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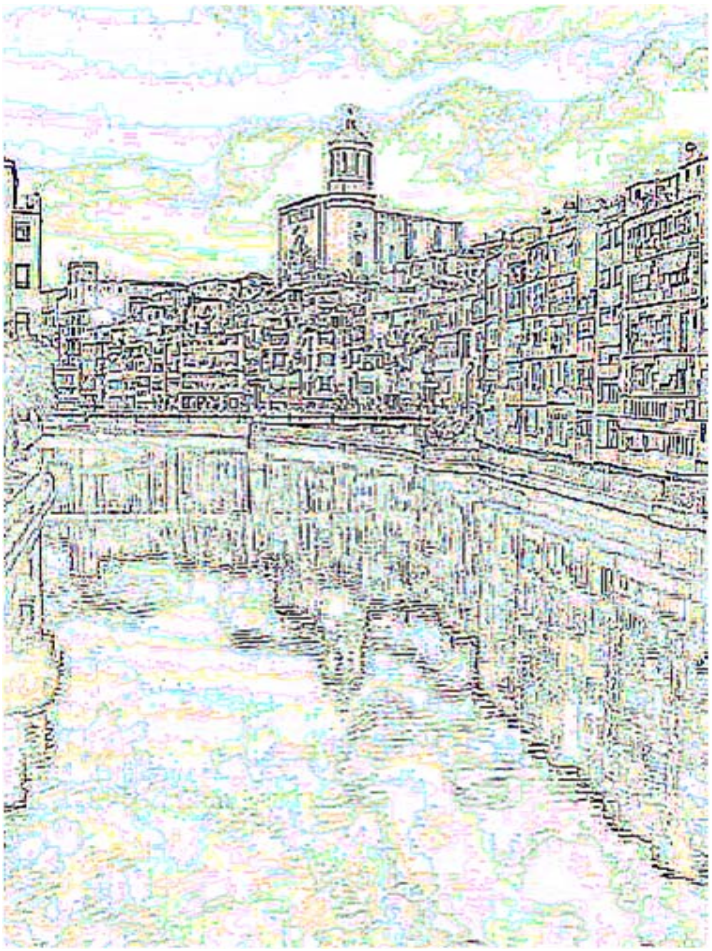
9th European Meeting on Environmental Chemistry



Programme and book of Abstracts

Escola Politècnica Superior Girona, Catalonia, Spain - 3-6th December 2008

9th European Meeting on Environmental Chemistry

Programme
and
Book of Abstracts

Escola Politècnica Superior, Girona, Catalonia, Spain
3-6th December 2008

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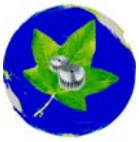

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EMEC 9 Programme

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Session Overview

Wednesday, 03/Dec/2008

5:00pm - 8:00pm	**Registration and Welcome Reception** Location: Poster's Hall

Thursday, 04/Dec/2008

9:00am - 9:15am	**Opening Ceremony** Location: Sala d'actes
9:15am - 10:00am	**Th: Plenary 1** - Arsenic in Waters and Soils: an Overview of its Origin, Behaviour, Mobility and Remediation Professor Jean-Claude Bollinger Chair: M. Angels Pèlach Location: Sala d'actes
10:00am - 11:00am	**Th-1: Oral session** Ecotoxicology Chair: Prof. Jean-Claude Bollinger Location: Sala d'actes
11:00am - 11:30am	**Th-2: Coffee break** Location: Poster's Hall
11:30am - 1:00pm	**Th-3: Oral session** Emerging contaminants Chair: Prof. Branimir, Stanko Jovancicevic Location: Sala d'actes
1:00pm - 2:30pm	**Th – Lunch** Location: Room 3rd floor
2:30pm - 3:15pm	**Th: Plenary 2** - Management of Waste Materials from Threat to Profit Professor Michael Cox Chair: Dr. Mª Isabel Villaescusa Location: Sala d'actes
3:15pm - 4:30pm	**Th-4: Oral session** Waste treatment and management Chair: Dr. Mª Isabel Villaescusa Location: Sala d'actes
4:30pm - 5:00pm	**Th-5: Coffee break** Location: Poster's Hall
5:00pm - 6:30pm	**Th-6: Oral session** Water treatment and reuse Chair: Prof. Michael Cox Location: Sala d'actes
6:30pm - 8:00pm	**Th-7: Poster Session and Refreshment** Location: Poster's Hall
7:30pm - 8:30pm	**ACE AGM** Location: Sala d'actes

Friday, 05/Dec/2008

9:00am - 9:45am	**Fr: Plenary** - Instrumental analytical chemistry for environmental applications Professor Guido Crisponi Chair: Prof. Josef Caslavsky Location: Sala d'actes
9:45am - 10:45am	**Fr - 1: Oral session** Analytical methods for environmental science Chair: Prof. Josef Caslavsky Location: Sala d'actes
10:45am - 11:45am	**Fr - 2: Coffee break and Poster Session** Location: Poster's Hall
11:45am - 1:00pm	**Fr – 3: Oral session** Analytical methods for environmental science. Water treatment and reuse Chair: Prof. Guido Crisponi Location: Sala d'actes
1:00pm - 2:30pm	**Fr – Lunch** Location: Room 3rd floor

2:30pm - 4:30pm	**Fr - 4 A: Oral session** Clean technologies and green chemistry Chair: Dr. Montserrat Filella Location: Sala d'actes
2:30pm - 4:30pm	**Fr – 4 B: Oral session** Pollutant chemistry Chair: Prof. Albert Lebedev Location: Lectures Room B
4:30pm	**Fr: Tourist Visit** Visit to Girona' s old city.
9:00pm	**Social Dinner** In Fornells Park Hotel

Saturday, 06/Dec/2008

9:00am - 9:45am	**St: Plenary** - Environmental issues related to abandoned mine sites Professor Giovanni Pardini Chair: Dr. Jan Schwarzbauer Location: Sala d'actes
9:45am - 11:00am	**St - 1: Oral session** Soil chemistry Chair: Dr. Jan Schwarzbauer Location: Sala d'actes
11:00am - 11:45am	**St - 2: Coffee break and Poster Session** Location: Poster's Hall
11:45am - 1:00pm	**St – 3: Oral session** Soil - water - atmospheric systems. Aquatic and marine chemistry
-	Chair: Dr. Giovanni Pardini Location: Sala d'actes
1:00pm - 1:30pm	**Closing Ceremony** Location: Sala d'actes
2:00pm	**Farewell Social Lunch** In Golf Girona restaurant

PLENARY SESIONS

ARSENIC IN WATERS AND SOILS: AN OVERVIEW OF ITS ORIGIN, BEHAVIOUR, MOBILITY AND REMEDIATION

Jean-Claude BOLLINGER

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The different forms of Arsenic and its versatile behaviour explain why there are so great concerns about this potentially toxic element. Accumulation of evidences for chronic toxicological effects of Arsenic in drinking water leaded the World Health Organisation to recommend lowering the regulatory limit. In European Union and in the USA, among other countries, these limits were recently downed from 50 to 10 µg total As/L. Moreover, Arsenic toxicity and mobility is highly related to its oxidation state: the reduced state As(III) is much more toxic, more soluble and mobile than the oxidised As(V).

Starting from the recent literature -- and from the studies realized since 12 years by the Arsenic Research Group at the University of Limoges -- we will present some information on various topics concerning this ubiquitous element, among others:

- *natural and anthropic origins*: Most metallic elements with an industrial interest are naturally present as sulphide deposits, frequently associated with arsenopyrite FeAsS. During ore processing, Arsenic is then discarded as tailings near the extraction sites. Many Arsenic-containing pesticides have been used (meta-arsenite, lead arsenate, etc), some are always in use (CCA for timber treatment, Roxarsone as an antibiotic additive to poultry feed).
- *weathering of Arsenic-rich minerals and mobility*: In mine tailings exposed during several years to rainwater under temperate climatic conditions, Arsenic present in primary sulphides can be mobilized and exported from the sites. Thereafter, Arsenic and the associated metal-bearing phases are mainly trapped into neo-formed phases, whose mineralogy depends on the water/rock ratio, pH and Eh. Of course, the stability of these Arsenic-rich secondary phases under oxic conditions is also highly dependent on environmental conditions.
- *speciation in rivers systems*: Interstitial water and groundwater composition often presents significant dissolved Arsenic content due to their pathway. Similarly, surface water can present high concentrations and fluxes of Arsenic, either dissolved or sorbed on suspended particulate materials. These solid particles are carried by surface waters and can participate downstream to the enrichment of sediments.
- *sorption behaviour*: In the environment, many solid mineral phases are able to sorb or trap Arsenic, they include many kinds of Iron and Manganese (oxy)(hydr)oxides. Such solid materials can also be synthesized, in order to remove Arsenic from contaminated water.
- *phytoremediation*: Many vegetal species, notably ferns, are well known as Arsenic accumulators, some have been patented in order to extract it from either contaminated soils or waters.

- *toxicity and human health effects*: Recent epidemiological studies in many parts of the world (Chile, Argentina, Central Europe, ...) have given new insights on the effects of chronic exposure to Arsenic, and on the nature of the metabolic species to be surveyed.

However, although these are important topics, we will NOT discuss here the development of analytical methods, the production of drinking water, nor the well-known case of hard chronic Arsenic poisoning is the Bengal delta basin, where several millions of inhabitants are exposed, with high death levels.

Reference:

"Arsenic in Drinking Water: Sources, Occurrence and Health Effects (a Review)"; I. VILLAESCUSA & J.C. BOLLINGER, *Re/Views in Environmental Science and Bio/Technology (RESB)*, in press (2008). doi: 10.1007/s11157-008-9138-7

MANAGEMENT OF WASTE MATERIALS – FROM THREAT TO PROFIT

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One of the major concerns of the 21st Century is the management of waste materials and the need for their reduction or recycle. This paper will look at the ways in which one particular waste material – combustion fly ash, a major waste product from the power industry, has been used to provide an alternative feed material in a number of different processes ranging from relatively low value high tonnage use in cement and concrete to more specialised high value products.

The world-wide production of combustion residues from power production and waste incineration has been estimated at 500Mt/y (1999) of which the EU contribution was 60 Mt. With the generation of electrical power continuing to increase and with coal still featuring as a major source of primary energy for the foreseeable future the production of combustion ashes will continue to be a concern world-wide. While in the EU about 50% of the residues are reused, mainly in the production of low-value building materials such as cement, concrete and road construction, world-wide the proportion is much lower and the majority of ashes are land-filled or stored for potential future use.

In 1998 an EU Thematic Network (PROGRES) was set up with the aim of investigating novel uses of combustion residues. The network consisted of 16 academic and industrial partners who were involved in studies of the reuse of combustion residues as a feed material for a range of industrial products. The substitution of primary raw materials by such wastes has two principle benefits, reduction of potential scarce resources and the reduction in solid residues for disposal. Application of coal combustion residues in the cement and concrete industry is well established with a number of industrial standards defining the extent and conditions of their use. However, even in this application the introduction of new and mixed fuels such as municipal wastes and biomass for power generation poses new questions on the suitability of these new generation ashes as a substitute feed material. In addition with the use of waste materials in such low value products there is a finite distance beyond which the cost of transportation outweighs the value of replacing traditional materials. Thus there is potential benefit to be gained in the development of high value products from such wastes where the cost of processing can be outweighed by the ultimate value of the product. The unlocking of such values from combustion residues was the main aim of the PROGRES project.

The major elemental components of coal combustion ashes are silicon and aluminium and obvious outlets for their use include various products such as ceramics, glasses and industrial silico-aluminate minerals. Applications to be discussed include the

production of zeolites; ceramic building materials; glass fibres; fire-resistant cements, and geopolymers. In addition ashes have been proposed as a substitute for mineral fillers in the rubber and plastic industry. The introduction of any new source material into established processes can pose difficulties, especially where existing materials are subject to precise specifications and standards. This has caused problems in some applications and if industries are to take advantage of such low-cost resources then existing specifications may have to be amended to accommodate them.

In addition to the major components combustion ashes also contain significant amounts of a number of valuable elements originally contained within the fuel. Incomplete combustion of the fuel as a result of the design of the combustor or operating conditions can lead to unburned carbon being present in the ash which can place some restrictions on some potential end uses. However the adsorbent properties of unburned carbon when separated from the combustion residue may be turned into a profit by production of activated carbon.
At one stage coal combustion ash was considered as an important secondary source of aluminium and a number of processes were developed to recover this element and thus provide a sustainable source of this important industrial metal. Other valuable elements that can be separated from coal combustion ashes include gallium and germanium, important elements for the electronic industry; and ash from heavy fuel oil combustion contains significant amounts of the alloying elements, vanadium and nickel. Thus combustion residues in the future could be a valuable resource for these important elements where recent studies have show that existing traditional resources have a limited lifetime at current usage.

In addition to discussing the use of combustion residues in the above applications, this paper will also consider the benefits and limits on the use of waste materials as an alternative industrial resource; the selection of appropriate end products; and some advantages and problems of the introduction of wastes into existing industrial processes.

INSTRUMENTAL ANALYTICAL CHEMISTRY FOR ENVIRONMENTAL APPLICATIONS

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Instrumental methods are widely used in environmental determinations and the *maximum allowable concentrations* are continuously decreasing in order to go with the known biological restraints and with the advancement of analitycal techniques, whose detection limits are constantly improving. In this context, in order to obtain reliable results, the analytical chemist cannot rely only on the technical apparatus but must keep the entire analytical procedure under control.

We will illustrate these kind of problems utilizing our experience with a particular technique, ICP-AES, proposing three different experimental situations:

- the control of the performance of a purification plant for wastewater treatment in a metallurgical factory;
- the analysis of inorganic pollution in the soil around an industrial plant;
- the determination of toxic metal ion concentration in different human tissues.

In the first case the treatments of the plant were with lime, with polyelectrolyte, with sulphyde and clearing up, and with sand filters and pH reduction. After this last treatment water was discharged into the sea. We collected the samples before the first treatment and after each treatment; On each sample pH, conductivity, solid content, chloride by potentiometric titration, sulfur, arsenic, cadmium, copper, iron, lead, zinc, manganese and mercury by ICP-AES were determined. In these determinations the major problems derived from matrix effects. These effects, connected to the high salt content of wastewater, were evaluated in detail and the problem circumvented by reproducing the matrix of samples in the standard solutions.

In the second situation we had to deal with the determination of inorganic pollutants in the area around an industrial plant. The pollution was examined by collecting soil samples, at different depths, on the whole area of the plant, which extended over 150,000 m^2. In the samples, after dissolution, lead, cadmium, copper, zinc, iron, boron, sulphur and phosphorus were determined by ICP-AES technique to identify the polluted areas within the whole factory and the various pollutants, and to quantify the concentration of each pollutant as a function both of the position in the factory area and of the depth, in order to evaluate the amount of polluted soil to be removed or reclaimed. In this case the whole analytical procedure was checked with awareness and validated through the analysis of NIST 2710 Montana Soil (Highly Elevated Traces).

As a third example we will present the use of ICP-AES to the determination of some toxic metal ions in various autoptic or transplanted organs (liver, heart, kidney, brain) of patients with different pathologies. The general procedure for drying, dissolving and

analyzing the tissue by ICP-AES was chosen among different literature procedures and optimized: we gave evidence of the drawbacks of some of the proposed drying and dissolving procedures The entire method was accurately validated on NIST 1577b Bovine Liver.

To sum up, the good practice to examine accurately the entire analytical procedure, pointing out and improving the less accurate steps for optimizing the whole process, will be illustrated on the above examples in which three completely different situations, each with different analytical problems, are evaluated with the same instrumental technique.

ENVIRONMENTAL ISSUES RELATED TO ABANDONED MINE SITES

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The entire mine lifecycle gives important benefits to mineral related industry but also contributes to regional development, heritage and culture. The economic impulse from this activity in terms of employment creation and increase of diverse technological and commercial activities favours the consolidation of a better standard of life. Mining has been practiced for hundreds or even thousands of years attracted by the regions rich metal deposits and the benefit for the society has been generally high, though the landscape in some cases has been heavily influenced by mining. Mining activity has also been often accompanied by unsafe working conditions, especially in old mines, which, once minerals decreased were simply abandoned, leaving waste rocks and tailings free to contaminate surrounding ecosystems.

Nowadays, the increasing pressure on our environment and the complexity of regulation require complying with the different aspects of waste management (monitoring, treatment, disposal), also taking into account that 29% of the total waste generated each year is from some type of mining activity. Despite the regulation for environmental protection during the mine lifecycle, the often low implication of current mining industry and the visible legacy of the impacting past mining activity produce a growing community opposition to opening mines. This public pressure is not confined to developed countries because the electronic communication and the easy access to media have made even remote communities increasingly conscious of the potential damage from uncontrolled mining activity.

That of abandoned mine sites is an outstanding environmental problem confronting the mining industry as it has been particularly slow to be tackled, also in developed countries. The potential cost of risk reduction on a wide scale, the lack of clearly assigned or assumed responsibility and the absence of criteria and standards for mine sites clean-up have delayed actions aimed at reclaiming these sites. Also, most of the attempts by international bodies to examine the issues and provide guidance to national institutions have failed. As a result, orphaned or abandoned mines or mines at risk are nowadays those mines for which the owner cannot be found or for which the owner is financially unable or unwilling to carry out clean-up. These mines pose environmental, safety and economic problems to communities, and also to the mining industry and governments in many countries.

These sites, however, are not well documented with respect to either their numbers or their associated environmental impacts and liabilities. Further research and compilation of information on abandoned mines is therefore necessary in terms of environmental

risk assessment and to enable sound decision-making, cost-efficient planning and sustainable remediation.

Indeed, in many European mining sites as in others worldwide, the problem of mine abandonment and its environmental implications is a serious current situation. Until the beginning of 80's many European extractive industries were accumulating mining residues from metal purification procedures in open tailing dams or even eliminating these residues through local water courses which resulted contaminated for decades. The impact of this activity prolonged through many years has been enormous and many of these examples may be seen today in ex-mining sites where pollution is extended to surface and groundwater, agricultural and recreational areas. However, the real extent of this impact is difficult to determine unless human resources and special funding are expressly directed to this purpose. At this regard, the European Network of Mining Regions was created and funded by EU Interreg IVC Programme, in order to promote guidelines of environmental protection, among others.

A revue of the work done indicates that there is no single definition of an "abandoned mine". This raises several questions associated to the many still unsolved issues around ex-mining sites.

- What exactly are abandoned mines?
- What are the environmental and social risks related to abandoned mines?
- What types of criteria are needed to prioritize these risks?
- Is a regional inventory a prerequisite for action?
- What are the legal liability issues?
- What types of financial mechanisms exist?
- Who will pay to mitigate these sites?
- How to deal with transnational mining impact, e.g. foreign downstream impacts?

The fundamental question is how many sites should really be considered at risk as constituting an environmental or community safety problem.

Some of the hazards are obvious. Old mine openings may be partially caved in or mine timbers rotted, presenting physical hazards when not properly closed and protected. Workings that underlie streets and buildings as well as ruined metal purification plants and tailings dams can collapse. Acidified streams and runoff by acid mine drainage from metallic mines can contaminate surrounding soils and biota with high concentrations of potentially toxic elements. Erosion of metal-particulate from remnants mine wastes may increase levels of trace elements in soils and pose important risk to human health due to further potential for increasing exposure along the food chain. Metal-contaminated dust may be moved from tailings deposits and waste piles to adjacent areas by wind erosion. Ancient mining activities can release gases that make air unsafe to breathe such as methane from coal mines, and carbon monoxide from hardrock mines. Waters from uranium or phosphate mines can carry radiation above normal background levels.

The picture of this situation claims interventions aimed at reclaiming mining contaminated sites. Some mining regions, shared by more than one country (e.g. Portuguese and Spanish Iberian Pyrite Belt) can have potential conflict, related with acid mine drainage along transnational hydrographic basins.

There is a huge difference between the situation of abandoned mines and the situation at current operational mine sites where the need for rehabilitation is now expected and often mandated. Here companies are identified and government have established legal, financial and technical procedures to ensure that mine sites are rehabilitated to make possible other economic uses after the mining operations cease. Despite that, a recent case like Aznalcollar demonstrates the vulnerability of these regulations. In abandoned mines the assignment of responsibility is different; it lies with unidentifiable or unwilling owner and has thus led to no action. But the problems must be dealt with and institutions must experience novel actions even in terms of imposing fiscal mechanisms levied on the entire mineral industry to pay for the clean up of those abandoned mines with not assigned responsibility.

Apart from any socio-economic aspect, the reclamation of abandoned mines will include some or all the following measures:

- Permanent sealing of underground workings and all mine openings, prevention of water and gas leakage that can cause adverse impact on neighboring environments.
- Ensuring that any open pit or open cut features are stable and do not pose risk to humans, animals or environment.
- Removal of all materials and equipment lying at surface.
- Demolition of surface building and structure, unless there are specific programs for a productive use of them (conversion in mine museum, conference and cultural events sites, arqueo-mineral park, etc..)
- Performing all steps necessary to ensure the safety of tailings and slurry ponds, soil heaps, waste dumps, stock piles, and any other type of waste coming from mining that might alter environmental dynamics and cause human hazard.
- Clearing areas formerly used for the mine surface facilities.

