraction windows, as low as 0.5 mDa in some instances.

In addition, the use of ChromaLynx XS software for non-targeted spectral deconvolution enabled further discovery and identification of a non-targeted pharmaceutical compound in natural river water during a pesticide screening run. This was confirmed by examination of the high energy MS^E fragment ion data, which exhibited characteristic fragments at the retention time for that compound.

AUTHOR INDEX