In case that rehabilitation has to be performed, it should include the following measures:

- Restoration of surface land including clean up of the premises, leveling the ground and revegetation.
- Establishing the nature of any water remaining in the open pit or galleries and treat it if necessary (liming).
- Rehabilitation of waste dumps.
- Establishing the nature of soils, the degree and extent of pollution from anomalous heavy metals concentrations and the hazard according to the current land use.
- Rehabilitation of contaminated water courses.
- Monitoring of results for a specified period after remediation of soils and water.

Although there have been few attempts for quantification, it is generally understood that the issue of abandoned mine sites is a major unresolved environmental and social problem for the industry, for communities and for governments.

ORAL SESSIONS

ASSESSMENT OF THE COMBINED TOXICITY OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCPS) ON THE RAINBOW TROUT LIVER CELL LINE RTL-W1

S. Schnell [1], N. C. Bols [2], C. Barata [1], C. Porte [1]

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Pharmaceuticals and personal care products (PPCPs) are an extraordinarily diverse group of chemicals used in veterinary medicine, agricultural practice, human health and cosmetic care. As for many synthetic chemicals in everyday use, the toxicological implications of the presence of PPCPs in the aquatic environment remain largely unknown. Acute toxicity tests have generally failed to detect the subtle action elicited by those compounds at environmentally relevant concentrations, and they have often overlooked the fact that toxicity can be influenced by additive and synergistic effects. Thus, the aim of this study was to further assess the cytotoxicity of different pharmaceuticals and synthetic musks, as well as their mixtures on the rainbow trout liver cell line RTL-W1. Eleven pharmaceuticals from different therapeutic classes, anti-inflammatory drugs (ibuprofen, naproxen, ketoprofen, diclofenac), serotonin re-uptake inhibitors (fluoxetine, paroxetine, fluvoxamine), lipid regulators (fenofibrate, clofibrate, bezafibrate, gemfibrozil) as well as five synthetic musks from the two major groups, nitro musk (musk ketone, musk xylene) and polycyclic musks (galaxolide, tonalide, celestolide) were selected for the study. Two fluorescent dyes were used to monitor cell viability. Metabolic activity was monitored with alamar Blue (resazurin) and cell membrane integrity was evaluated with 5-carboxyfluorescein diacetate (CFDA-AM). Among the tested compounds, estimated EC50s (effective concentration causing 50% decline of cell viability) denoted that polycyclic musks (7-25 μM) followed by antidepressives (7-50 μM) showed the highest potential to induce cytotoxicity, whereas lipid regulators (20-380 μM), anti-inflammatory drugs (160-260 μM) and nitromusks (100-240 μM) had the lowest toxicity. Within a given therapeutic class, combined toxicity of mixtures was additive, following in most cases the concentration addition concept. However, the combined toxicity was higher than additive for those mixtures that included one compound from each class (i.e. dissimilar mixtures). Overall, this study shows that in the aquatic environment, toxicity of PPCPs on non target organisms may occur at concentrations lower than expected due to synergistic effects between the different toxicants.

A COUPLED MODEL OF DYNAMICS OF PERSISTANT ORGANIC POLLUTANTS IN MANILA CLAM (TAPES PHILIPPINARUM)

S. Raccanelli [1], S. Libralato [2]

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Persistent organic pollutants (POPs) discharged and accumulated in sediments of coastal areas might be directly bioaccumulated by benthic organisms such as Manila clam (*Tapes philippinarum*). Clams are also a commercially important species subjected to intense fishing and cultivation in many temperate coastal ecosystems. As an example, the Venice Lagoon (Italy) produces approximately 40000 ton/year of clams that are exported throughout Europe. Therefore, modelling studies of POPs bioaccumulation in Manila clam might be useful also in the light of managing the human risk associated to its exploitation and consumption.
In this work we present a coupled bioenergetic-bioaccumulation model for Manila clam, that permits for a full exploitation of empirical data, for a better understanding of observed temporal-spatial patterns, and might represents a tool useful for analysing management options.
We set-up an ecotoxicological model by coupling a bioenergetic growth model for Manila clam with a model of the accumulation of POPs in body tissues. Clam growth dynamics is represented in the bioenergetic module as a function of water temperature, food availability and initial size. The growth module was integrated with a bioaccumulation one representing POPs concentration as a function of environmental concentrations, chemical properties and biological processes (i.e. respiration, food uptake, metabolization, excretion).
The coupled dynamic model is calibrated by using concentration of POP congeners in clam flesh measured during natural detoxification field experiments with clams collected in polluted industrial area of the Venice Lagoon. During two experiments, conducted in summer 2004 and winter 2006, were collected 14 samples in 120 days of detoxification for each experiment.
This ecotoxicological model provides a basis for representing dioxin dynamics in clam flash under different environmental conditions, provides estimates of specific metabolic detoxification rates and thus it can be used for providing scenarios for human risk management.

SHORT TERM COPPER TOXICITY ON MICROCYSTIS AERUGINOSA AND CHLORELLA VULGARIS BY FLOW CYTOMETRY MEASUREMENTS

S.Hadjoudja [1], C.Vignoles [2], V. Deluchat [1], JF.Lenain [1], A.H.Le Jeune [1], M. Baudu [1]

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Abstract. Copper sulphate is an common algaecide applied to ponds in order to keep phytoplanktonic blooms under control, especially those prone to cyanobacterial development. Among phytoplanktonic species, cyanobacteria seem to be particularly sensitive to copper. An increase in sensitivity of cyanobacteria to copper treatments has frequently been observed. In order to better understand the ecotoxicological effects of copper on phytoplanktonic species, the sensitivity to this chemical treatment of two unicellular species with similar shape and size, a cyanobacteria *Microcystis aeruginosa* and a chlorophyceae *Chlorella vulgaris* are tested in this study under laboratory conditions. The aim of this work was to provide a comparative study between these two freshwater species and to determinate the relationship between biological responses and the initial free copper concentration in the synthetic media under controlled conditions.
According to the biotic ligand model (BLM) derived from the free ion activity model (FIAM), under laboratory conditions metal bioavailability and toxicity depends firstly on the physicochemistry of the media which affects metal speciation and secondly on the accumulated element in the microorganisms . Thus, for each phytoplanktonic species, copper toxicity was estimated according to (1) the chemical speciation of copper in the external environment, and (2) the resulting biological effects. The initial free copper exposures were directly related to their biological effects. To determinate the initial free ion concentration, the speciation of copper in the media was controlled by a defined chemical composition of the medium , Good's (MOPS) and metal (EDTA) buffers. Initial free copper concentration was derived from the calculated speciation of the metal in the synthetic media. For each species, the biological responses were determinated by two sets of flow cytometry data i.e. cell pigment autofluorescence and inhibition of enzymatic activity with fluorescein diacetate fluorescence (FDA). The curve dose response were analysed to determinate statiscally EC_x values i.e. the concentration of copper inducing a reduction the biological response by x % compared to the control.
The results of this study showed: (1) regardless of the cell type, as copper concentrations increased, esterase activity decreased, although slower than the autofluorescence of the pigment assay commonly used as cytotoxicity test, (2) a difference in sensitivity to copper between the two species after 24 and 48h of copper exposure, (3) *M. aeruginosa* was more sensitive to copper exposure than *C. vulgaris*. This work highlights the importance to control the metal speciation for an effective evaluation of the metal toxicity on aquatic organisms in natural freshwater and demonstrate the importance of using monospecie population to estimate metal toxicity.

APPLICATION OF YEAST GENOME-WILDE ANALYSIS TO TOXICOLOGY RESEARCH OF GLYPHOSATE BASED FORMULATIONS

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In the last decade, new genomic methods and tools have been applied in toxicology research to understand mechanisms of action of both single and mixtures of chemicals on biological systems. Rich functional information can be obtained by phenotypic analysis of yeast mutation collection perturbed by a given environmental stressor in an experimental approach termed chemical-genetic profiling.
Glyphosate is one of the most applied non-selective herbicides in the world, but data on the toxicity of the glyphosate based formulations is scarce. Commercially available glyphosate based formulations contain different ingredients, mainly surfactants, which vary in nature and concentration. Toxicity properties of pure glyphosate comparing with its formulation might be different.
The aim of the presented work was to apply a recently developed method for semi-quantitative determination of chemical-genetic interactions to the toxicology study of mixture of chemicals, such as pesticide formulations. By comparing the results for two glyphosate based formulations, we tried to understand mechanism of actions of tested formulations and determine contribution of the supposedly inert ingredients in formulations to overall toxicity.
We performed chemical-genetic profiles for two glyphosate based formulations registered in Slovenia, *Boom efekt* (Pinus) and *Touchdown System4* (Singenta). Genome-wide chemical-genetic profiles were generated by testing the sensitivity of ~4800 *Saccharomyces cerevisiae* single-gene haploid deletion mutants to examined formulations. Growth curves were also performed by measuring optical density of selected mutants growing on media containing the formulations or pure technical grade glyphosate.
Generally, pure technical grade glyphosate was much less toxic to yeast than its formulations, with *Touchdown System4* being more toxic than *Boom efekt*. By comparing chemical-genetic profile of both formulations it was shown that both perturb pathways of aromatic amino acid metabolism in yeast and besides common targets, both formulations have specific biological targets.
Yeast genome-wild chemical-genetic profiling allows relatively quick and easy searches for genes involved in the resistance or susceptibility to given environmental stressor. Chemical-genetic profiles of *Boom efekt* and *Touchdown System4* differ, indicating large contribution of the so called inert ingredients in formulations to overall toxicity.

SELECTIVE ENANTIOMERIC ENRICHMENT OF HEXABROMOCYCLODODECANE IN HUMAN BODIES

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Hexabromocyclododecane (HBCD), a brominated alicyclic hydrocarbon, is the principal flame retardant in polystyrene foams and is used as thermal insulation in the building industry. Technical HBCD is produced industrially by addition of bromine to *cis-trans-trans*-1,5,9-cyclododecatriene, with the resulting mixture containing three predominant diastereoisomers α-, β- and γ-HBCD. Normally, the γ-isomer is the most dominant in the commercial mixtures (ranging between 75 and 89%), followed by α- and then β-isomer (10-13% and 1-12%, respectively). But, the α-, β- and γ- HBCD diastereoisomers are chiral and must be present as enantiomeric pairs. The physical-chemical properties of HBCD are similar to other persistent organic pollutants; in fact the log K_{ow} of HBCD is 5.6 and that valour places in the optimum range for bioaccumulation. Due to their lipophilic and persistent character, HBCD accumulate in the human body. But, little information is available regarding HBCD concentrations in human samples. Moreover, although limited data on human exposure to HBCD exists, no information is available on its enantiomeric pattern. The aim of this study was to determine HBCD isomer levels in human breast milk from Spain. Moreover, for the first time, enantiomeric fractions (EFs) were calculated in order to investigate potential selective enantiomeric enrichment in human bodies.

HBCD was detected in 30 out 34 human milk samples, at concentration levels up to 188 ng/g lipid weight (lw). Although there are few reports regarding HBCD concentrations in human breast milk, our values are higher than those available for other countries such as Sweden, Norway, Canada, USA or Japan, which are always below 20 ng/g lw. As regards the isomeric pattern, there is a predominance of the γ-isomer, with a low contribution of the α-isomer, and the β-isomer being below the limit of quantification. Only in two samples, this isomeric pattern was different, showing a clear dominance of the α-isomer versus the γ-isomer. This inconsistency in the isomeric pattern may be due to individual variability in metabolizing capacity or other unknown factors such as the frequency of exposure to HBCD. Moreover, for the first time, HBCD enantiomeric analysis was carried out in human breast milk samples. The most interesting finding was obtained for the two samples were α-isomer predominate. In these cases, abundance of (-)α-HBCD was higher than that of (+)α-HBCD. EFs were calculated and obtained values (0.102 and 0.204) showed a clear enrichment of (-)α-HBCD in these samples, indicating a selective enantiomeric enrichment in human body. These data has not been described before in the literature. However, further studies in a great number of human breast milk samples are required in order to check this differential enantiomeric behaviour.

CHOLESTEROL-LOWERING STATING DRUGS – AN ENVIRONMENTAL THREAT?

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Cholesterol lowering statins are a group of pharmaceuticals, which are the most frequently prescribed agents for reducing morbidity and mortality related to coronary heart disease. Lovastatin (Mevacor®), pravastatin (Pravachol®) and simvastatin (Zocor®) have been introduced to the market since 1987. Lovastatin is a natural product; simvastatin and pravastatin are semi-synthetic products [1]. Statins exist in two forms, lactone and hydroxyl acid in general. In vivo, the hydroxyl acid forms are the active drugs to lower plasma cholesterol while the lactone forms are inactive (prodrug) [2].

Due the widespread use of statins and their large scale production municipal sewage treatment plants as well as sewage treatment plants of the pharmaceutical industry might therefore be important point sources of contamination. Lipid regulators have been found in different environmental compartments [3]. A multiresidue analytical method is prerequisite to provide reliable figures on the fate of pharmaceuticals (and statins among them) in STPs and surface water and to assess drug removal, partition and fate in the environment [4].

Statins stability in different solvents, temperatures and pH, their photo-behavior, environmental persistence and toxicity of products has been investigated in our research.
A solid phase extraction was developed to enrich the analytes from aqueous samples. The method with advantages in terms of sensitivity for determination of pravastatin, lovastatin and simvastatin was put forward. A positive mode ionisation technique within LC/MS/MS instrument was used for ionisation of all the three compounds. Limits of detection for pravastatin was 19 ng/L, for lovastatin 14 ng/L and for simvastatin 16 ng/L, respectively. Method was linear up to 1000 ng/mL. The experimental values showed statins interconversions between lactone and hydroxyl acid form, even at the room temperature, various pH and presence of sun light. The interconversion ratio varied according to different conditions from 2 to 30 %. This occurrence has been supervised in order to avoid its influence on the results of quantification. Biodegradibility test proved that statin compounds tend to possess environmental persistence.

[1] X-S. Miao, C. D. Metcalfe, *J. Chrom. A* **998** (2003) 133-141.
[2] Hwang L.S., Yang D-J, *J Chrom. A* **1119** (2006), 277-284.
[3] Hernando M.D., Aguera A., Fernandez-Alba R., *Anal. Bioanal Chem.* **387** (2007), 1269-1285.
[4] J Zuccato E.,Castiglioni S., Bagnati R., Calamari D., Fanelli R., J. *Chrom. A* **1092** (2005), 206-215.

DEGRADATION PRODUCTS OF POLYURETHANES WITH ENHANCED DEGRADABILITY

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Polyurethanes (PU) are the world's sixth most abundant synthetic polymer; they show a wide range of properties and therefore they could be found in many products ranging from automobiles to furniture and upholstery. They are synthesized by simple reaction between a monomer containing at least two isocyanate functional groups (e.g. toluenediisocyanate) with another monomer containing at least two alcohol groups (most often polyol) in the presence of a catalyst. Polyurethane formulations cover an extremely wide range of stiffness, hardness, and densities, but majority of PU production comprises flexible polyurethane foams. At the end of their life-cycle the polyurethane-made or polyurethane-containing products are mostly deposited on waste dumps, where they stay for a long time due to high PU resistence, and slowly degrade under the influence of environmental factors; photodegradation and hydrolysis together with biodegradation are the main processes. The degradation products then enter the environmental compartments, where they could negatively effect.

The degradability of polyurethanes could be improved by the addition of the biodegradable filler – most often biooriginated and biodegradable polyol, which partly substitutes the synthetic polyol during PU synthesis. The amount of degradation products of such modified polymers increases substantially; therefore we focus our attention on their identification.

Polyurethane foams (PUFs) with enhanced biodegradability were synthesized at Institute of Material Chemistry of Faculty of Chemistry, Brno University of Technology using (i) carboxymethyl cellulose, (ii) acetylated potato starch, (iii) cellulose acetate, (iv) 2-hydroxyethyl cellulose and (v) wheat protein as biodegradable fillers. These PUFs together with reference PUF without any filler were subjected to accelerated degradation either by hydrolysis or by UV light. In the first case, degradation products were identified directly in the hydrolysate using LC/MS and ESI-MS^n; in the second case volatile degradation products were trapped using SPME and identified by GC/MS. Various fragments of polyurethane chains were identified in hydrolysates and quite often increase of ecotoxicity was observed in comparison to reference PUF. Photodegradation leads also to many products; their identification by library search was in many cases unsuccessful and manual interpretation of mass spectra had to be used. If cellulose-based fillers were used, highly toxic 2,4-toluenediisocyanate was identified as one of the degradation products.

Acknowledgement: This study was supported by the Grant No. MSM 0021630501 from the Ministry of Education, Youth and Sport of the CR.

DECONJUGATION OF STEROIDS IN WASTEWATER TREATMENT: SCOPE OF THE PROBLEM AND BEHAVIOUR IN BATCH STUDIES

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Steroid estrogens of anthropogenic origin have been identified as the major contributors to endocrine disrupting activity in both sewage effluent and river systems. Their presence in the aqueous environment attributed to their incomplete removal during wastewater treatment.

In order to reduce the estrogenic load entering receiving waters, reduction at source and/or improvements to wastewater treatment are necessary. As steroids are excreted from the human body, reduction at source is not feasible. Therefore, knowledge of their fate and removal under wastewater conditions is essential to assess the impact of operational parameters which may be utilised to improve removal efficiency.

Steroids are predominantly excreted from the body in either the glucuronide of sulphated conjugated form. However, research has focused on the unconjugated (free) steroids as they constitute the dominant form in wastewater. A need exists for assessing the behaviour of these precursor conjugates, particularly with recent studies observing conjugated steroids in wastewater and river samples.

Discussed herein is the justification for focusing steroids in their conjugated form and how the evolution in environmental analysis has led to increasing interest in studying conjugated steroids. The current knowledge on fate and behaviour in wastewater and river matrices are provided along with preliminary data on the transformation of conjugated steroids in batch studies using activated sludge grown on synthetic sewage in laboratory-scale Husmann simulation and crude wastewater obtained from the field.

Deconjugation proved to be a biotic process, dependent on the conjugate moiety, positioning of the conjugate on the steroid body and possibly the type of steroid (natural or synthetic in origin). Results indicate that in order to remove steroids during wastewater treatment and prevent entrance into river systems, there is a need to optimise wastewater treatment for deconjugation of the recalcitrant sulfate moiety from the parent steroid.

COMPARISON OF POCIS AND SPMD FOR IN-SITU SAMPLING OF MODERATELY HYDROPHOBIC MOLECULES

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Polar organic chemical integrative sampler (POCIS) and semipermeable membrane device (SPMD) are among the most commonly used passive samplers for the monitoring of organic micropollutants in water [1]. POCIS is used to monitor hydrophilic molecules (log Kow < 4), such as pharmaceuticals or pesticides [2]. SPMD is designed for sampling hydrophobic molecules (log Kow > 2), like polychlorinated byphenyls (PCB) or polycyclic aromatic hydrocarbons (PAH) [3].
The objective of the present work was to compare the efficiency of these two samplers to monitor molecules of moderate hydrophobicity (log Kow < 5) in freshwater systems impacted by wastewater treatment plants (WWTP) inputs. The studied molecules include 10 betablockers (acebutolol, atenolol, betaxolol, bisoprolol, metoprolol, nadolol, oxprenolol, propranolol, sotalol, timolol), 5 estrogenic hormones (estrone, 17α-estradiol, 17β-estradiol, estriol, 17α-ethynilestradiol) and 5 alkylphenols (4-tert-octylphenol, 4-nonylphenol, 4-nonylphenol-monoethoxylate, 4-nonylphenol-diethoxylate, 4nonylphenoxyacetic acid).
Five sampling campaigns were carried out in France: on the Saône River (November 2007), the Jalle River (March 2008), the Ardières River (June 2008), the Seine River (September 2008) and the Bourbre River (September 2008). POCIS and SPMD were exposed in surface waters upstream and downstream WWTP inputs, as well as in the WWTP effluent, which corresponds to an increasing gradient of contamination. Grab samples were periodically collected from each site during the exposure periods. Samplers were exposed between three days and three weeks in order to compare the accumulation kinetics and linearity. Repeatability was studied by the exposure of triplicates samplers. We also tested in situ the benefit of using performance reference compounds (PRC).
The samplers were then processed to recover the accumulated contaminants. Different extraction procedures were developed according to the sampler: an elution of the adsorbant is performed for POCIS, whereas SPMD is dialysed in an organic solvents mixture. We compared recoveries for different volume and nature of solvents to obtain satisfying recovery for the different classes of molecules studied. The extracts were analysed by LCMSMS. The performances of the optimized analytical methods are discussed with regards to recoveries and repeatability obtained for each molecule and passive sampler. At last, the two samplers are compared in terms of practical use, cost, accumulation kinetics and linearity range, as well as concentration factor and quantification limits. The first results show that POCIS is more efficient than SPMD for the insitu sampling of betablockers and hormones.
[1] Vrana et al, Trends Anal. Chem. 24 (2005) 845868
[2] Alvarez et al, Environ. Toxicol. Chem. 23 (2004) 16401648
[3] Huckins et al, Chemosphere 20 (1990) 533552

LEVELS OF PBDEs AND OTHER PERSISTENT ORGANIC POLLUTANTS IN COMPUTER USERS FROM GREECE

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Polybrominated diphenyl ethers (PBDEs) are a class of widely used flame retardants, used in various consumer products such as plastics, textiles and computers to prevent flammable gas formation. PBDEs can easily leach out of these materials and volatilise into the environment, ending up in high concentrations in biota and humans. They were first detected in humans in 1998 in breast milk and their concentrations have been increasing through the 90s and 00s (de Wit, 2002). Recent research has shown that occupational exposure may play a more important role than dietary intake in the accumulation of PBDEs in human body, mainly through the inhalation of contaminated air. It has been observed that computer clerks have higher PBDE levels in their blood than control groups (Sjodin *et al*., 1999), which indicates that PBDEs used in computers and electronics may contaminate the working environment and accumulate in workers.

We collected 30 human serum samples from workers of a computer company in Athens, Greece and 30 serum samples from a control population with no computer use and analyzed them for PBDEs, PCBs and organochlorine pesticides (OCPs) by GC-MS, using the method described by Covaci and Voorspoels (2005) with a slight modification to include concurrent analysis of PCBs and OCPs. A questionnaire on dietary habits, computer and other electronic equipment use was completed by the participants to explore any possible correlations between lifestyle habits and PBDE levels.

Total PBDE levels (sum of 8 congeners) ranged from 0.15 to 60.6 ng/g lipid, with a median of 1.27 ng/g lipid. These concentrations are on the lower end of those that have been reported for other European countries. Median ∑PBDE concentrations were higher in the case group (computer clerks) than in the control group, which could be an indication of occupational exposure. However, when considering individual key PBDE congeners 47 and 209, the concentrations were similar between the two groups. ∑PCB concentrations ranged from 31.8 to 254 ng/g lipid, with a median of 110 ng/g lipid. pp'-DDE concentrations ranged from 53.8 to 1649 ng/g lipid, with a median of 268 ng/g lipid. This is the first study to our knowledge reporting PBDE levels in human serum from an occupationally-exposed subset of the Greek population.

Covaci, A., Voorspoels, S. (2005). Optimization of the determination of PBDEs in human serum using solid-phase extraction and gas chromatography-electron capture negative ionization mass spectrometry. *J. Chromatogr B*, 827, 216-223
de Wit C.A. (2002). An overview of brominated flame retardants in the environment. *Chemosphere*, 46 (5), 583-624
Sjödin, A., Hagmar, L., Klasson-Wehler, E., Kronholm-Diab, K., Jakobsson, E., Bergman, A., (1999). Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. *Environ. Health Perspect*. 107, 643-648

ELECTRODIALYTIC REMEDIATION OF AIR POLLUTION CONTROL RESIDUES IN BENCH SCALE

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Air pollution control (APC) residue from municipal solid waste incineration (MSWI) is considered a hazardous waste due to its alkalinity and high content of salts and mobile heavy metals. Various solutions for the handling of APC-residue exist in different regions; however, most commercial solutions are concerned with deposition. A demand for more environmentally friendly alternatives exists. Electrodialysis could be such an alternative, and the potential is being explored. This work presents a bench scale study of the feasibility of treating APC-residue from a dry system by electrodialysis. A system resembling conventional electrodialysis was designed and adjusted to fit the high solids content feed solution (10% APC residue, 90% water). Experiments were made in bench scale with raw residue (natural pH > 12), water pre-residue (natural pH > 12), acid pre-washed residue (pH 10), and acid-treated residue (pH 2). Our results show that the soluble fraction of the toxic elements Pb, Cu, Cd and Zn was removed from the feed solution and concentrated in the concentrate solution. Furthermore, the leaching (leaching test at L/S 2) of these elements was substantially reduced during treatment (fig. 1). Between 57 and 83% of the APC residue was dissolved during treatment. The highest dissolution was seen for acid treated residue and the lowest for water pre-washed residue.

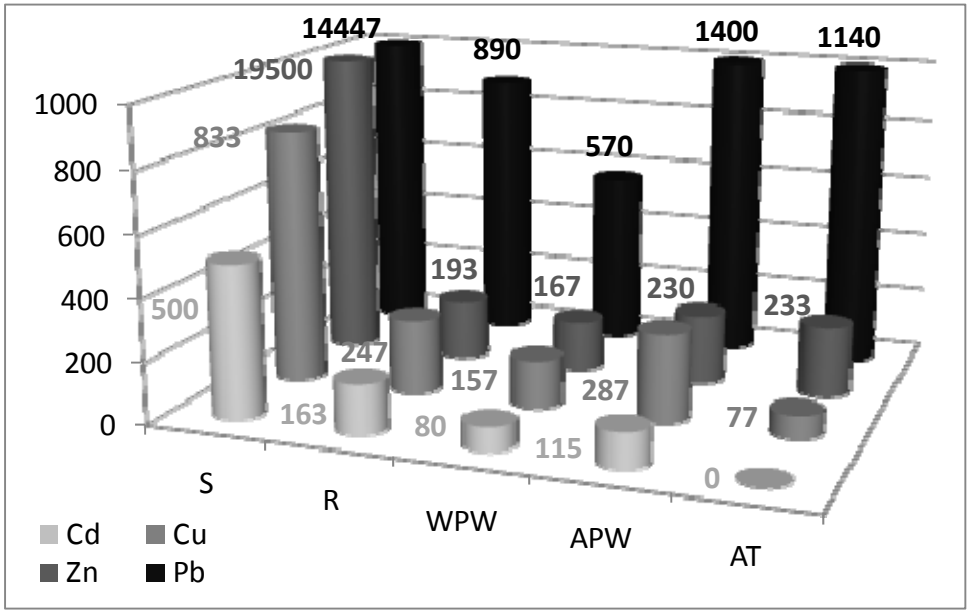

Fig. 1: Leaching of Cd, Cu, Zn and Pb before (S) and after treatment (µg/L). Raw residue (R), water pre-washed residue (WPW), acid pre-washed residue (APW), and acid-treated residue (AT). Note that initial concentrations of Pb and Zn are out of scale.

GREEN CHEMISTRY APPROACH IN TREATMENT OF WASTE WATER EMULSIONS FROM METAL-PROCESSING INDUSTRIES

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The metal-processing industries produce a large volume of waste soluble oil-in-water emulsions together with other small organic molecules present as additives. After being used the fluids become less effective because of thermal degradation and contamination and must be replaced periodically. Used emulsions are returned to the producer who needs to treat them in accordance to local regulations.
The objective was to treat, recycle or dispose of the oily waste in the most efficient and environmentally sound manner. In this study, oily waste water from a local metal-processing industry was treated to break the emulsion by means of flocculation, coagulation, filtration, adsorption and bioremediation. The emulsion came from different workshops and was in different conditions concerning degradation. An oil-in-water emulsion was homogenized in a 300 m^3 tank. The emulsion contained 1–5% of oil as well as many kinds of additives and other impurities.
Scale up was from laboratory samples and probes (10 L) via pilot level (2 m^3) up to the industrial level (600 m^3). Flocculation and coagulation was achieved by mixture of inorganic salts, amphoteric polyelectrolyte and precipitator. Reduction of volume was achieved by means of sand filtration and adsorption with polyfunctional fillers. Obtained waste water was drain into a sanitary sewer in accordance to the local regulations. Bioremediation was used to break-down of oil. Dewatered cake together with filtration sand was spread evenly over the biopile. Bioremediation was enhanced by biostimulation, bioventilation and every 30 days by reinoculation with about 1m^3 of fresh biomass of zymogenous microorganisms produced in a mobile bioreactor.
Total volume of treated emulsions was 600 m^3. Flocculation, coagulation, filtration and adsorption as a first step of the process reduced waste volume 10 times. About 60 t of dewatered cake together with moistured filtration sand and saturated adsorption columns were gained for bioremediation. To bioremediation was submitted around 7150 kg hydrocarbons. For 90 days of bioremediation TPH (Total Petroleum Hydrocarbons) dropped from about 30 dry mass to less than 0.5 g/kg dry mass. At the end of process part of microorganisms that consume hydrocarbons were around 95%.
Our two step process for treatment of metal-processing emulsions showed:
After first step of our process COD (Chemical Oxygen Demand), crucial parameter of contamination of water was reduced from starting 100000 to 100 mg/L which means that efficiency of the process was 99.9%.
For period of near 3 months about 7 tons of hydrocarbons gained from waste water emulsion was transformed into CO_2, H_2O and biomass by the action of active zimogenous microbial consortium which is almost 95% efficiency.
The result of realized treatment was humified material gained by bioremediation.
Developed proceeding of metal-processing oil-in-water emulsions treatment is in all parts consistent with green chemistry principles.

DEVELOPMENT OF A NOVEL PROCESS FOR THE REMOVAL OF SELECTED ORGANIC COMPOUNDS FROM WASTE STREAMS

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The European Pollutant Emission Register (EPER) database lists 50 chemicals or classes of chemical which are defined as being especially hazardous to human health or the environment. The focus of this study is to devise a novel method of treatment for a single selected organic chemical listed on the EPER database which is also present in industrial wastewater streams. Of the 25 organic chemicals on the database, phenol was selected due to its relatively high water solubility, potentially damaging environmental impact and significant release quantities into industrial wastewaters each year. The proposed process for removal of phenol consists of an initial adsorption step followed by a secondary catalytic oxidation step. The work to date has focused on the first step; adsorption of phenol onto zeolite-beta and the modification of zeolite beta to facilitate catalysis. Uptake of the phenol has been assessed as a function of contact time, pH, initial aqueous phenol concentration and silica to alumina ratio within the adsorbent material. It was found that phenol uptake takes place within the first 10 minutes of contact with a maximum uptake level of 17.4 mg g^{-1} being achieved. Phenol removal was found to have a significantly negative relationship with increasing temperature and a positive relationship with increasing silica ratio but with no definable relationship to the pH of the adsorbate solution. The Freundlich model of adsorption provided the best correlation for phenol uptake on the zeolite-beta. The zeolite was also successfully modified with copper which was found to have a favourable relationship with phenol adsorption and good aqueous stability within a pH range of 5 to 9. Further research work in the second step of the process will assess the ability of the copper modified zeolite to catalytically oxidize the adsorbed phenol.

NEW BACTERIAL DESTRUCTOR OF ALKYLPYRIDINE DERIVATIVES

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Pyridines constitute an important group of industrial contaminants. These compounds are formed in coal chemistry, present in wastes of petrochemical and pharmaceutical enterprises, widely used as solvents, dyes and pesticides. Due to their heterocyclic moiety they are better soluble in water than their carbocyclic analogues and may easily penetrate ground waters. The most promising method of pyridine containing wastes treatment involves microorganisms. The present work deals with the search, isolation and cultivation of a strain able to destruct methyl and dimethyl derivatives of pyridine. GC-MS was applied to understand the pathways of catabolism of 2-methylpyridine, while MALDI was used for the characterization and identification of the strain.

The study of pyridines transformation was based on the results of the dynamic of growth of the strain in mineral media. Pyridines were introduced as the only source of carbon, nitrogen and energy. Purge and trap technique with Agilent 5973 quadrupole instrument was used to identify volatile compounds. LECO Pegasus IV TOF instrument in GC-MS and GC-GC-MS mode was used to study semi volatile products. Methylation was used to make polar compounds amenable for the analysis. Autoflex (Bruker) MALDI TOF instrument was used for the characterization and identification of the strain destructor and its comparison with the related strains of microorganisms.

The new strain was isolated from the soil contaminated by pyridine containing wastes of a chemical enterprise “Acrikhin”. The strain was tested to study its efficiency in destruction of pyridine and its methyl and dimethyl derivatives. The efficiency appeared to be remarkable. Mineralization takes place in 24 hours while the initial levels of pyridine may be as high as 1.5 g/l, of 2-methylpyridine – 2 g/l, of 4-methylpyridine – 1.5 g/l, of 2,6-dimethylpyridine – 3 g/l. Microbiological analyses allowed referring the new strain as Arthobacter sp. This result was confirmed by genetic method – sequencing of 16S rRNA. To make the final identification of the species we launched a comparative study of the MALDI mass spectra of eleven strains from the Russian State collection of microorganisms (Pushchino) belonging to Arthrobacter family. The best mass spectra were recorded with the strain cultivated on Difco agar with sinapinic acid as a matrix. All the strains produced quite different peptide fingerprint, although it was possible to divide the species into three groups. Three cultures of this family possess a characteristic triplet in the spectrum due to the presence of three peptides with the masses about 7000 Da. The same feature is present in the spectra of the new strain. The second part of the study dealt with the pathways of catabolism of 2-methylpyridine. Various mass spectrometric techniques were used for this purpose. Purge and trap method, as well as liquid-liquid extraction followed by GC-MS analysis were used to detect volatile and semi volatile products. The transformation of the original substrates starts with hydroxylation of the pyridine cycle. At the second stage another oxygen atom penetrates the molecule. Alternatively electrophilic addition of water to the double bond takes place. When two hydroxyl groups are in the intermediate the cleavage of the cycle takes place. Keto acids were detected in the reaction mixture as intermediates. Sixteen products were detected and identified in the reaction media. Their structures allowed proposing a scheme of degradation of 2-methylpyridine. Oxidative rather than reductive mechanism rationalizes the observed products.

MERCURY IN SEDIMENTS OF THE ESTUARY OF THE NERBIOI-IBAIZABAL RIVER (BAY OF BISCAY, BASQUE COUNTRY): TRENDS IN TIME AND SPACE FROM 1998 TO 2007

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The Nerbioi-Ibaizabal estuary (Bilbao, Bay of Biscay, Basque Country) constitutes the most industrialised and populated area of the whole Cantabrian cornice. In the seventies, the system was severely polluted due to historical mining and industrial activity during the last century. Closure of important pollutant enterprises, together with implementation of environmental protection policies have resulted in a gradual recovery of the estuary. Sediments remind nowadays, however, not only as a reminder of historical pollution, but also reflect the current activity in the estuary.

Mercury was found in unacceptable high concentrations in sediments collected in several points of the estuary in 1998. The aim of this study is to investigate the evolution in time and space of the total concentration of mercury in sediments of the Nerbioi-Ibaizabal estuary, in order i) to check if the presence of this metalloid in the estuary remains or not in a potentially problematic level and ii) to identify trends and potential pollution sources.

Total concentration of mercury was measured in surface sediments collected in different points of the estuary (four in the main chanel, four in tributaries and five in semi-closed docks) during several sampling campaigns between March 1998 and July 2007. The longest time series includes 13 sampling campaigns in one of the points located in the main chanel.

The sediments were analysed by cold vapour atomic absorption or fluorescence spectroscopy after acidic extraction assisted by microwave or ultrasound focused energy and preconcentration by cryofocussing. The results have been analysed in terms of geographical and temporal trends and the pollution level has been compared to that of other similar environments. In addition, international standards, such as the geoaccumulation index, together with background values proposed for the area have been used to estimate the quality of the sediments from an toxicological point of view.

As a general conclusion, it can be stated that mercury concentration in sediments of the estuary shows a significant decreasing trend along the period investigated. Several points, however, still exhibit mercury concentrations substantially higher than the background value estimated for the area.

Acknowledgements: This work has been financially supported by the Basque Government through the ETORTEK BERRILUR II (IE06-179) project. A. Gredilla and S. Fdez-Ortiz de Vallejuelo are grateful to the UPV/EHU for their pre-doctoral fellowship.

UNDERSTANDING THE MECHANISMS OCCURRING DURING THE REMOVAL OF ARSENIC BY COAGULATION FLOCCULATION AND ELECTROCOAGULATION

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Since the reduction of the maximum contaminant level of arsenic in drinking water from 50 to 10 $\mu g.L^{-1}$, several different removal processes were developed and optimized. The most promising processes for arsenic removal are coagulation flocculation and adsorption because of their low costs and high efficiency. Coagulation flocculation is a well known and easy-to-handle process, it uses easily available, cheap and not hazardous coagulants and it is always an important step in a potabilization treatment plant; it was thus preferred to adsorption. However, an alternative coagulation flocculation process, called electrocoagulation, in which cations are produced by the electrodissolution of soluble anodes, was also developed and optimized because it presents the advantage to avoid the addition of chemical reagents such as cationic coagulant.

The optimization of the coagulation flocculation process using $FeCl_3$ as coagulant was realised on reconstituted water spiked with the maximum total arsenic concentration acceptable before treatment (100 $\mu g.L^{-1}$ as As(III) or As(V)) and taking into account residual turbidity and Fe(II), Fe(III), As(III), As(V) concentrations. For $[Fe^{3+}]$ = 37 $mg.L^{-1}$ and pH > 6,0, residual As(III) and As(V) concentrations were respectively 2.5 ± 0.2 $\mu g.L^{-1}$ and ≤ 0.8 $\mu g.L^{-1}$ and residual turbidity and total iron concentration respected the European potabilization standards. Comparison with the electrocoagulation process underlined i) lower treatment dose to apply ($[Fe^{3+}]$ = 25 $mg.L^{-1}$), ii) self regulation of pH, iii) better As(III) removal (residual concentration of 0.8 ± 0.1 $\mu g.L^{-1}$) during electrocoagulation process.

However, nowadays, few studies deal with the comparison of the mechanisms occurring during the both processes. Thus, a series of experiments was realised to try to reproduce pH and coagulant electrocoagulation conditions in coagulation flocculation and also to try to understand the mechanisms (adsorption, precipitation and coprecipitation) taking place during the removal: i) study of the adsorption of As(III) and As(V) on preformed iron(III) hydroxide flocs, ii) coagulation flocculation experiments with Fe(II) and a mixture of Fe(II) and Fe(III) iii) coagulation flocculation experiments at the same pH conditions as electrocoagulation. Finally, the zeta potential measurements helped understanding these mechanisms.

REMOVAL OF ORGANIC MERCURY FROM WATER BY ADSORPTION ON THIOL-FUNCTIONALIZED MESOSTRUCTURED SILICA

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Mercury compounds, which are highly toxic, are present in the environment from mining, urban wastes and industrial processes. Among them, organic mercury is the most toxic form. The research carried out in this work focused on the removal of different types of organic mercury(II) compounds (methylmercury chloride, phenylmercury chloride, dimethyl mercury(II)) from water and water/ethanol mixtures by adsorption on thiol-functionalized mesostructured SBA-15 silica.

This adsorbent is an hybrid organic-inorganic material with excellent properties for removing inorganic Hg(II)[1]. Silica SBA-15 material, prepared by using self-assembly methods, exhibit mesoporous ordered structures, with high specific areas and high pore volumes to act as good adsorbents. Besides, these materials are superficially modified with an organic monolayer that contains specific thiol sites for mercury anchorage.

To test the effectiveness for organic mercury, batch experiments have been perform to obtain adsorption isotherms at room temperature by modifiyng initial Hg(II) aqueous concentration. The results show that adsorption capacity decrease in the order: $HgCl_2 > CH_3HgCl > C_6H_5HgCl \approx (CH_3)_2Hg$. In addition, methylmercury chloride has been chosen to test the pH influence on the adsorption capacity of thiol-functionalized mesostrutured silica materials. The adsorption capacity remains approximately constant in a wide range of proton concentration from 1M to pH 12. As example, a characteristic TEM image of adsorbent pore structure and an experimental adsorption isotherm obtained for CH_3HgCl are shown in Figure 1.

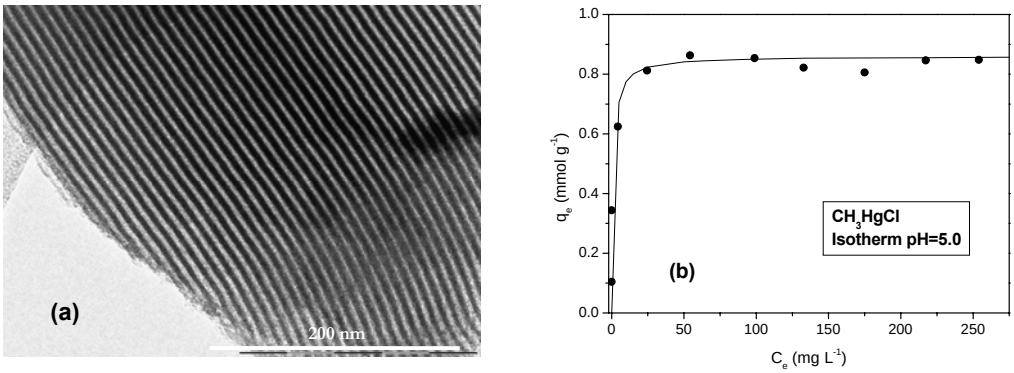

Figure 1. a) TEM image of SBA-15-SH b) Adsorption isotherm obtained for CH_3HgCl at pH=5.

Authors thank to the regional government of Madrid that has financed this work through the research project "REMTAVARES" (S-0505/AMB/0395) and URJC-CM-2007-CET-1674. Authors also thank to the "Ministerio de Educación y Ciencia" for the financial support through the projects CTM2005-01053 and "CONSOLIDER INGENIO 2010" (CSD2006-44).

[1] Aguado, J.; Arsuaga, J.M.; Arencibia, A. *Microp. Mesop. Mater.* **2008,** 109, 513.

USE OF ZEOLITES IN THE TREATMENT OF WATER POLLUTED BY SULFAMIDE ANTIBIOTICS

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An actual and underestimated problem is the environmental pollution due to drug release by humans and feedstocks. Generally, after administration, drugs (i.e. antibiotics, hormones, antiepileptics, pain-killers) are excreted from the organism for the most part unchanged. Drug residues are detected in the outlets of waste water treatment plants or in the agricultural wastes as a consequence of manure spreading. Whether drugs are not adsorbed by soils, they move along the soil profile towards the groundwaters. Antibiotics, used in the treatment of diseases or as growth-promoting additives in animal feeds (banned from European Community in 2006 but still permitted in USA), are the most diffuse classes of veterinary drugs. Among these, sulfamides are the fifth most widely used group of veterinary antibiotics within the EU and are considered ubiquitarious pollutants. Because of their unique adsorption and ion-exchange properties, zeolites are versatile materials, commonly applied as adsorbent, molecular sieves or catalysts. With the aim to perform a cheap and environmentally friend clean-up system of waters contaminated by antibiotics, in this study we have investigated the adsorption and degradation properties of Y-Faujausite and Mordenite zeolites towards three sulfamides (sulfadiazine, sulfamethazine, and sulfachloro-pyridazine). Only zeolites with the channel size comparable to sulfamides molecular dimensions were chosen. Adsorption properties were determined varying Si/Al ratio in the zeolite framework. All sulfamides were completely and quickly ($t_{1/2}$ < 1 min) adsorbed from water on hydrophobic Y zeolites with 200 Si_2O_3/Al_2O_3 ratio. The maximal amounts of antibiotics adsorbed on Y zeolite obtained after 10 adsorption cycles ranged beetween 15-30% of zeolite dry weight. Hydrophobic Mordenite with 200 Si_2O_3/Al_2O_3 ratio was more effective in the adsorption of sulfachloropyridazine (80% of the initial value adsorbed at room temperature, > 90% at 65°C) if compared to sulfadiazine and sulfamethazine. The maximal amounts of sulfachloropyridazine obtained after 5 adsorption cycles on Mordenite at 65 °C was about 20% of zeolite dry weight and a degradation product was detected. Despite of large amount of sulfamides adsorbed on Y and Mordenite zeolites, the adsorption of antibiotics was not reversible in water (2–3% of desorbed sulfamides). X-ray analyses confirmed the presence of sulfamide molecules inside of zeolite channels as showed by the cell parameter variations calculated before and after adsorption. Finally, FT-IR analyses helped to interpret the interaction mechanism that involves N-H bond of sulfonamide group and O of the framework. The high adsorption capacity, the fast and irreversible adsorption of the three sulfamides make hydrophobic Y zeolite a good candidate for the clean-up of water contaminated by sulfamide antibiotics.

ENHANCEMENT OF POLLUTANTS OXIDATION FROM THE $SO_4^{\circ-}$ RADICAL GENERATION IN WATERS

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Previous work in our group showed that the sulphate radical generated from the UV irradiation of persulfate ions enable complete mineralization of acetic acid compared to the numerous by-products formed from oxidation by OH° radicals. In this study, the sulphate radical was produced from the irradiation by an electron beam accelerator of waters in the presence of persulfate ions. Under these conditions, both OH° and $SO_4^{\circ-}$ radicals were formed :

$H_2O \rightarrow OH^\circ, e^-_{aq}, H^\circ$ (ionisation)
$e^-_{aq} + S_2O_8^{2-} \rightarrow SO_4^{\circ-} + SO_4^{2-}$

Experiments performed on aqueous solutions of phenol confirmed the positive effect of the $SO_4^{\circ-}$ radicals generation for the removal of the initial molecule and its by-products. The results have been simulated with good accuracy (Copasi® software).Sulphate radicals also react with the solvent to form OH° radicals :

$SO_4^{\circ-} + H_2O \rightarrow SO_4^{2-} + OH^\circ + H^+$

In the second part of the work, ferrous or ferric ions were added in the system in order to tentatively catalyze the formation of the sulphate radicals. Under these conditions, the efficiency was highly improved and the radiation dose necessary to the total removal of phenol could be divided by 3. This could be explained by the additional reaction of ferrous ions with persulfate :

$Fe^{II} + S_2O_8^{2-} \rightarrow SO_4^{\circ-} + SO_4^{2-} + Fe^{III}$

Finally, this combined advanced oxidation process has proved also its interest in the oxidation of municipal and industrial wastewaters compared to the treatment without any reactant.

The original data obtained in this study show that the production of sulphate radicals complementary to the wellknown OH° radicals could improve the reactivity of AOPs. The use of persulfate ions could offer new prospects for radical oxidation systems in lowering the energy required for a given purpose.

SCREENING OF PHARMACEUTICALS AND OTHER ORGANIC POLLUTANTS IN AGRICULTURAL IRRIGATION AND THEIR POTENTIAL CROP UPTAKE IN TORROELLA DE MONTGRI, SPAIN

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Irrigated agriculture represents the bulk of water demand and it is usually the first sector impinged by water shortage. In order to sustain food production an efficient use of all water resources is needed. Reuse of wastewater treatment plant (WWTP) effluent is a sustainable crop irrigation alternative. Nevertheless these effluents may be a source of different classes of contaminants such as human and veterinary pharmaceuticals, personal care products (PPCPs), disinfection by-products (DBPs), pesticides, polycyclic aromatic hydrocarbons (PAHs) amongst others. There is a potential for the contaminants present in the effluent to be uptaken by the irrigated crops and thus entering into the human food chain. Uptake of veterinary medicines, PAHs and pesticides from soil into plants has been documented, making the risk assessment of great importance[1,2].

The aim of this work was to evaluate the occurrence of 60 contaminants belonging to different chemical classes in chlorinated reclaimed water (Torroella de Montgri WWTP) and river water (Ter river) used for crop irrigation in the NE Spain over 2-years monitoring period (2007-2008). In addition, the loading mass discharged into agricultural soil of these pollutants corresponding to different crops, namely maize, *Zea mays,* apple, *Malus domestica,* and alfalfa, *Medicago sativa*, was estimated from crop irrigation regimes. Table 1 shows the figures of merit for analytical techniques employed in the analysis of these pollutants. 26 out of 60 contaminants studied were detected in both river and reclaimed water, 9 DBPs (0.09 to 24 ng L^{-1}), 6 pharmaceuticals (0.01 to 7.98 ng L^{-1}), 4 PCPs (0.002 to 6.9 ng L^{-1}), and 2 flame retardants (0.027 to 7.98 ng L^{-1}). The occurrence of these pollutants is due to discharges of both WWTP effluents and untreated sewage discharges upstream the river catchment

Table 1. Analytical techniques employed in pollutant determination and discharge in agricultural soil for the different crops studied

Compound	Preconcentration Technique	Analysis	LOD (ng L^{-1})	LOQ (ng L^{-1})	Estimated load (mg Ha^{-1} y^{-1})
Trihalomethanes	HS-SPME	GC-ECD	1-350	2- 474	28 - 250
Nitrosamines	SPE	GC-NPD	0.09 - 0.9	0.15-2	28- 50
Pharmaceuticals	SPE	GC-MS	0.08 - 0.47	0.11 - 0.5	205 - 364
PCPs	SPE	GC-MS	0.03 - 0.18	0.046 - 0.24	198 - 227
Flame retardants	SPE	GC-MS	0.36 - 0.46	0.37 - 0.61	87 - 120
Pesticides	SPE	GC-MS	0.15- 8.6	0.19 - 23	102 - 117

HS-SPME. Headspace solid-phase microextraction. SPE. Solid-phase extraction
GC-ECD, GC-NPD, GC-MS: Gas chromatography coupled to electron capture detection, nitrogen phosphorous detection, mass spectrometry.

1. Nikolaou, A., Meric, S., Fatta, D. Ocurrence patterns of pharmaceuticals in water and wastewater environments. Anal. Bioanal. Chem. (2007) 387: 1225-1234
2. Khan, S., Aijun, L., Zhang, S., Hu, Q., Zhu, Y. Accumulation of polycyclic aromatic hydrocarbons and heavy metals in lettuce grown in the soils contaminated with long-term wastewater irrigation. J. Hazardous Materials, 152 (2008) 506 - 515

DETERMINATION OF POLY(VINYLPYRROLIDONE) IN WASTE WATER SAMPLES BY PYROLYSIS-GAS CHROMATOGRAPHY / MASS SPECTROMETRY

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Poly(vinylpyrrolidone) (PVP) is synthetic polymer widely used in a variety of industries, because of its unique spectra of properties, particularly good solubility not only in water but also in a large number of organic solvents, low toxicity, high complexing ability and good film-forming characteristics. Because of its low toxicity, PVP is intensively used in the pharmaceutical industry as binder in many tablets. PVP also gets application in the cosmetic, detergent and brewing industries. As a result of its very frequent usage and its suggested environmental stability, it is proposed that PVP has to be detected in the polluted water samples. However, an appropriate analytical method for detection of this polymer is missing so far. In this work an analytical method for detecting trace levels of PVP in waste water samples was developed applying off-line pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).
The concentrations of PVP in the analyzed water samples were calculated on the basis on main degradation (pyrolytic) product, *N*-vinyl-2-pyrrolidone (NVP). Different amounts of the commercial PVP were pyrolized in off-line conditions (500 □C and 1 h), in order to establish correlation between the initial amount of polymer and the amount of NVP. Degradation products were dissolved in dichloromethane and identified by GC/MS. The amount of NVP in pyrolyzates was determined by GC. Calibration curve was constructed using commercial NVP and corrected by an internal standard, 4-*tert*-butylcyclohexanone. The amount of NVP generated during pyrolysis was between 8.5 and 10.1 mass %, calculated to initial mass of PVP, which was ranged from 20 to 1000 □g. The pyrolytic calibration was used for the calculation of PVP levels in the spiked and waste water samples. Spiked water samples (□200 mg PVP per 1 dm^3 of distilled water) were pre-extracted consequently with hexane and diethyl ether and after that water phase was evaporated and dissolved in methanol. Pyrolysis of the methanolic solutions showed that the amount of PVP was ranged between 92.3 and 96.5 mass %, calculated to the initial mass of polymer which was dissolved in distilled water. The obtained results indicated that "pre-extraction" can be used in order to decrease the amount of organic substances which are also capable to be pyrolyzed, without significant loss of PVP. The presence of PVP in two waste water samples (municipal waste water from Aachen, Germany and industrial waste water from Pancevo, Serbia) was investigated in the last part of this work. Both samples (250 cm^3) were pre-extracted in the same way as the spiked samples and after that evaporated and dissolved again in distilled water (25 cm^3). GC/MS analysis of the pyrolytic products showed that PVP was present in both waste water samples. The calculated concentrations of PVP amounted 7.1 mg/dm^3 (water from Aachen) and 2.9 mg/dm^3 (water from Pancevo). In summary, an effective and robust method based on pyrolysis techniques was developed for the determination of PVP at trace levels in waste and surface water systems.

A NOVEL NANOBIOSENSOR FOR DETERMINATION OF THE HERBICIDES GLUFOSINATE, GLYPHOSATE AND ITS METABOLITE AMINOMETHYLPHOSPHONIC ACID

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Glyphosate and glufosinate are broad-spectrum herbicides used extensively for control of long grasses and broad-leaved weeds. The increase in the use of these herbicides has lead to their residues being found in soil, atmosphere, agricultural products, as well as in ground water. However, because their effects on non-target organisms and overall environmental impact have not been fully investigated, questions regarding the environmental safety with their increasing use have to be addressed. As a result, the Food and Agricultural Organization (FAO) of the United Nations has set a maximum residue limit (MRL) of glyphosate in the range of 0.1–5.0 mg kg^{-1} for fruits and grains and MRL of glufosinate at 0.05 mg kg^{-1} for grains [1]. The challenge of monitoring these herbicides in situ requires new and improved analytical devices featuring low limits of detection, sensitivity, rapidity, and ease of operation to detect foodstuffs for glyphosate and glufosinate contamination. In this context, biosensors appear as suitable alternative or complementary analytical tools. Nanobiosensor for the determination of glufosinate, glyphosate and its major metabolite aminomethylphosphonic acid (AMPA) is therefore reported in this paper. The nanobiosensor was constructed by electrochemically depositing poly(2,5-dimethoxyaniline) (PDMA) doped with poly(4-styrenesulfonic acid) (PSS) onto the surface of a rotating gold disk electrode followed by electrostatic attachment of the enzyme HRP onto the PDMA-PSS nanocomposite film. The PDMA-PSS and HRP/PDMA-PSS films were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), UV-VIS spectroscopy and Fourier transform infrared (FTIR) spectrocopy. Hydrogen peroxide was used to measure activity of the enzyme before injection of the herbicides and spiked samples into the electrolyte solution. Glufosinate, glyphosate and AMPA analyses were realized on spiked soya bean samples within a concentration range of 1.0-78.0 µg L^{-1}. Detection limits were 0.1 µg L^{-1} for both glyphosate and glufosinate while that of AMPA was 1.0 µg L^{-1} without sample clean-up or preconcentration.

[1]. FAO. Food and Agriculture Organization. Food Standards Programme. http://www.codexalimentarius.net/download/report/655/al29_24e.pdf (2006)

FTIR REFLECTANCE OF ASTROBIOLOGICALLY SIGNIFICANT MINERALS AND THEIR MIXTURES: IMPLICATIONS FOR THE STUDY OF MARS SURFACE ENVIRONMENT

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Reflectance spectroscopic studies have provided some of the most remarkable advances in our understanding of Mars surface environment, such as detecting the presence of various types of water-related minerals[1]. The Martian regolith is made up of an apparently homogenized dust having (broadly) basaltic composition, with admixed local rock components, oxides (e.g. hematite), water-bearing phyllosilicates and salts (mainly sulfates). Quartzofeldspathic materials also have been identified. However, much is still unknown about Martian chemical-mineralogical assemblages, which is fundamental to interpreting its environmental (and paleoenvironmental) settings[2-4]. NASA's Mars Science Laboratory (MSL) is a rover that will assess whether Mars ever was, or is still today, an environment able to support microbial life[5]. It is the first mission with an environmental station located on the rover and with a mission's duration of one Martian year, which allows the study of Mars seasons. The Rover Environmental Monitoring Station (REMS) is one of the MSL instruments, which has been designed for measuring ambient pressure, humidity, wind speed and direction, UV radiation, and air and ground temperature (GT)[6]. GT will be recorded by using three thermopiles. The bandwidth of each thermopile is: 8-14, 14,5-15,5, 16-20 microns. Specifically, the GT-sensor is dedicated to measure the brightness temperature of the Martian surface, integrating the IR energy coming from the ground, and making an estimation of the emissivity. In order to evaluate the impact on the measurement of ground minerals, the FTIR reflectance of a set of selected minerals and basalt were measured, for different mixing amounts, and covering the working wavelength range of the REMS' GT sensor. The minerals were selected from verified standards (SARM, NCS, USGS) and terrestrial analogs (e.g. Jaroso, Sorbas, Atacama); they consist of hematite, goethite, magnetite, jarosite, halite, smectite/montmorillonite and jasper. Samples were cut into small pieces, grounded in an agatha mortar, and sieved to get a powder smaller than 45μm (in accordance with Martian regolith dust). All mineral powders were dried in order to fit the Mars arid surface conditions before their final analysis using a Nicolet Nexus FTIR (Thermo). The working range for the reflectance data acquisition was from 3.34 to 25 microns. The results obtained indicate significant percentage increases or decreases of reflectance in the whole wavelength range (e.g basalt-hematite *vs.* basalt-magnetite) and specific variations restricted to some spectral bands (e.g. basalt-smectite *vs.* basalt-jasper). This confirms the necessity of taking into account the chemical-mineralogical assemblages (and textures) for any study of Mars surface environment.

1 Cloutis E.A. et al. (2008) *Icarus* 195 (2008) 140–168
2 Bandfield JL et al. (2004) *J Geophys Res* E100:1–14
3 Martínez-Frías et al. (2006) *Rev Environ Sci Biotechnol* 5: 219-231.
4 Martínez-Frías et al. (2007) *AMBIO: Journal of the Human Environment* 36-5: 425-427.
5 http://mars.jpl.nasa.gov/msl/
6 Gómez-Elvira, J. and REMS Team (2008) *Lunar and Planetary Science* XXXIX (2008) 1647.pdf

DETERMINATION OF PARTICLE-ASSOCIATED NITROSAMINES IN THE ATMOSPHERIC ENVIRONMENT OF ZONGULDAK, TURKEY

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A gas chromatography-mass spectrometry (GC-MS) method has been proposed for the determination of mutagenic and carcinogenic nitrosamines in particulate matter (PM). The method includes collection of the particulate matter ($PM_{2.5}$ and PM_{10}) using dichotomous Partisol 2025 sampler, extraction of the compounds from aqueous solution with dichloromethane/n-propanol after sonication with water prior to their GC-MS analysis in both EI and PNICI mode. The obtained recoveries of nitrosamines ranged from 92.2 to 98.8 % and the precision of this method, as indicated by the relative standard deviations (RSDs) was within the range of 1.2 and 3.4 %. The detection limits obtained from calculations by using GC-MS results based on S/N=3 were within the range from 0.01 to 0.12 ng/m^3.

In the present study, airborne fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particulates collected in Zonguldak province during summer and winter times were analysed for nitrosamines by the proposed method and the method was shown to be suitable for the determination of these compounds at the levels of ng/m^3 in air and airborne particulate samples. The predominant nitrosamines determined in PM were N-nitrosodibutylamine, N-nitrosodiethylamine, N-nitrosodimethylamine, N-nitrosomorpholine, N-nitrosodipropylamine. The concentration levels of nitrosamines fluctuate significantly within a year with higher means and peak concentrations in the winter compared to that of summer times.

ANALYSIS OF ORGANIC SULFUR COMPOUNDS IN BIOGAS

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During the fermentation of agricultural wastes and energy crops in biogas plants, reduced organic sulfur compounds are released in addition to the produced biogas. Due to their high reactivity, the sulfur compounds may cause operational problems during the further use of the biogas in combined heat and power production plants or in fuel cells apart from odour problems. Additionally, the volatile sulfur organic compounds may have adverse effects on analytical devices or sensors applied for process control. The objective of our project was, hence, to (i) develop analytical methods for the analysis of reduced organic sulfur compounds in biogas, gas condensate and process liquid of biogas plants and (ii) to monitor selected samples of lab-scale continuous stirred tank and leach-bed reactors fed with various substrates. The analysed organic sulfur compounds are: ethanethiol, dimethyl sulfide, carbon disulfide, 1-propanethiol, 2-propanethiol, ethylmethyl sulfide, diethyl sulfide, dimethyl disulfide and dimethyl trisulfide. For the development of the analytical procedure, model solutions are employed. Quantification of the compounds is based on internal isotopic standards. Organic sulfur compounds in biogas samples were enriched using solid phase micro extraction (SPME) prior to GC-MSD analysis. For aqueous samples of biogas condensate, direct SPME in the liquid phase is compared to SPME in the headspace (HS) of liquid samples as well as HS analysis without further enrichment. Due to the complex matrix of the process liquid, only HS-GC-MSD and HS-SPME-GC-MSD is applied to this type of samples. Reactors run as co-fermentaters of maize silage and cattle of pig manure are compared to mono-fermentaters of maize silage. Preliminary studies reveal that the occurrence of organic sulfur components depends on the substrate of fermentation as well as on process parameters such as organic loading rate and temperature regime. Due to their high volatility and the effective SPME sample enrichment most compounds are found in biogas samples. Determined concentrations range from 10 to 300 ng L_{gas}^{-1}.

SELECTED MUSK COMPOUNDS IN AQUATIC ECOSYSTEM

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Musk compounds (MCs) are artificial odorous organic chemicals used in overwhelming majority of fragranced consumer products instead of natural musks. From economical and technological points of view natural musks, compared to synthetic musks, are not considered favourable for the industrial use. MCs are added to everyday products such as laundry detergents, air fresheners, hand creams, soaps, perfumes, all personal care products, fabric softeners or household cleaners. They enter the surface water from the waste water or from waste water treatment plants where they get mostly after the application in domestic households. Subsequently they accumulate in aquatic biota and finally they can appear also in drinking water. In last decade these compounds have attracted the attention as they were found to be persistent (Musk xylene, Musk ketone) or potentially persistent (Tonalide® - AHTN, Galaxolide® - HHCB) in the environment. Musk Xylene (MX) and Musk Ketone (MK) have been included in priority lists under the European Commission Existing Substances Regulation (ESR), which is the European programme for identifying risks from chemicals to human health and the environment.

This study was focused on the occurrence of musk compounds in the aquatic ecosystem. In addition to above mentioned musks also following fragrances produced in the AROMA Company, Prague were monitored: 2-cyclohexyl ethanole, 2-cyclohexyl acetate, 3-phenyl-1-propanole (HSA), 2-terc. butyl cyclohexyl acetate (Arocet), 2-terc. Amyl-cyclohexyl-acetate (Arofir), 4-terc. amyl-cyclohexanone (Aroflorone), 2-sec. butylcyclo-hexanone (Aromentone), allyl-3-cyclohexyl-propionate (Ananolide).

Waste water and sewage sludge from the Brno city Wastewater Treatment Plant (WWTP) and from smaller WWTP situated in the area of University of Veterinary Medicine (UVM) in Brno were sampled; also fish from the Svratka river close to discharge of WWTP was sampled. Either passive sampling using SPMDs or SPME were applied for isolation of target compounds from waters. Sewage sludge was extracted by three technigues (Soxhlet extraction, PSE, MWAE). Fish samples were homogenized with sodium sulfate and extracted using Soxhlet extraction. Extracts were cleaned-up by GPC and column chromatography (mixed column, Florisil and Silica 1:1). For final analysis GC/MSD technique was employed using splitless injection and selected ion monitoring.

In the waste water at the Brno WWTP the highest concentration show Arocet, Arofir, HHCB and AHTN. At WWTP situated in the area of UVM MC were detected only in influent. MX:MK:HHCB:AHTN were present approximately in this ratio – 2:1:170:30.

Analyses of real sludge samples from WWTP Brno - Modřice proved only the presence of AROCET in a mix sludge; no other compounds were identified in digested sludge which may indicate their fast biodegradation.

In biota were found MK 35,58 – 325,91 □g/kg of fresh tissue, MX 108,95 – 166,41 □g/kg f.t., HHCB 63,32 – 870,23 □g/kg and AHTN 103,93 – 196,73 □g/kg f.t.

Acknowledgement: This study was supported by the Project OC- 83, COST Action 636.

METAL SPECIATION: MEASURING WITH AGNES AND INTERPRETING WITH CONDITIONAL AFFINITY SPECTRA

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Trace metal speciation science[1] is continuously progressing with both, new measuring methods and new interpretative frameworks.

In particular, AGNES (Absence of Gradients and Nernstian Equilibrium Stripping)[2] determines free metal ion concentrations for amalgamating metals. The judicious selection of AGNES' parameters, leading to practical deposition times[3], is critical for the technique. In this respect, the knowledge of the lability characteristics of the complexes (relating their diffusive and dissociation capabilities) is also very helpful. Apart from validation against consolidated techniques (ISE, Scanned Stripping Chrono-potentiometry[4] and Resin Titration[5]), the development of AGNES has included its implementation with microelectrodes [6], rotating disk electrodes, screen printed electrodes and a careful analysis of intermetallic compounds between Znº and Cuº (which was essential for free Zn^{2+} determination in wine). Several applications to environmental systems are studied: free Zn determination in Mediterranean seawater[7] and in the Ebro river, Pb^{2+}complexation to several fractions from anthropized water and complexation of Cd, Zn and Pb to Purified Aldrich Humic Acid[8].

On the interpretative front, as a complementary alternative to isotherms or average equilibrium functions, the affinity spectrum (the distribution of affinities that characterises the binding properties of the ligand) associated to monocomponent and multicomponent isotherms can be found by using adequate inversion formulas[9]. Experiments performed at a fixed pH values allow the reduction of competitive isotherms into monocomponent ones, whose Conditional Affinity Spectra (CAS) [10] allow a visualization (guiding physical interpretations) of the characteristics of the associated binding isotherms. For instance, in the case of NICA[11], we have shown that each monomodal distribution (at each pH) or CAS might include two peaks or a peak and a shoulder. This behaviour justifies the remarkable adaptability of this competitive isotherm to experimental data [12,13].

[1] J.Buffle, Complexation Reactions in Aquatic Systems. An Analytical Approach., Ellis Horwood Limited, Chichester, 1988.
[2] J.Galceran, E.Companys, J.Puy, J.Cecília, J.L.Garcés, J. Electroanal. Chem. 566 (2004) 95.
[3] E.Companys, J.Cecília, G.Codina, J.Puy, J.Galceran, J. Electroanal. Chem. 576 (2005) 21.
[4] R.F. Domingos , C.Huidobro, E.Companys, J.Galceran, J.Puy, J.P.Pinheiro, J. Electroanal. Chem. 617 (2008) 141.
[5] G.Alberti, R.Biesuz, C.Huidobro, E.Companys, J.Puy, J.Galceran, Anal. Chim. Acta 599 (2007) 41.
[6] C.Huidobro, E.Companys, J.Puy, J.Galceran, J.P.Pinheiro, J. Electroanal. Chem. 606 (2007) 134.
[7] J.Galceran, C.Huidobro, E.Companys, G.Alberti, Talanta 71 (2007) 1795.
[8] E.Companys, J.Puy, J.Galceran, Environ. Chem. 4 (2007) 347.
[9] J.L.Garces, F.Mas, J.Puy, J. Chem. Phys. 120 (2004) 9266.
[10] J.L.Garces, F.Mas, J.Puy, J. Chem. Phys. 124 (2006) 044710-1.
[11] L.K.Koopal, T.Saito, J.P.Pinheiro, W.H.van Riemsdijk, Colloids Surf. A 265 (2005) 40.
[12] J.Puy, C.Huidobro, C.David, C.Rey-Castro, J.Salvador, E.Companys, J.L.Garces, J.Galceran, J.Cecilia, F.Mas. Submitted to Colloids Surf. A, 2008;
[13] J.Puy, J.Galceran, C.Huidobro, E.Companys, N.Samper, J.L.Garces, F.Mas. Submitted to Environ. Sci. Technol., 2008;

THE USE OF OIL SHALE ASH FOR AGRICULTURE: EXPLORING THE ENVIRONMENTAL SIGNIFICANCE OF MATRIX EFFECTS

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The main principles of the EU waste policy are sustainable use of natural resource and recycling of wastes. Therefore, the utilization of solid wastes, e.g., fly ash (FA) from power plants; to improve soil properties is an important issue for sustainable development. The FA can provide plant nutrients and serve as a liming agent to neutralize soil acidity. The most common mineral ingredients of agricultural importance in oil shale FA are: CaO (30-44%) as a liming agent, SiO_2 (27-32%), K_2O (2,7-7.0%) as a fertilizer, and Fe_2O_3 (5.2-5.5%). However, FA contains elevated concentrations of trace elements that could adversely affect plant and soil quality. The environmental impact of pollutants is related to their availability for transport and bio-uptake, rather than their total concentration in the soil or waste material. The aim of the present study is to characterize the environmental aspects of utilization of oil shale FA in agriculture by investigating water treatment processes, e.g., leaching of the main matrix components as well as toxic trace metals in soil-ash system.

Samples of agricultural soils, particularly Rendzic Leptosol and Podsolic Gleysols were treated with water separately and in a mixture of oil shale FA by using different approaches, e.g., 1) typical one step leaching scheme or 2) pre-treatment of material with a small amount of water which was followed by a regular leaching test, keeping the total amount of water constant. The transport of soil and FA matrix components to water phase was highly dependent on the leaching conditions, being more effective when the pre-treatment scheme was used. Due to the interaction of ingredients in soil-ash mixture the matrix components were intensively retained in solid phase. The sensitivity of certain metal compounds to matrix behaviour under environmental conditions was found to be specific. In general, the most mobile metals were found to be chromium, zinc, and cadmium. Thus, the composition of FA, the parent soil characteristics and the conditions of interactions between soil and waste matrices are important factors determining the mobility of toxic ingredients in a terrestrial system. For the safe recycling of oil shale wastes in agriculture, it is recommended to take into account the leaching of trace elements from combustion ash amended soils.

PHOTODEGRADATION OF PHARMACEUTICAL COMPOUNDS

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Ibuprofen and ketoprofen are widely used as non-steroidal anti inflammatory drugs (NSAIDs). These compounds are applied for the treatment of rheumatoid arthritis, distress, fever etc. The widespread usage of the NSAIDs causes their presence both in sewage and natural waters [1, 2]. They are only partly eliminated by classical processes used in Sewage Treatment Plants (STP) due to their low or non biodegradability. It is therefore of great interest to investigate alternative processes implying light irradiation to eliminate these compounds from water: UV (ultraviolet) and UV/VUV (ultraviolet/vacuum ultraviolet) photolysis. Additionally, UV radiation may be used for water disinfection, too [3].

In this work, our aim was to examine the photodegradation of ketoprofen and ibuprofen. We discussed the direct UV and UV/VUV photolysis of ibuprofen and ketoprofen as single compound and as mixture in aqueous solutions. We also examined the effect of the dissolved oxygen.
Analyses were carried out by HPLC-UV/Fluorescence to determine the kinetics of photolysis for both compounds, and by GC-MS for ibuprofen to determine the structure of photoproducts.

Upon irradiation at 254 nm, the complete decomposition (96-99%) has been reached in 1 hour for ibuprofen and 90 seconds for ketoprofen. The presence of dissolved oxygen accelerates the photodegradation of ibuprofen, whereas no effect was observed for ketoprofen. The photoproducts of ibuprofen have been determined.

Ketoprofen is also known to have photosensitizer properties [4]. As a result, we have observed that the UV photodecomposition of ibuprofen became three times faster when irradiated in the presence of ketoprofen both in UV and UV/VUV photolysis experiments.

The photolysis of these compounds in natural samples will also be described.

[1] M. Petrović, S. Gonzalez, Damià Barceló, Trends in Analytical Chemistry, 22 (2003) 685-696.
[2] T. Ternes, M. Meisenheimer, D. McDowell, F. Sacher, H.-J. Brauch, B. Haist-Gulde, G. Preuss, U. Wilme, N. Zulei-Seibert, Environ. Sci. Technol., 36 (2002) 3855-3863.
[3] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671.
[4] F. Boscá, M.A. Miranda, Journal of Photochemistry and Photobiolology B: Biology 43 (1998) 1-26

IMPROVED V_2O_5-TiO_2/SO_4^{2-} CATALYSTS FOR THE SELECTIVE OXIDATION OF METHANOL TO DIMETHOXYMETHANE

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During the last decade, we have observed a growing concern for the minimization of CO_2 emissions in the atmosphere and their influence on the global warming via the greenhouse effect. Among the others the introduction of fuel-cell vehicles can significantly cut down the CO_2 emissions if compared to the conventional internal combustion engines. A still open challenge for the application of the fuel cell technology is the transport of H_2. One convenient method could be the on-board reforming of methanol to hydrogen, but the high toxicity of methanol is a too big restraint for a broad application. The solution is to substitute methanol with less dangerous liquid compounds and dimethoxymethane (DMM) is a great candidate.
Considering the promising results obtained using dispersed V containing phases over titania supports as catalysts for the selective oxidation of methanol to dimethoxymethane (DMM), we report in this work on the preparation and characterization of V_2O_5-TiO_2/SO_4^{2-} (VTiS) catalysts.
Different preparation methods were optimized to modulate the final SO_4^{2-} content in the samples. The addition of SO_4^{2-} is known to enhance the surface acidity and the redox properties the vanadium oxide phase that are directly connected with the catalytic activity of the VTiS catalysts.
The obtained materials were deeply characterized by complementary physical-chemical techniques (BET, ICP, XRD, FTIR, XPS, TGA, pyridine adsorption calorimetry and FTIR, TPR).
V_2O_5 appeared to be well dispersed on the surface of TiO_2 as shown by XPS results of the calcined samples. Only the samples prepared by mechanical grinding vanadium oxide showed aggregates detected by XRD. A single reduction peak centred around 850 K was detected by TPR for the samples prepared by co-precipitation and sol-gel, while a larger peak at higher temperatures of reduction (890 and 980 K) was collected for the samples prepared by mechanical grinding, according to the presence of bigger and less reducible vanadium oxide particles.
The oxidation state of vanadium was shown to vary with the preparation methods while titanium was always present at its maximum oxidation state. V^{5+} and V^{4+} were found in all samples, while V^{3+} was observed only for the catalysts prepared by mechanical grinding. The presence of V^{3+} was related to a higher concentration of SO_4^{2-} ions that can facilitate the vanadium oxide reduction once the catalysts are exposed to high vacuum and XPS electron beam.
In general the surface and redox properties of dispersed vanadium oxide were influenced by the preparation method and concentration of sulphate ions. It was possible to tune the SO_4^{2-} amount (and consequently the acidity) by choosing the right preparation route and calcination temperature.

REMOVAL OF 2-NITROPHENOL FROM AQUEOUS STREAMS

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Phenolic compounds arising from a variety of industrial waste streams are classed as priority pollutants according to the European Pollutant Emissions Register database (EPER). Currently, technologies for treating phenol containing industrial wastewaters include catalytic wet air oxidation, biological degradation, UV- oxidation, adsorption technology using activated carbon as adsorbent. Considerable interest has also developed in the use of alternative adsorbent materials. In this research work unmodified beta zeolite and copper-exchanged beta zeolite were investigated with a view to examining their potential as adsorbents for the removal of 2-nitrophenol from aqueous solutions. To evaluate the effectiveness of unmodified and modified beta zeolite for the removal of 2-nitrophenol, the kinetics, thermodynamics and influence of pH on the adsorption processes were investigated. Kinetic experiments were undertaken on unmodified beta zeolites in order to determine the equilibrium time for the adsorption process. In the case of the unmodified beta zeolites, the findings revealed that equilibrium 2-nitrophenol uptake reached a level of 70-80 mg g^{-1} at 24°C with complete uptake occurring in less than 20 minutes irrespective of initial 2- nitrophenol concentration. Thermodynamic evaluation indicated that the adsorption process is mildly exothermic with higher uptake at lower temperature. The optimum pH range for adsorption of the 2-nitrophenol on unmodified beta zeolite was in the pH range pH 4.0 to pH 6.5. The effect of varying the silica-alumina ratio of the beta zeolite on the 2-nitrophenol uptake level was also examined using four different beta zeolites with ratios of 25:1, 75:1,150:1 and 300:1, with uptake levels increasing with increasing Si/Al ratio. The influence of copper-exchanged beta zeolites on 2- nitrophenol uptake level was assessed revealing an increase in uptake level (approximately 80-100 mg g^{-1}) for all of the copper–exchanged beta zeolites.

INVESTIGATION OF BIOREMEDIATION POTENTIAL OF BACTERIA AND FUNGI FOR CRUDE OIL DEGRADATION

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Bioremediation potential of bacteria and fungi isolated from mud samples belonging to alluvial formation of the Danube River (waste water channel) of Pančevo industrial zone has been investigated. Total isolated microorganisms were divided into three parts and sown in an appropriate medium. One part was added with actidione antifungicide so that only bacteria propagated in it. The second part was added with streptomycin antibiotic. In that part fungi propagated. The third part (with no additives) contained consortium of fungi and bacteria.

Paraffinic type of crude oil, in inorganic medium in phosphate puffer, was a substrate for assessment of bioremediation potential of the mentioned microorganisms. The experiments of the simulated oil biodegradation lasted 30, 60 and 90 days. Parallel with that, blind experiments containing none of the mentioned organisms were conducted.

The changes in the contents and composition of the petroleum were monitored. Extracts were isolated from the samples using the Soxhlet method. They were assayed for the group composition (alkanes, aromatics, polar fractions and fatty acids) by method of column chromatography. Alkane fraction was analyzed by gas chromatography-mass spectrometry (GC-MS) techniques. The most intense oil degradation was achieved in the experiments with bacteria, somewhat weaker with consortium of fungi and bacteria, and the weakest bioremediation potential in these experiments was shown by fungi.

OXIDATIVE DEGRADATION OF PERSISTENT ECOPOLLUTANTS: PRO ET CONTRA

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Oxidative degradation is considered as an alternative to biodegradation of persistent pollutants. However chemical degradation is environmentally benign only if the process meets certain criteria, the most important of them being oxidant, intermediates and products.

In the study oxidative degradation of alkylphenol ethoxylates and some other phenol derivatives is described. Hydrogen peroxide activated by iron ions was used as oxidizing agent. Systems with both ferric and ferrous ions have been studied. Tensiometry and HPLC techniques were shown to be useful for study of kinetics of ethoxylate oxidative decomposition. Colorimetry was applied to study nitrophenol decomposition.

Advantages and disadvantages of the oxidant are discussed. A main drawback is a significant amount of iron salts remaining in the solution after the degradation. An attempt to overcome the disadvantage by using solid sources of iron was made. The systems were shown to be moderately active towards dinitrophenol oxidation but inactive towards more resistant alkylphenol ethoxylates.

Optimum conditions of oxidative degradation were found. Reagents ratio, pH, temperature were shown to be essential for the process.

Degradation intermediates and products were investigated by several techniques. The products were proved to be non-toxic, mainly water and acetic acid were found.

Oxidative degradation of phenol derivatives can be applied for water clean-up in a combination with biodegradation or even instead of it.

DEGRADATION OF AN AROMATIC CARBOXYLIC ACID IN WATER BY THE FENTON AND PHOTO-FENTON PROCESSES

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Advanced Oxidation Processes (AOPs) are gaining in importance as alternatives to conventional methods of elimination of organic contaminants from wastewater. Among AOP processes, the Fenton reaction, and especially the photochemically enhanced Fenton reaction (photo-Fenton), are considered most promising for the remediation of wastewaters from chemical, pharmaceutical and dye industries.[1] The Fenton reaction efficiently produces highly oxidizing species (*i.e.* hydroxyl radicals) from hydrogen peroxide and an iron(II) salt (eq. 1), whereas photochemical reactions enhance recycling of iron(III) to iron(II) in comparison with the dark process.

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^- + HO^{\cdot} \quad (1)$$

In this work, we have investigated the kinetics of the oxidation and mineralization of 2,4-dihydroxybenzoic acid (DHBA), a product of the degradation of aromatic pollutants of industrial wastewaters. Consumption of DHBA and formation and degradation of by-products have been analyzed by a combination of UV-visible spectrophotometry, HPLC, HPLC-MS, IC and TOC.

In contrast to the oxidation of DHBA by TiO_2 photocatalysis where no hydroxylated aromatic intermediates could be detected,[2] hydroxylation of the aromatic ring was observed during the DHBA oxidation by both Fenton and photo-Fenton reactions: 2,3,4-trihydroxybenzoic acid (2,3,4-THBA) was the main intermediate formed at the beginning of the reaction. Oxalic acid (OA) was the only low molecular weight carboxylic acid detected in significant amounts. Under the experimental conditions used, the concentrations of both 2,3,4-THBA and OA reached a plateau in the case of the Fenton reaction, whereas they were completely mineralized during the photo-Fenton reaction. As expected, mineralization was affected favorably by increasing both the oxygen concentration and the H_2O_2 initial concentration.

As observed for other compounds, only 40% DHBA mineralization was reached under the best conditions investigated for the Fenton reaction. This was mainly due to complexation of Fe(III) produced in Reaction 1 by carboxylic acids, especially oxalic acid (formation of a stable ferrioxalate complex).[1] Under irradiation, photolysis of the iron(III) complexes results in the photoreduction of iron(III) to iron(II) and the Fenton reaction proceeds further.

The Fenton-like oxidation of DHBA (using an iron(III) salt) was delayed compared to the Fenton reaction, as recycling of Fe(II) was slowed down due to complexation of iron(III) by DHBA (charge transfer band centered at 514 nm). 2,3,4-THBA also complexed iron(III). The importance of the formation of these complexes on the oxidative degradation of DHBA was investigated.

[1] See e.g., J. J. Pignatello, E. Oliveros, A. Mackay, *Crit. Rev. Env. Sci. Technol.*, **36** (2006) 1-84; [2] F. Benoit-Marquié, E. Costes-Puech, A. M. Braun, E. Oliveros, M.-T. Maurette, J. Photochem. Photobiol., A: Chem., 108 (1997) 65-71.

THERMAL DESORPTION OF POLYCHLOROBIPHENYLS FROM CONTAMINATED SOILS AND THEIR HYDRODECHLORINATION USING Pd- AND Rh-SUPPORTED CATALYSTS

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This paper reports about a combined technology for soil decontamination from PCBs using the thermal desorption technique coupled with the catalytic hydrogenation of recovered PCBs. The reactor is a bench scale rotating desorption furnace through which dinitrogen is flushed and used as carrier gas of desorbed PCBs. The latter are condensed into an hexane or hexane-acetone (1:1 v/v) solution that is then hydrogenated using phosphate-supported Pd or Rh as catalyst. The analysis of the treated soil, under variable operative conditions (temperature and desorption time), shows that the total (99.8%) decontamination from PCBs occurs. The recovery yield of the desorbed PCBs is better than 75% and the subsequent hydrogenation reaches 63% of the collected PCBs.

THE PHOTO-FENTON PROCESS : EFFECTS OF CHLORIDE AND SULFATE ANIONS ON THE REDUCTION OF Fe(III) AND ON THE DECOMPOSITION OF H_2O_2

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Of the advanced oxidation processes (AOPs), the Fenton's reaction ($Fe(II)/H_2O_2$) is an effective and inexpensive process to treat wastewaters containing biologically refractory organic substances. The efficiency of the Fenton process is due to the formation of highly reactive hydroxyl radicals by the reaction of H_2O_2 with Fe(II). One of the drawbacks of the Fenton process is that the overall rate of oxidation of organic pollutants is considerably slowed down after conversion of Fe(II) into Fe(III). It is now well-known that the combination of the Fenton's reaction with UV light (also called as the Photo-Fenton process) largely enhances the rate of oxidation organic compounds. The enhancement of reaction rates is due to the photoreduction reactions of Fe(III) species which lead to a regeneration of Fe(II) and to the production hydroxyl radicals. Recent works showed that the rate of oxidation of organic pollutants by the photo-Fenton process depends on various parameters such as UV intensity, pH, the concentrations of reactants, and the reactivity of OH radicals with the organic and inorganic solutes present in the water.

Large quantities of inorganic anions are often present in wastewater or introduced in the water as reactants (iron salt, acid), and their influence on the oxidation of organic chemicals by the photo-Fenton is yet unknown. Therefore, the effects of Cl^- and SO_4^{2-} on the photo-Fenton process have been investigated in the present work. The photolysis experiments were conducted under monochromatic irradiation (253.7nm), in a batch reactor at $pH \leq 3$ and at 25°C. pH and ionic strength have been adjusted with $HClO_4$ and $NaClO_4$. The effects of anions on the rates of decomposition of H_2O_2 and of photoreduction of Fe(III) have been systematically investigated.

The data showed that the overall rates of photoreduction of Fe(III) and of decomposition of H_2O_2 depend on the concentrations of Cl^- or SO_4^{2-} and on pH. The effects of Cl^- or SO_4^{2-} anions on the overall reaction rates could be mainly attributed to the formation of chloro and sulfatocomplexes of Fe(III) and to the formation of inorganic radicals ($Cl_2^{\bullet-}$ and $SO_4^{\bullet-}$) which are less reactive than hydroxyl radicals. A kinetic model including hydrolysis and complexation reactions of Fe(II) and Fe(III) species, photoreduction of Fe(III) species, reactions of Fe(II) and Fe(III) species with H_2O_2 and reactions initiated by the formation of inorganic radicals ($OH^{\bullet}$, $Cl_2^{\bullet-}$, $SO_4^{\bullet-}$) has also been tested to simulate the experimental concentration-time profiles for Fe(II) and H_2O_2.

TRANSPORT OF SILVER ION THROUGH SUPPORTED LIQUID MEMBRANE USING DC18C6 LIGAND AS CARRIER IN TOLUENE

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The silver compounds and silver-containing preparations have found increasing use in industry and medicine. Silver may enter the receiving bodies via industrial wastewaters because its impurities in copper, zinc, arsenic and antimony ores. Moreover, the interaction of silver with essential nutrients, especially Se, Cu, vitamin E and Vitamin B12 has focused attention on potentially toxic nutrients. Thus, there is a need to develop new techniques either for its recovery, separation and concentration, or for its purification.

Several technologies can be used to remove or recover toxic metals from liquid effluents such as precipitation, solvent extraction and ion exchange. During the past decade, supported liquid membranes (SLMs) have received increasing attention as alternatives to liquid–liquid extraction and other (membrane) separation techniques for the selective removal of ions, organotin ecotoxicants or neutral molecules from dilute solutions.

The aim of this study is to investigate the extraction of silver ion through a supported liquid membrane. A micro-porous Fluoropore PTFE membrane with an effective pore size of 0.2 μm, a thickness of 150 μm and a porosity of 85% were used as supporting mediums to hold toluene solutions containing the ion carriers DC18C6. The membrane was cut into rectangular pieces of 40x70 mm in dimensions and was soaked in the corresponding carrier solution for 60 min. The membrane was then removed from the organic solution, cleaned with filter papers to take away excess carrier and placed in a SLM cell.

The sources with 200 ml in feed and strip side were stirred magnetically at 250 rpm to avoid concentration polarization at the membrane surfaces. All experiments were carried out at ambient temperature. Samples were taken at regular time intervals from the feed and strip compartments and analyzed by flame AAS.

The optimum experiment conditions for silver ion transport were decided as follows: 0.01M DC18C6 dissolved in toluene as carrier solution in PTFE support, $Na_2S_2O_3$ as stripping solution and 50 ppm Ag^+ dissolved in 0.015M HNO_3 as feed solution. The stripping phase silver transport rate was found between 30 to 40 percent as a result.

PHENOLIC MICROPOLLUTANTS SORPTION FROM AQUEOUS SOLUTION BY POLYMERIC RESIN MACRONET MN200

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Phenol-containing wastewater presents a serious environmental problem since biological degradation of phenol occurs too slowly or does not occur at all. Phenols are commonly encountered in wastewater of a number of industries, such as high temperature coal conversion, petroleum refining, resin and plastics. At present several methods, such as microbial degradation, chemical oxidation, incineration, solvent extraction, reverse osmosis and irradiation, are being used for removing phenols from wastewater. Adsorption by activated carbon (AC) is one the most frequently used method. In recent years, polymeric adsorbents have been increasingly regarded as an alternative to activated carbon due to their feasible adsorption–regeneration properties.

The present work evaluates the removal of phenolic compounds from aqueous solutions by polymeric resin Macronet MN200 under batch kinetic, equilibrium and fixed bed experiments. Phenol and aniline were studied as mono and bi-component system. It was demonstrated that under basic conditions (pH 11) the phenol removal was low for polymeric resin MN200 (25 mg g^{-1}). However, under acid conditions (pH 3) the experimental loading capacity of phenol was approximately 90 mg g^{-1}. In the case of aniline the loading capacity was 10 mg g^{-1} at pH 3, and then increases to 80 mg g^{-1} at pH 7. Three isotherm models were used to represent the equilibrium data.
The kinetic experiments were carried out under the best sorption conditions obtained in the previous batch experiments. Studies with MN200 resin showed the same sorption rate for phenol and aniline, at both mono and bi-component systems; in all cases 3 hours was the time necessary to reach the equilibrium conditions (initial concentration of 50 mg L^{-1}). Analyses of the respective batch rate data with two kinetic models, the homogenous particle diffusion model (HPDM) and the shell progressive model (SPM) were carried out. Sorbent phase was confirmed as the rate-determining step of the sorption process. Effective particle diffusion coefficients (Deff) were determined from the rate data proposed by both models.
Fixed bed experiments showed a considerable reduction of the waste volume produced (70-75%). In order to saturate the resin 350-380 BV were necessary, while 5 BV were necessary for its complete regeneration. According to the results, the sorption process of phenol and aniline by MN200 resin at pH 7.0 is an available option to remove phenolic compounds from aqueous solution.

ROLE OF NITRILOTRIACETIC ACID -Fe(III) COMPLEX (FeNTA) ON THE ACTIVATION OF 2-AMINOBENZOTHIAZOLE PHOTODEGRADATION AND BIODEGRADATION BY *RHODOCOCCUS RHODOCHROUS*.

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Aminopolycarbocylic acids (APCAs) are ubiquitous in natural waters and wastewaters. They have the ability to form very stable, water soluble complexes with many metallic di- or trivalent ions. The iron complex FeNTA (nitrilotriacetic acid -Fe(III)) is a good model of natural organic mater–iron complexes present in the natural water. In addition, it is used as a chelating agent, substitute of phosphates in detergents; as a result of this massive use, NTA can be rejected in the environment. FeNTA has been previously shown to increase drastically the rate of photo- and biodegradation of 2-aminobenzothiazole (ABT), an organic pollutant, by *Rhodococcus rhodochrous*[1].
The objective of this work was to understand how FeNTA was increasing the rate of ABT degradation. For this purpose, the fate of FeNTA was investigated during the ABT photo and biodegradation processes. First it was shown, using *in situ* ^{1}H NMR, that the complex FeNTA was biodegraded by *Rhodococcus rhodochrous* cells but not the ligand alone (NTA). This result indicates that FeNTA was transported and biotransformed inside the cell. The same products were obtained during the photo and biodegradation processes of FeNTA, including IDA (iminodiacetic acid), glycine and formate, likely because they both involve oxidoreduction mechanisms. When comparing the different experiments, the soluble iron, measured by spectrophotometry, was decreasing when microbial cells were present. About 20% of the initial iron was found inside the cells. These results allowed us to propose detailed mechanistic schemes of FeNTA degradation by solar light and by *R. rhodochrous*[2]. The mechanism proposed for FeNTA biodegradation, although its remains highly speculative, suggests that the intracellular iron reduced as Fe(II) could activate enzymes involved in the biodegradation pathway of ABT, and more particularly mono or dioxygenases.

1. **A. Bunescu, P. Besse-Hoggan, M. Sancelme, G. Mailhot, and A-M. Delort.** 2008a. Comparison of microbial and photochemical processes and their combination for degradation of 2-aminobenzothiazole. Appl. Environ. Microbiol. **74**: 2976-2984.
2. **A. Bunescu, P. Besse-Hoggan, M. Sancelme, G. Mailhot, and A-M. Delort.** 2008b. Fate of the Nitrilotriacetic acid-Fe(III) complex (FeNTA) during photodegradation and biodegradation by *Rhodococcus rhodochrous.* Appl. Environ. Microbiol *in press*

EFFECT OF CARBONATE IONS ON THE DEGRADATION OF N-CONTAINING COMPOUNDS IN TIO_2 PHOTOCATALYTIC SYSTEMS

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Bicarbonate ions are ubiquitous in aqueous compartments. In photocatalytic processes, generally, the presence of inorganic anions, and especially of bicarbonate ions, has been shown to negatively affect the photocatalytic degradation of organic pollutants. This phenomenon is attributed to reactions between inorganic anions and hydroxyl radicals, which are responsible for the oxidation of organics. These reactions mainly lead to a scavenging effect. To date, the information regarding the real effects of these ions in photocatalysis is still limited. Phenomenon may be more complex and the involvement of inorganic radicals is nowadays also proposed. Thus, in a recent study, a reaction with carbonate radicals has been proposed to explain the significant increase of the rate of aniline photocatalytic degradation by Degussa P25/UV in the presence of carbonate ions at pH > 9.0.

In this study, the effect of bicarbonate ions on the photocatalytic degradation of fenuron (pesticide) and diclofenac (pharmaceutical) were examined. The photocatalytic degradation of two pollutants was compared in the presence of two photocatalysts, either P25-Degussa (P25) or PC500-Millennium (PC500). The concentration of $NaHCO_3$ was varied within 0 – 100 mM and pH is controlled around 8.2. Pollutants were measured by HPLC (concentration between 10 and 50 µM). The by-products of photocatalytic degradation of two pollutants were also identified in this work, using liquid chromatography-atmospheric pressure chemical ionisation mass spectrometry.

This study demonstrates that the presence of bicarbonate ions may have a significant impact on pollutant degradation. Carbonate radicals may be involved in the process, leading to the formation of specific degradation products with both probe compounds used. We put forward the assumption that carbonate radicals would be more likely formed with PC500 rather than with P25. Moreover, as far as carbonate radicals are involved, and according to literature data, the second order reaction rate constant with diclofenac is supposed to be at least 50 fold higher than that with fenuron. This constitutes an explanation for the difference observed in the systems P25/pollutants/ HCO_3^-.

ANIONIC SURFACTANTS EFFECT IN HEAVY METALS SOLUBILITY

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Heavy metals contamination of soil is mainly due to industrial, urban, and farming activities. These pollutants are persistent in soil and pose a long-term risk to ground water quality and ecosystem functioning. Therefore, risk assessments and environmental regulations for polluted soils should take into account the mobility of heavy metals in soils. Surfactants are introduced in the environment by wastewater discharge, point-charge pollution or deliberate action.. Anionic surfactants, which in wastewater originate mainly from detergents, may solubilize metals through complexation and thus modify their fate and transport in soil.

Batch assays were performed to evaluate the effect of anionic surfactants on metal concentrations in soil solution. Anionic surfactants, Aerosol 22 (A22), Biopower (BP) and Sodium Dodecyl Sulphate (SDS), were added to five soils differing in organic carbon content among other properties. To evaluate the effect of surfactants on mobility of heavy metals, a consecutive extraction was carried out: first with surfactants aqueous solutions at a concentration corresponding to ten times their critic micellar concentration (CMC) and secondly with MilliQ water. The concentration of heavy metals in the equilibrium solution was determined by ICP-AES, as well as the concentration of dissolved organic carbon (DOC) and the UV absorbance. The specific UV-absorbance (SUVA, L g^{-1} cm^{-1}), a measure of aromaticity (the relative contribution of aromatic structures to DOC), was calculated by normalizing the UV absorbance (A^{254}, cm^{-1}) for the DOC concentration ([DOC], mg L^{-1}):

$$SUVA = \frac{A^{254} \cdot 1000}{b \cdot [DOC]}$$

For the three anionic surfactants assayed, the concentration of Cu, Zn and Pb increased in soil solution after addition of the surfactants. The relative effect (compared to a control extracted with mQ) depended on the metal, the soil and the surfactant. The largest effect was observed in general for A22, which increased the solution concentrations of Cd, Zn, Cu and Pb in the equilibrium solution for most soils over 10-fold, presumably through complexation of metals with the dicarboxy-ethyl group of the surfactant. Besides, the measurements of DOC and SUVA indicated that the surfactants may solubilize soil organic matter and thus mobilize metals that are sorbed on organic matter.

The results for the second extraction step, performed with MilliQ water, showed that organic matter release to soil solution remains larger than in control assays, and concentrations of heavy metals were still elevated compared to the control – indicating a residual effect of the surfactants – but much smaller than during the first extraction step.

In ongoing research, we assess the effect of surfactants on metal mobility under more realistic conditions, in soil columns with a continuous supply of surfactant at lower (field relevant) concentrations.

THERMAL AND ULTRASOUND TREATMENT OF ACTIVATED SLUDGE: FATE OF CADMIUM AND COPPER

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Wastewater treatment with activated sludge processes (ASP) generates large quantities of excess sludge which must be eliminated. This disposal is subject to various social and economic problems. Thus, interest for solutions allowing sludge volume and mass reduction is growing up. Ultrasonic and thermal treatments are among the most promising recent technologies for reducing sludge production in wastewater treatment plants [1]. Previous work focused on the effectiveness of sludge reduction by ultrasounds and temperature during activated sludge process [2; 3].

The presence of heavy metals in the excess sludge poses serious problems, and considerably hampers the final disposal alternatives, especially in the agricultural use (soil improvement/amendment). Recent studies [4; 5] investigated the adsorption of heavy metals on previously sonicated sludge. The behaviour of copper and cadmium towards sonicated sludge was linked with the physico-chemical modifications induced by the ultrasonic treatment : surface properties, dissolved organic matter… However, no data is available in the literature concerning heavy-metals loaded sludges behaviour during ultrasonic and thermal treatment respectively.

In this study, the fate of cadmium and copper during thermal and ultrasound treatments of activated sludge was studied in respect with mixed liquor physico-chemical modifications. Biochemical composition showed solubilization of sludge biopolymers. Granulometric measurements demonstrated that ultrasound and temperature induced respectively floc disintegration and macro-floc defloculation. The uptake of the two metals by sludge flocs was improved with increasing temperature. The two metals had different behaviours during ultrasonic treatment: mass transfer improvement due to ultrasonic cavitation together with the extended surface area offered by sonicated flocs increased cadmium uptake by sludge flocs. At the same time, the increase of soluble organic ligands limited copper uptake.

REFERENCES

[1] H. Ødegaard, Sludge minimization technologies - an overview, Water Science and Technology. 49 (2004) 31-40.
[2] X.Q. Cao, J. Chen, Y.L. Cao, J.Y. Zhu, X.D. Hao, Experimental study on sludge reduction by ultrasound, Water Science and Technology. 54 (2006) 87-93.
[3] E. Paul, P. Camacho, D. Lefebvre, P. Ginestet, Organic matter release in low temperature thermal treatment of biological sludge for reduction of excess sludge production, Water Science and Technology. 54 (2006) 59-68.
[4] J. Laurent, M. Casellas, C. Dagot, Heavy metals uptake by sonicated activated sludge: relation with floc surface properties, Journal of Hazardous Materials. (2008). In Press. DOI:10.1016/j.jhazmat.2008.05.066
[5] N. Commenges-Bernole, J. Marguerie, Adsorption of heavy metals on sonicated activated sludge, Ultrasonics Sonochemistry. (2008). In Press. DOI:10.1016/j.ultsonch.2008.05.006

ANALYTICAL CHARACTERISATION OF ORGANIC POLLUTANTS RELEASED BY INDUSTRIAL EMISSIONS TO RIVERINE SYSTEMS

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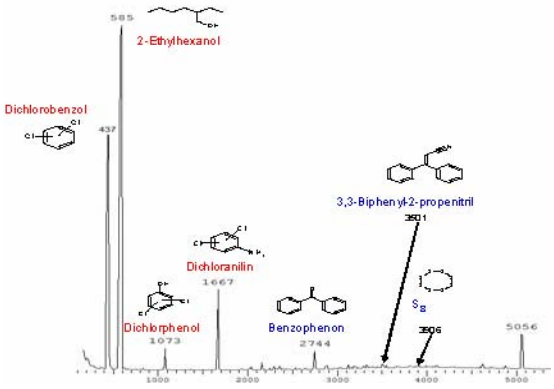
Industrial emissions contribute significantly to the organic pollution of riverine systems. Such effluents are characterized on the one hand by a high structural diversity and huge amounts, on the other hand by a normally spatial restricted appearance as a result of point source emission. Both the structural diversity and the more local importance of industrial emissions led to the neglect of these contamination in the past.

Therefore, we performed extended organic analytical investigations on effluents of different industries using a non-target-screening approach based on GC/MS. A first objective was to identify specific compounds which might act as trade related indicators or marker compounds. Secondly, the stability of pollutants were investigated by comparison of the substance spectra before and after sewage treatment processes. And thirdly, the first environmental fate of specific pollutants in the riverine environment has been monitored. These analyses has been performed on effluents from food, paper, petro, fertilizer and further industries.

Two out of these industries were selected for this presentation -industrial settings related to chemical and petrochemical branches. Non-target screening analyses revealed a wide spectra of organic contaminants that were partially able to be linked to synthetic products or synthetic pathways. Numerous compounds exhibited high structural similarity indicating a collective origin. Examples of such specific compounds comprise: triphenylphosphinoxid, fluorochloroanilines, trifluoromethylacetophenone, methylarylsulfones, chloroindol, 3,3-diphenyl-2-propenenitrile (see figure). All these compounds will be discussed in detail also regarding their envrionmental relevance.

On two industrial sites we were allowed to sample individual subunits of the industrial complex as well as the inflow and outflow of the treatment plant disposing the total plant complexes. Based on these analysis also indicators for discharge of untreated effluents e.g. as the result of accidents were identified and evaluated. Further on, quantitative determination and the calculation of loads for individual components allowed a compound specific insight into its mass fluxes. Based on these load calculations the efficiency of the industrial sewage treatment plants were investigated with respect to the individual organic pollutants.



Chromatogram of an outflow sample derived from a chemical plant

DISTRIBUTION AND CHEMICAL FRACTIONATION OF COPPER IN VINEYARD AND HOP FIELD SOILS

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In order to control fungal diseases, Cu-based fungicides have been extensively used in agriculture which resulted into increased Cu concentrations in soils. This work focused on the distribution and chemical fractionation of Cu in selected Czech vineyard and hop field soils. The application of Cu-based fungicides resulted into soil Cu concentrations well above 150 mg kg^{-1}. Higher concentrations were observed in hop field soils (up to 180 mg Cu kg^{-1}) compared to vineyard soils. Furthermore, increased Cu concentrations were observed closer to the treated plants and in superficial layers, which represents its tight binding to soil organic matter and Fe-, Mn-(hydr)oxides as proved by chemical fractionation analyses. Most of the studied samples from the arable layers did not meet the regulatory limits for Cu in agricultural soils set by the Ministry of the Environment of the Czech Republic and the warning limits set by the European Commission. A surprisingly high Cu concentration (up to 170 mg Cu kg^{-1}) was found in the soil from a non-active vineyard, suggesting that contamination of soils from abandoned vineyards should be investigated before changing their use in agriculture. Furthermore, standardized single-step extraction procedures, 0.01 M $CaCl_2$; and 0.05 M EDTA (ethylenediaminetetraacetate) were carried in order to evaluate the potential availability of Cu in these soils. This study showed that the $CaCl_2$ extraction is not suitable for predicting Cu availability in alkaline vineyard soils as it did not correlate with exchangeable Cu. Soil pH proved to be the dominant factor influencing the vertical mobility of Cu in the studied soils. Chemical fractionation results showed that only a small portion of total Cu (< ~10%) was present in the most labile (exchangeable) soil fraction. A significant amount of Cu was associated with the reducible soil fraction, probably because Cu oxychloride was mainly applied. The results showed that contamination of vineyard and hop field soils can present a serious environmental and toxicological concern, especially if young vines or other shallow rooting crops would be subsequently planted on them. Although not as extensive as vine cultivation in Europe, hop production present an important agricultural practice in several countries (e.g., Czech Republic, Germany) and the contamination of hop field soils can pose a risk for the surrounding environment.

This work is part of the post-doc project GAČR 526/08/P042 (Czech Science Foundation).

MICROBIALLY-INDUCED LEAD (Pb) IMMOBILISATION IN CONTAMINATED SOILS

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Lead (Pb) contaminant is attracting particular attention because of its widespread use in mining, industry and agricultural activity and wide distribution in the earth's crust. However, it is widely recognized that the mobility and bioavailability of Pb in soil is more important than total Pb concentration. Therefore, mitigation of Pb availability is critical issue for remediation of Pb in contaminated soils. Immobilisation of Pb with phosphate (P) compounds in the Pb contaminated water or soil is relatively inexpensive and highly effective. The effectiveness of P compounds in immobilizing Pb from contaminated soils primarily depends on their solubility. Insoluble phosphate compounds can be solubilised in soils by enhancing the activity of P solubilising bacteria (PSB). The objectives of this study are to select the most effective PSB from P amended soils and Pb contaminated soils and to examine the potential value of the PSB in the solubilisation of P in soil and the subsequent immobilization of Pb.
Nineteen different bacterial strains were isolated from P amended and Pb contaminated soils using the standard National Botanical Research Institute's phosphate (NBRIP) growth medium. The isolated bacteria were incubated with tricalcium phosphate for 14 days to assess P solubilisation, acid phosphatase enzyme activity, organic acid production and pH. The PSB isolated from P amended soils solubilised more than 350 mg/L of P while the PSB from Pb contaminated soil produced more than 250 mg/L of P. P solubilisation was correlated with pH and organic acid production, indicating that the major mechanism of P solubilisation by bacteria is considered as the pH reduction by production of organic acid.
From the P solubilization test, PP bacterial strain isolated from Pb contaminated soil was selected for soil incubation test. Pb contaminated soil was incubated with three P amendments (tricalcium phosphate (TP), hydroxyapatite (HA) and soft rock phosphate (NP)) at 25 □ for 2 weeks. Soils were kept at 60 % water holding capacity and at the end of the incubation period the soil samples were extracted with 1 M NH_4NO_3 solution (often used as a measure of metal availability in soils) to measure Pb concentration. Soil plus phosphate amendment, soil + bacteria and soil only + sterile water served as controls. The PSB inoculation reduced NH_4NO_3 extractable Pb in soil with and without phosphate addition, and the effect of PSB was more pronounced in the in the soft rock phosphate amended soil (Figure 1).

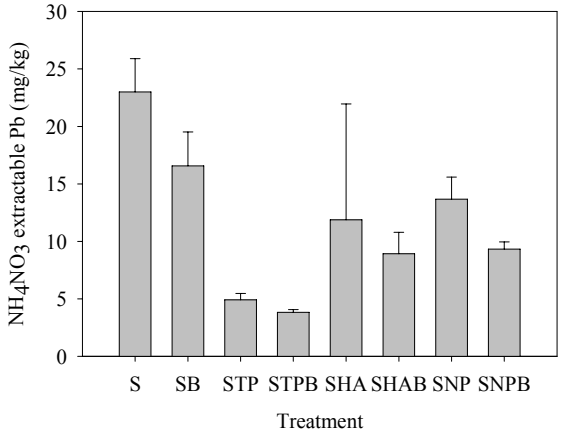

Figure 1. NH_4NO_3 extractable Pb concentration after soil incubation (B means bacterial inoculation.)

The data indicate that the PSB isolated from Pb contaminated soil (i.e. PP PSB) shows great potential to immobilise Pb and can be used to mitigate Pb mobility in Pb contaminated soils.

GEOCHEMICAL ASSESSMENT OF SOIL CONTAMINATION IN THE AREAS OF NARVA POWER PLANTS (ESTONIA)

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Two largest in the world thermal power plants (Estonian and Baltic TPPs) burning oil shale for electricity production are the main sources of environmental pollution in Narva region in North-Eastern Estonia. The atmospheric emission during oil shale combustion and leaching of trace elements (including hazardous) from ash landfills near TPPs leads to contamination of air, soils and groundwaters in this area.

The geochemical mapping is one of the approaches which permits to evaluate the soil contamination. The low-scale multielemental geochemical mapping based on the regular grid was initiated in order to estimate the topsoils pollution in Narva region.

100 topsoils samples were digested in aqua regia and in a 4-acid solution (HNO_3, $HClO_4$, HF and HCl) at high temperature for low to ultra-low elements concentration determination. Concentrations of 43 chemical elements were measured by ICP-MS in both types of solutions. In comparison with the previous studies the number of measured elements increased significantly what allowed to evaluate the dissimination of the new set of chemical elements including hazardous in the topsoils.

Evaluation of spatial distribution of chemical elements and application of the multuvariate statistical technique (principal components R-mode factor analysis) for interpretation of geochemical data permitted to separate the natural and technogenous factors in formation of anomalous concentration of chemical elements in the topsoils.

Extractability of chemical elements was studied using 6-steps sequential extraction of both initial oil shale and contaminated soils. It demonstrated the high leachability of water-soluble As and Pb from the soil samples and oil shale's ash in the first step of the sequential extraction. As, Co, Cr, Pb and Zn were also bound to a considerable degree in the iron-oxide phase and Zn was mostly bound in the sulphide phase of the ash samples.

The geochemical data showed that in the distribution of the major chemical elements in the topsoils in Narva region the natural factors are dominating. In dissimination of As, Cd, Hg and Pb the atmospheric deposition with the fine particles of ash formed in the result of oil shale burning plays the main role. The concentrations of Cr and Pb are close or exceed (As) the concentrations allowed for the soils for the residential area for these metals /metalloids.

Acknowledgements. The authors are very grateful to the Ministry of Foreign Affairs of Norway, the Norwegian Financial Mechanism and Estonian Target Financed Research Programme No. SF0332652s04 supported the collaborative Norwegian-Estonian projects "Risk based environmental site assessment of waste from the oil shale industry" and "Environmental impact of oil shale combustion ashes on topsoils in Narva Powerplants region: combined geochemical and ecotoxicological approach".

INVESTIGATION OF ORGANIC SUBSTANCE FROM THE PEAT OF VLASINA LAKE - ECOCHEMICAL ASPECT

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The peat of Vlasina lake (area 10.5 km^2) is of fluvial origin. During the construction of the dam on the Vlasina river in 1949 it was flooded. Bearing in mind that the Vlasina lake water is used for water supply the knowledge of both organic and inorganic peat substances is of extreme ecological importance.
Four peat samples were collected vertically beginning from the surface: 1) 0-25cm; 2) 25-40cm; 3) 70-80cm and 4) 100-120cm (submerged in water at sampling).
The study of peat organic substance comprised: determination of organic substance quantity; extraction of free and associated (bound) hydrocarbons, aliphatic hydrocarbons and aromatic hydrocarbons and NSO compounds (applying the column chromatography, SiO_2/Al_2O_3); extraction of fulvic- and humic acids from acid and alkaline peat extract solution according to Internatonal Humic Substances Society procedure (IHSS 1983) (***www.ihss.gatech.edu***). CG/MS analyses were performed for identification of all bitumen fraction compounds.
The previous research showed the quantity of free bitumen on all samples was substantially higher than associated one. The results of *n*-alkane fraction analyses of all bitumen indicated the peat organic substance was of biogenic origin, with active participation of microorganisms, primarily bacteria, but participation of algae, fungi and yeast could not be excluded (Đurka et al., 2005).
The work will show the identification results of one fraction part of saturated hydrocarbons (hopane) and aromatic hydrocarbons of free and associated bitumens. GC/MS hopane analyses (m/z 191) established prevailing 17 β(H) hopane series, in the range C_{27}-C_{31} (without C_{28}). $\beta\beta C_{30}$ hopane (biolipid isomer) is prevailing in relation to more stable thermodynamic geolipid $\beta\alpha C_{30}$ and $\alpha\beta C_{30}$. Prevalence of biolipid 22R in relation to 22S at homohopanic isomer C_{31} confirms that the peat organic substance is in the initial diagenesis phase. The identificated hopanes are indicators of microbiological origin, primarily bacteria. Geolipid 18 β(H)-trisnorhopane (Ts) was not confirmed in any of free bitumen samples whereas 17α(H)-trisnorhopan (Tm) and 17β(H)- trisnorhopane were identified.
By analyses of aromatic bitumen fractions 2,2-dimetil-1,2,3,4-tetrahydropicene was identified. Its presence is connected with early diagenetic transformations of β-amyrin, compound typical for angiospermic plants as one main component of waxes isolated from higher plants.
The obtained results of hopane fraction investigation and aromatic hydrocarbons are in complete compliance with already published conclusion that the peat organic substance is of biogenic origin, namely that the peat of Vlasina lake is ecologically preserved environment.

Acknowledgments: We thank Dr Herman Wehner (retired professor at Federal Institute for Geosciences and Natural Resources, Hannover, Germany) for conducted GC-MS analyses, and the Alexander von Humboldt Foundation and the Ministry of Science and Technological Development of the Republic of Serbia for supporting this research.

1. www.ihss.gatech.edu
2. Đurka D., Pfendt P., Jovančićević B., Cvetković O., Wehner H. (2005) Natural bitumens versus oil pollution in the Vlasina lake peat, *Environmental Chemistry Letters*, 3: 39-42.

RELATIVE EFFECTS OF SODIUM AND POTASSIUM ON SOIL HYDRAULIC CONDUCTIVITY AT A WINERY WASTEWATER APPLICATION SITE

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Surface and subsoil layers from a land application sites for winery wastwater were used in laboratory experiments on repacked soil cores, to evaluate the relative effects of sodium and potassium in percolating solutions on soil hydraulic conductivity. In both the surface and subsurface layers at SAR/PAR values of 5, the value of relative hydraulic conductivity remained high and close to a value of 1 at all electrolyte concentrations,

In the surface soil, the decrease in relative hydraulic conductivity with reduction in salt concentrations in PAR 20 and 40 are much smaller than with corresponding SAR 20 and 40 solutions, when divalent cation was calcium or magnesium.

In the subsurface soil, the decrease in relative hydraulic conductivity with reduction in salt concentrations in PAR 40 are also much smaller than with the corresponding SAR 40 solutions, when the divalent cation was calcium or magnesium. In this subsurface soil, there was little difference between SAR/PAR solutions of 20, when the divalent cation was calcium. However, the decrease in relative hydraulic conductivity with reduction in salt concentrations in PAR 20 are much smaller than with corresponding SAR 20 solutions, when the divalent cation was magnesium.

These results indicate a greater soil stability in the presence of potassium relative to sodium in the surface and subsurface soils at this land application site, at the higher SAR/PAR values of 20 and 40. There were no differences at SAR/PAR values of 5. The implications of these studies for wastewater management at a winery wastewater land application site are discussed.

PARTITION AND DISTRIBUTION PROCESSES OF DDT, PCB AND PAH BETWEEN SEDIMENT AND WATER

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The spatial distribution of DDT, PCB and PAH in environmental system is affected by transport processes. Dynamic processes of partition and adsorption/absorption are one of the dominant ways of contamination of water by DDT, PCB and PAH.

The research in this paper analyses and presents mathematic relation of interaction, partition and adsorption/absorption processes of DDT, PCB and PAH in solid/liquid phase system, sediment-water. Model which optimally describes complex nature processes of interaction and distribution of DDT, PCB and PAH in sediment and water are developed threw implemented and accepted concept in literature and based on the original detected concentration of DDT, PCB and PAH in water and sediment. The locality of research field is Novi Sad and surroundings.

Persistent organic pollutants (POPs) represent group of toxic, persistent semi volatile and volatile chemicals capable to be bioaccumulated and biomagnificated in environmental complements and in biological chains. Paper doesn't discuss balanced partition between water and biomaterial.

For the mathematical approach, three partition coefficients have been used: octanol/water partition coefficient (K_{OW}), organic carbon/water partition coefficient (K_{OC}), as well as K_d which symbolizes the solid-water partition coefficient.

Determination of DDT, PCB and PAH in water, sediment and soil was observed during time period from 2001. - 2007. In all examined samples of water, sediment and soil, there have been detected residue levels of DDT, PCB and PAH.

Key words: DDT, PCBs, PAH, partitioning/distribution processes.

CRITICAL LOADS OF LEAD AND CADMIUM FOR SURFACE WATERS IN BULGARIAN BEACH FORESTS

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According to the International Convention for Trans-boundary Air Pollution Decrease and the Frame Directive for Waters 2000/60/EU in European countries the International Cooperative Programme for calculation of critical loads for terrestrial and aquatic ecosystems (ICP Modeling and Mapping Critical Loads and Levels) is in use, in which Bulgaria also takes part. The main purpose of this study is to determine the admissible heavy metal depositions of aquatic ecosystems according to several criteria: different localities, level of pollution, analytical methods etc. The prior attention is paid to the pollution of waters by Lead and Cadmium.

The research has been carried out for 8 aquatic ecosystems with stream and steady waters used as drinking water, water for industry and irrigation as well as recreation. The results from the monitoring of acidity, suspended materials, carbon and heavy metals concentration in the precipitations, surface waters and sediments have been used to calculate the depositions of Pb and Cd in different test variations. The heavy metals removal by the biomass and the vertical migration by drainage waters have been determined too. Atomic absorption spectrometry and ICP atomic emission have been used as measuring methods for Pd and Cd. A software product based on Steady State Mass Balance Method has been developed to calculate the critical loads of Pb and Cd.

The obtained results have shown that in 2006 when Atomic absorption spectrometry has been used acid precipitations polluted with heavy metals occurs regularly. The dam still waters are more susceptible to deposition of Cd compared to the stream waters of the studied rivers, of which the admissible critical loads are higher while the susceptibility of Pb depositions of both types of water are equal. The admissible critical loads of heavy metals, however, are considerably higher due to precipitation of the waters in four of six studied aquatic ecosystems. The precipitations levels are in a good correlation with depositions of heavy metals. The critical loads of Pb and Cd in the regions with lowest depositions of heavy metals are not exceeded for both water types.

After using ICP atomic emission spectrometry in 2006 the values of Lead and Cadmium deposition have been lower than when atomic absorption spectrometry has been applied. There were not exceedances of critical loads of Lead but critical loads of Cadmium have been exceeded in 50 % of the cases studied.

This work was performed at the Sofia University of Forestry sites and funded by the Ministry of Education and Science with a grant N BY-H3 -01/05 "Critical loads of lead and cadmium for aquatic ecosystems and their exceedances by the real depositions".

MECHANISM OF TROPOSPHERIC CARBOXYLIC ACIDS DEGRADATION PHOTOINDUCED BY H_2O_2 : CLOUD REACTIVITY

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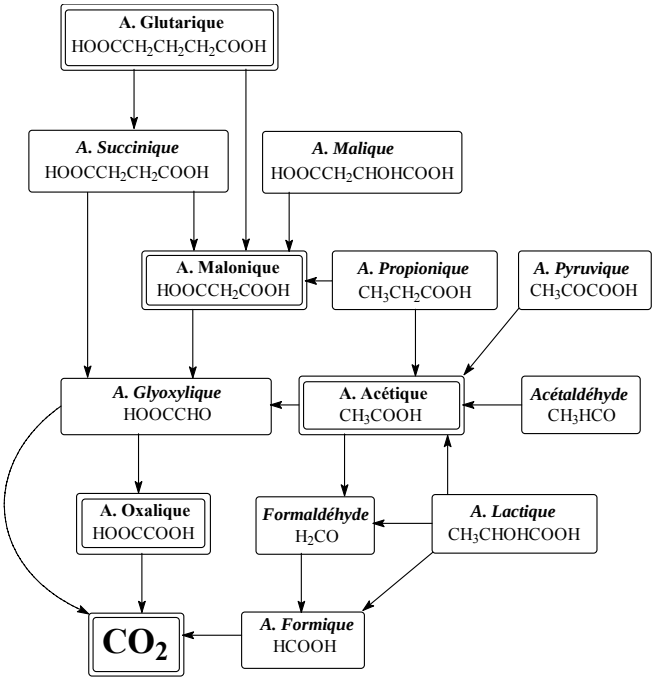
Carboxylic acids have been abundantly measured in the tropospheric aqueous phase, particularly in rain samples and also in cloud, fog waters and snow and even in polar ice samples. For example, Marinoni et al. (2004) have measured Total Organic Carbon (TOC) in cloud aqueous phase sampled at the puy de dome station (France). The concentration of TOC ranges from 1.2 to 8.9 mg l^{-1} with a median of 3.6 mg l^{-1}. A significant fraction of the TOC is composed by carboxylic acids (CA) with an average of 36%. Among the CA, the mono-carboxylic acids represent the larger fraction with 71% (formic, acetic, lactic, glycolic, glyoxylic, propionic) compared to the dicarboxylic acids representing 29% (oxalic, glutaric, succinic, maleic, malonic and tartaric). If the identification and the concentration of CA in the atmosphere have been well studied, their mechanisms of formation and transformation are not well documented.
As a consequence, the main goal of this study is to identify the ways of degradation of the main atmospherically significant CA identified in the atmosphere by the attack of $^{\bullet}OH$ radicals. H_2O_2 has been used as a photochemical source of $^{\bullet}OH$ radicals due to its major role in the formation of such radicals in the atmosphere. The degradation of 13 CA, photoinduced by H_2O_2, has been studied separately. The mechanism of degradation has been established for each CA and the half life in our experimental conditions has been evaluated and compared between each CA. These theoretical results have been compared with field studies and a general chemical scheme for the degradation of glutaric acid (C_5) has been established until its total degradation into CO_2.



From these results it is obvious that some CA appears to be key compounds in the oxidation of the organic matter in the atmosphere. Some of them, like oxalic acid, can be used as a good indicator of the oxidation state of the air masses and as a consequence of the atmospheric pollution.

Reference:
A. Marinoni, P. Laj, K. Sellegri and G. Mailhot 2004. Cloud chemistry at the puy de Dôme: variability and relationships with environmental factors. Atmos. Chem. Phys., 4, 715-728.

CONTAMINATION IN ENVIRONMENTAL COMPARTMENTS BY DDA, A POLAR DDT METABOLITE

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The environmental fate of main DDT metabolites, in particular of DDD and DDE have been investigated intensively over the last decades. However, the polar metabolite DDA has been widely neglected in environmental studies so far. Due to its carboxylic group DDA is the best water soluble DDT metabolite which results in a high contamination risk potential for the hydrosphere. Therefore, this study focussed on the environmental pathway of DDA in surface and ground waters as well as in corresponding riverine sediments taken at an industrial point source and highly contaminated by DDT and its metabolites. Aim of this study was to give a comprehensive overview on the state of DDX pollution and to estimate the risk potential with respect to DDA for a groundwater system which is destined for drinking water production.

In detail, sediment samples, river water and ground water samples from the investigated riverine infiltration area as well as from the contamination plume were analysed by GC/MS. Interestingly, in the plume samples several unknown DDT related compounds were identified for the first time as environmental contaminants. With respect to the particulate samples not only the extractable fractions of the sediment contamination were analysed but also the particularly bound DDX residues were detected using continuative chemical degradation techniques. Based on the results, potential precursor metabolites of DDA were classified as labile or strongly bound to particulate material. Calculation of the sediment mass and concentration revealed an absolute risk potential of approx 10 kg of directly available precursor metabolites and of approx 4 kg of DDA in labile-bound fractions.
Remobilisation experiments under oxic and anoxic conditions showed a fast release of the considerable amount of DDA confirming the high risk potential of labile bound DDA and DDA precursors. Furthermore, a retention experiment with spiked sediment revealed no retardation capacity for DDA in soil, hence, contamination of groundwater by DDA due to river infiltration is feasible.
Compound specific stable carbon isotope analyses were performed on the water samples in order to gain information on possible degradation processes of DDA in the aquifer, but no isotopic shift was detected that indicates transformation of DDA in the groundwater.

Generally, DDA representing a polar DDT metabolite has to be considered for a water contaminant and as long-term impact of DDT pollution in the aquatic environment because of its negligible retention in soil and due to a high formation potential of precursor metabolites in sediments.

ROLE AND IMPACT OF Fe(III) CARBOXYLATE COMPLEXES ON THE PHOTODEGRADATION OF 2,4-D AND 2,4-DCP IN AQUATIC COMPARTMENT

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Iron is considered to be the most abundant transition metal in the environment. Dissolved iron can exist in two different oxidation states in water Fe(III) and Fe(II), and it plays a central role in many biological, chemical and photochemical processes. However, Fe(III) is rapidly removed from the photic zone of surface waters by precipitation and particle scavenging. In contrast, Fe(II) is highly soluble in water.
Carboxylic acids have received considerable attention as one of the most common dissolved organic compounds present in natural environment. Many studies indicate that carboxylates can form strong complexes with iron and these Fe(III) complexes are recognised to be photoreactive. Moreover, it is known that the presence of such organic compounds in water increases the phenomenon of photodissolution of iron and as a consequence the photoreactivity of the mixture.
In the present work, we studied the photochemical properties of Fe(III)-carboxylate complexes, including Fe(III) with citric acid, tartaric acid or pyruvic acid complexes. First, the photogeneration of $HO^{\bullet}$ radicals have been determined in aqueous solution with the three complexes. Then, 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenol (2,4-DCP) were used as model compounds to evaluate the photochemical properties of the different iron-carboxylate complexes. The quantum yields of Fe(II) formation and 2,4-D and 2,4-DCP disappearance were determined and the main parameters affecting the photoreaction (wavelength, oxygen concentration, pH, …) were studied in this work.
The same mechanism of 2,4-D degradation for the three complexes is observed and correspond to the mechanism described in previous work using different Advanced Oxidation Processes (generating $HO^{\bullet}$ radicals). 2,4-D is selectively degraded in 2,4-DCP, which through different photodegradation products could be mineralized into H_2O, Cl^- and CO_2.
Our results show that the presence of Fe(III)-carboxylate complexes could have a considerable impact on the fate of organic pollutants in aquatic environment and that such compounds must be considered in the production of oxidant radicals in natural waters. The photoreactivity of chosen complexes, one tri-carboxylic (citric), one di-carboxylic (tartaric) and one mono-carboxylic (pyruvic) were compared. It appears that the mono-carboxylic complex with pyruvic acid is the most reactive for the degradation of organic pollutant such 2,4-D.

POSTER SESIONS

ADSORPTION OF VANADIUM FROM WATER USING NEUTRALIZED RED MUD

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Vanadium is, as microelement in bauxite mineral, placed like vanadium pentoxid V_2O_5 (around 260 ppm). In the process of separating bauxite, in reaction with sodium hydroxide, about 30% of vanadium goes to solution like sodium vanadat, while the rest is separated in the red mud [1].

Aluminium Plant is placed near to Podgorica and it is considered to be main pollutant of Zeta valley, especially groundwaters.
Red mud is the by-product of alumina production from bauxite and it contain abundant finely divided Fe-, Al- and Ti- oxide and oxyhydroxides and also large amounts of sodium hydroxide and sodium carbonate that leaves it highly caustic. The red mud used in this study obtained from the Aluminium Plant, Podgorica, Montenegro.

Among the vanadium removal technologies adsorption is very important.

Red mud is used as an unconventional novel adsorbent for removing many metals from water [2].

The aim of this paper was to investigated the vanadium adsorption capacity of seawater-neutralized red mud (Bauxol). The effect of contact time on vanadium adsorption is determined.

The investigation of contact time on vanadium adsorption is show that the removing starts shortly after the shaking starts (after 15 min.) and increases over time until a steady state is attained after roughly 2h. After 2 h Bauxol can remove roughly 96% of vanadium. After this time there is no significant change in concentration up to 24 h.
Analyses have been carried out on iCAP 6000 Series ICP-OES Spectrometer.

Reference:
1. Perović,S. , Procjena uticaja otpadnih supstanci proizvodnje aluminijuma na kvalitet površinskih i podzemnih voda, Magistarski rad, *Univerziter u Beogradu. Beograd*, (2001) 42
2. D. Mohan, C. U. Pittman Jr., Arsenic removal from water/wastewater using adsorbents—A critical review, *Journal of Hazardous Materials,* 142 (2007) 1–53

ANALYSIS OF CHROMIUM IN EVALUATION OF BIOAVAILABILITY AND RISK ASSESSMENT

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Soil is a very important part of food chain as well as a potential source of contaminants. The pollution of agricultural soil by heavy metals is defined by their concentration still, more influencing parameters are metals bioavailability which additionally depends on soil structure, its adsorption potential, acidity and redox potential. All these factors play important roles in controlling the transport of heavy metals to the plants, atmosphere and hydrosphere exhibiting their impact in different extent.

Objective of this work was to investigate the capacity of agricultural soil for chromium binding and chemical conditions that could increase its solubility and mobility. In order to investigate the influence of acidity and redox potential an incubation experiment was performed.

Soil samples were spiked with standard solutions of Cr(III)-nitrate, on four concentration levels (40, 80, 120 and 200 ppm). Within each concentration levels, four samples, with different pH values (5.98 as real, 5.00 and 7.0) were analyzed. Additionally, redox conditions as aerobic, with about 80% of retention water holding capacity and anaerobic were analyzed. After incubation period of 60 days experiment was continued.

For prediction chromium behaviour in soil, the knowledge of its potential bioavailability is essential an can contribute in evaluation of its distribution, adsorption, association with different geochemical structures and mobility. In that order, sequential extraction in three stages (1M solution of ammonium – acetate, 0.1 ME solution of hydroxylamine – chlorohydrate and mixture of 0.2M oxalic acid and ammonium – oxalate), prior to the measurements (ETAAS), was applied in this work. This methodology appeared to be very useful in further evaluation of the chromium mobility and toxicity.

APPLICATION OF AN ACID MINE DRAINAGE MICROBIAL CONSORTIUM TO THE BIOFILTRATION OF HYDROGEN SULFIDE CONTAINING EFFLUENT

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A microbial culture collected in a drainage pool at the decommissioned Lousal pyrite mining facilities (Portugal) was applied for preliminary evaluation as component of a biofiltration unit for the removal of sulfur reduced gaseous compounds in biogas, obtained from an anaerobic digester treating olive mill wastewater.
To this effect an experimental bench reactor was set-up with a feed of hydrogen sulfide gas of 0.5 Lh^{-1}. pH and redox were monitored during the run of the experiment. The pH value was maintained at 2.7, without external control.

The highest concentration of sulfate formed (80 mM) was attained by the third day, dissolved sulfide increased steadily until a value of 30 mM in the 4th day of the experiment and a sudden increase was registered by the 8th day. Redox potential decreased steadily during the run of the experience reaching a value of –141 mV by the 8th day. No oxygen or air was added to the culture during the run of the experiment.

BIOGENIC VOC EMISSIONS FROM OIL PALM AND NATURAL RAINFOREST CANOPIES IN BORNEO

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Volatile isoprenoids emitted by vegetation can contribute to the chemistry of ozone and secondary organic aerosol formation in the troposphere. The type and amount of volatile isoprenoid emitted is plant-species specific, and once emitted, the compounds have different reactivities and different oxidation products in the atmosphere. Therefore large-scale land-use change involving change of plant species over large areas has the potential to affect regional air chemistry and quality. For several years, plantation crops such as oil palm have been replacing tropical forests in SE Asia. Oil palm emits isoprene, but there is little information on isoprenoid emissions from native tropical forest tree species in this region, nor do we understand how air quality changes as oil palm replaces natural dipterocarp forest. Here we present first results of emissions of isoprene from native forests and oil palm plantations in Borneo. Extensive leaf-level measurements showed that isoprene emissions from oil palm range from 0 to 100 $\mu g\ g^{-1}$ dry wt h^{-1} (14.5±0.3 mg m^{-2} ground h^{-1}) but monoterpene emissions are negligible. Isoprene and total monoterpene emissions from native forest trees range from 0 to >100, and from 0 to 40 $\mu g\ g^{-1}$ dry wt h^{-1}, respectively (1 to 6 mg m^{-2} ground h^{-1} and 0.1 to 0.7 mg m^{-2} ground h^{-1}, respectively) from natural forest canopies. According to the NOx/VOC regime, oil palm plantations could have an effect on the chemistry of tropospheric ozone formation. Oil palm is grown extensively in the tropics, so these results are relevant for large areas of the globe.

CHARACTERIZATION AND COMPOSITON OF MUCUS OF SABELLA SPALLANZANII GMELIN

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The present work is part of a Regional Project namely "ACTIBIOMAR" focused on the valorisation of marine biomass. The research topic is the utilization of some marine organism as source of bioactive molecules.
We have focused our attention on the species *Sabella spallanzani* Gmelin, one of the best known and abundant Mediterranean sabellids. The proposed marine organisms show physiological and morphological features such as high tolerance to environmental variability, high growth rates and easiness of rearing. These polychaetes are able to remove bacteria from water under natural and artificial conditions, as recently reported in the literature.[1,2,3] The accumulation capability suggests the employment of this species as biofilters of microbially contaminated waters in aquaculture.
Considring that several aspects as chemical properties, production and roles of the mucus, or its dynamics of formation and variability over time are not known, in the present study we describe the elemental composition, viscosity and PCBs contamination of *Sabella spallanzanii* mucus.
In general, invertebrates use mucus as an external surface coating to reduce friction or hydrodynamic drag, and to limit water loss; in addition mucus can serve as an aid in locomotion and feeding, a mating rope, or a "scaffolding" that provides anchorage and protection for eggs and a barrier against infection. Mucus production constitutes a key factor determining the ability of many polychaete species to survive in their environment. Sabellids polychaetes use mucus to cementate different substances in tube building, mixing faeces, pseudofaeces and sediment. In addition mucus plays an important role in protection and absorption of metabolites.
200 adults specimens of *S. spallanzanii* were collected in the harbour of Brindisi (Southern Adriatic Sea, Italy) using SCUBA equipment. In order to stimulate the secretion of the mucus, all the individuals have been removed from the tube where they live and kept for 30 min in a Petri dish. Secreted mucus was collected and centrifuged at 12000 x g for 30 min at 4 °C. Results showed that mucus viscosity was 2.57± 0.2 Cps at 20°C. The water content was 96 ± 0.3% and carbohydrates (glucose equivalents) were 0.32 ± 0.02. The elemental composition of it and its possible contamination from PCBs was also studied.
Results on the composition of the body and tube of *S. spallanzanii* will be also discussed.

[1] M. Licciano, L. Stabili, A. Giangrande. *Water Research 39* (**2005**) 4375-4384.
[2] L. Stabili, M. Licciano, A. Giangrande, G. Fanelli, R. A. Cavallo. *Marine Environmental Research 61* (**2006**) 74-92.
[3] D. Cavallo, A. Pusceddu, R. Danovaro, A. Giangrande. *Marine Pollution Bulletin 54* (**2007**) 602-625.

CHARACTERIZATION OF THE AIR QUALITY IN BELGRADE: EXAMPLE OF A TRANSITION ECONOMY CITY

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Urban air pollution and its impact on urban air quality has been considered as a serious environmental problem with both urban and large scale impacts. While traffic and traffic related pollutants are the main source of air pollution in most cities in the industrialized western world, in countries with economy in transition domestic heating, outdated production technologies and old car fleet are the main source of urban air pollution.

To interpret the trends in urban air quality of Belgrade, the capital of Serbia, we analyzed monthly average concentrations of BS, SO_2, NO_2, O_3, PM_{10} and CO from the official monitoring network of automated monitoring stations for the period 2003-2007. We aslo used a set of air quality idices (AQI) normalized to Serbia's national ambient air quality standards, for comparisons between the measured pollutants and to better describe the status of air pollution in this area, for the period August 2007-July 2008.

The results showed that concentrations of SO_2 (pollutant strongly related to burning of sulfur-containing fossil fuels) substantially decreased during this period, but the levels are still very high in comparison with other European cities. The levels of NO_2 show a decreasing trend and are still not so high as in the most industrialized countries, indicating that traffic is apparently still not as dense as in the more developed cities. Black smoke and PM_{10} still have very high values, especially during the heating season, and their AQI values have the greatest contribution to the bad overall air quality in the city. There are indications, however, that a sizable proportion of these is of natural origin. More research is needed for a true quantificaiton.

NO_x/SO_2 ratio, an indicator of the changing structure of urban air pollution sources, significantly increases with economic development. Although for Belgrade this ratio gradually increased from 1.7 in 2004 to 2.98 in 2007, it still has a value below 5, which is typical for transition economy cities.

In most respects, air pollution in Belgrade has characteristics of most East-European cities in the past decade, of countries in transition in which economic conditions have a strong effect on the atmospheric environment. Gradual deacrease of the consumption of solid fuels for heating of homes and industrial use, and improved quality of the car fleet slightly improved the air qulity in the period studied. Adoption of new environmental legislation, closing inefficient industries and power plants, introducing gas heating and modernization of the car fleet could result in significant air-quality improvement over the Belgrade metropolitan area.

COMBINED PROCEDURE FOR 2,6-DINITROPHENOL REMOVAL FROM WASTEWATER

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Nitrophenols are important and versatile organic compounds in industrial, agricultural and defense applications. They are frequently used as intermediates in the manufacture of explosives, pharmaceuticals, pesticides, pigments, dyes, rubber chemicals and so on. Therefore, the monitoring of nitrophenols is essential for environmental pollution control [1].
The aim of this work was to reduce the concentration of 2,6-dinitrophenol from wastewaters under the maximum limit admited by international regulations.
The experimental methods for 2,6-nitrophenol removal are: adsorption on granular activated carbon, electrochemical reduction in electrochemical reactor type cellule H and combined procedure: adsorption on activated carbon plus electrochemical reduction. The adsorption experiments were performed under stirring using granular activated carbon NORIT GAC 1240. The electrochemical reduction experiments were performed in an electrochemical reactor type cellule H, equipped with an Ti anode, an graphite cathode and a NAFION 350 millipore membrane and a pump, which assure the electrolyte recirculation. The combined procedure consists in the addition of activated carbon in the electrochemical reactor.
The experimental processes are pursued by different methods: cyclic voltammetry (CH instruments 630C and AUTOLAB PGSTAT 12), spectrophotometry in UV-Visible (Unicam Helyos B), total organic carbon determinations (TOC-DR2800 Hach Lange).
The effects of pH, 2,6-nitrophenol concentration and temperature about the processes, were also examined.
As expected, the best results have been obtained in combined adsorption and electrochemical reduction experiments (almost total removal of 2,6-dinitrophenol from solutions).

References:

[1] D-P. Zang, W-L. Wu, H-Y. Long, Y-C. Liu, Z-S. Yang, Int. J. Mol. Sci. **2008**, 9, 316-326.

DETERMINATION OF MOLECULAR MECHANISM CAUSING SIDE EFFECTS OF SELECTED NEONICOTINOIDS USING CHEMICAL GENOMICS

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Introduction: Neonicotinoid insecticides are a rather new generation of nicotine-related compounds that are used for insect pest management. Neonicotinoids act on central nervous system by blocking postsynaptic nicotinic acetylcholine receptors, but they are relatively safe to mammals because of their selective binding on insect, and not mammalian, receptors. Nicotinic acetylcholine receptor is a well-studied cellular target, but little is known about the mechanism of off-target effects of neonicotinoids.

Objective: To identify novel biological targets of neonicotinoids, we have been investigating the effects of two neonicotinoids, imidacloprid and acetamiprid, on model organism yeast *Saccharomycess cerevisiae,* using chemical genomics approach. *S.cerevisiae* resembles many cellular processes in higher organisms and therefore yeast-generated hypotheses can often be successfully applied to humans. Chemical genomics approach allows genome-wide analysis of the cellular effects of neonicotinoids, an approach currently not possible in human cells or other mammalian model organisms.

Results: We examined the effects of imidacloprid and acetamiprid on the growth rate of 4800 nonessential haploid single deletion mutant yeast strains. The profile of over-sensitive and over-resistant mutants indicates the cellular processes that are affected by a neonicotinoid. Data analysis of the preliminary experiment in which yeast strains were exposed to semi-inhibitory concentration of imidacloprid revealed that mutants of genes involved in histone exchange are hypersensitive to this neonicotinoid, indicating potential functional connection. Since histone exchange is a crucial step in spermatogenesis, it is a plausible hypothesis that imidacloprid could affect spermatogenesis in higher organisms by inhibiting histone exchange. Next, we exposed the yeast strains to the dispersing agents used in the Confidor configuration, dimethyl sulfoxide (DMSO) and N-methyl-2-pirrolidone, to differentiate between the effects of the active substance and those of the dispersing agents. The results indicate that the effects of these chemicals could explain the majority of the effects observed using Confidor preparation. Further work will be required to test this yeast-generated hypothesis in mammalian cells.

Keywords: neonicotinoids, chemical genomics, *Saccharomycess cerevisiae,* acetamiprid, imidakloprid

ECOTOXICOLOGICAL EVALUATION OF COMPOUNDS USED IN POLYMERS PRODUCTION

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The materials commonly called plastics are all synthetic polymers. Nowadays, these materials are produced commercially on very large scale and have a wide range of properties and uses. New polymeric compounds are finding their way to all areas of human activities and replace traditional, currently used materials. Monomers, additives and catalysers are main compounds used for their syntheses. All these substances could influence the ecotoxicity of resulting materials. From the environmental point of view it is necessary to monitor ecotoxicological impact not only of synthetic polymeric materials but also of their components.

The presented study is aimed on the ecotoxicity evaluation of selected monomers, additives of polymers and catalysers. Environmental legislation demands the evaluation of the ecotoxicity of all types of chemicals. This requirement is given in Czech as well as in the European legislation. In the last year the new regulation named REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) has started to stand in EU countries. From this point of view, ecotoxicity belongs to very important characteristic of chemicals.

In our study following substances were ecotoxicaly tested; monomers: 1,1,2-trichlorethylene, 1,1,2,2-tetrachlorethylene, triethyleneglycoldimethacrylate, acrylamide, 2-hydroxyethylmethacrylate; additives of polymers: 2-Br-5-Cl-pyridine, 2-Br-5-Cl-pyridine-N-oxide and sodium salt of 2-merkapto-5-Cl-pyridine-N-oxide and tin-octoate $Sn(Oct)_2$, (catalyser). For the purpose of evaluation of the ecotoxicity of above mentioned chemicals two alternative toxicity tests, Thamnotoxkit F^{TM} on sense organisms *Thamnocephalus platyurus* and Daphnotoxkit F^{TM} on sense organisms *Daphnia magna* were used. The most of mentioned substances were ecotoxicaly evaluated also via phytotoxicity test. *Sinapis alba* root growth inhibition toxicity test and *Allium cepa L* root growth inhibition toxicity test were used. Test on Sinapis alba represents standard test. The values of 24hLC50 and 48hLC50 obtained for *Thamnocephalus platyurus* and *Daphnia magna* testing organisms and 72hIC50 values gained for *Sinapis alba* and *Allium cepa* testing plants are the basic data for the ecotoxicological assessment of the chemicals and for their classification following the Czech legislation. Ecotoxicity of tested monomers increased in following sequence: 1,1,2-trichlorethylene, 1,1,2,2-tetrachlorethylene, acrylamide, triethyleneglycoldimethacrylate, 2-hydroxyethylmethacrylate. Ecotoxicity of additives of polymers went down in following sequence: sodium salt of 2-merkapto-5-Cl-pyridine-N-oxide, 2-Br-5-Cl-pyridine-N-oxid and 2-Br-5-Cl-pyridine. The obtained results will be presented.

Acknowledgement: This work was supported by the grant MSM 0021630501 from the Ministry of Education, Youth and Sport of the CR.

EFFECT OF ARTIFICIAL AGEING ON Cu, Zn, Cd, Pb AND Ni FRACTIONATION, MOBILITY AND ACCESSIBILITY IN ARTIFICIAL SOIL MIXTURES.

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The article describes the effects of artificial ageing on fractionation, mobility and accessibility of metals (Cu, Zn, Cd, Pb and Ni) in three different artificial soil mixtures. Temperature changes were used as a model abiotic factor in a laboratory-scale ageing simulation. The artificial ageing was simulated with 5 sequential cycles, composed of a 5-day exposure to high temperature (105°C) and by a 5-day exposure to low temperature (-25°C). Artificial soil mixtures were prepared by mixing natural mineral soil phase and sewage sludge pellets from a wastewater treatment plant (10, 30 and 50% (w/w) addition). For aged and non-aged soil, metal fractionation with a 6-step sequential extraction (modified Tessier´s sequential extraction), mobility (TCLP), plant accessibility (DTPA) and oral bioavailability (PBET) were determined. Aging treatment consistently lowered metal mobility by 80-100% in all soil mixtures. Bioavailability of metals also decreased after the artificial ageing process, but to a lower extent. Oral availability of Zn and Cu in the small intestine phase remained approximately the same after ageing, while oral availability of Cd, Pb and Ni decreased in both phases.

HEAVY METALS SOIL POLLUTION RELATED TO NON-FERROUS INDUSTRY

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Copsa Mica is one of the sites with the highest degree of pollution in Romania.Pollution in this town area was almost entirely caused by two factories: CARBOSIN (which produced carbon black for dies and tires from 1936 until 1993) and SOMETRA (a non-ferrous smelter plant that is still operational and uses ecological hazardous technologies).

SOMETRA is largely responsible for the most health problems of Copsa Mica's population due to its emissions of sulphur dioxide, the solid particles in suspension and heavy metals which are present in the atmosphere, in water, in soil and in vegetation. As the local population produces, sells and consumes a great number of agricultural products, food chain analysis was performed in order to establish the levels of contamination with lead, zinc and cadmium.

The aim of this study was to establish the soil contamination with lead, cadmium and zinc in the target area; soil contaminated by heavy metals may pose a threat to human health if the heavy metals enter the food chain.

Soil samples were collected from both surface and 20 cm depth, being then processed through microwave-assisted mineralization. Analyses were performed using an atomic absorption technique with graphite furnace and flame atomization, with an Shimadzu AA 6300 AAS instrument.

The obtained results demonstrated that the heavy metals content in Copsa Mica area is much higher than the results obtained in an unpolluted reference area. The maximum contamination levels with lead were recorded surprisingly not in the vicinity of the smelter plant, but in a location situated at five kilometers distance. For cadmium and zinc, the maximum levels were recorded near the pollution source, being higher than the maximum allowed limits.

INDUSTRIAL WASTE WATER TREATMENT BY USING GRAPE STALKS RESIDUES AS LOW COST BIOSORBENTS

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The toxic effects of heavy metals in the environment are well known and governments introduce strict regulations with regard to metal discharge, mainly from industrial processes. Toxic metals are not biodegradable and can be accumulated on living tissues causing serious diseases. Recently, certain waste products from industrial or agricultural operations have been recognised as new cheap sorbents in the removal/recovery of toxic metals. These materials represent a cheaper alternative as compared to conventional sorbents frequently used. Grape stalks waste belongs to these products generally known as biosorbents.

In the present work, the usefulness of grape stalks wastes generated in the wine production has been investigated as metal sorbent for Pb(II) and Cd(II) from aqueous solutions using column experiments. In both cases, the influence of metal concentration and particle size on metal removal has been studied at constant initial pH around 6. The change in the initial metal ion concentration (in the range from 0.25 to 0.5 mmol. dm^{-3}) has a significant effect on breakthrough curve. Hence, we observed that metal loading rate increases as the feed concentration is increased. However, the total concentration loaded per gram of grape remained constant (0.22 mmol for lead and 0.17 mmol for cadmium). Moreover, studying the influence of particle size (in the range from 0.3 mm to 1.4 mm) we observed that if the particle size decreases metal loading rate decreases as well, whereas the total concentration of metal loaded per gram of grape increases ..

In industrial waste, very often there is more than one metal present in solution and the sorption performance can be modified. In this context, mixtures of both metals, cadmium and lead, have been studied for different ratios of metal concentrations. It has been observed that cadmium does not significantly affect lead sorption while cadmium sorption is affected by lead in the range of concentrations studied.

Desorption processes are important for two main reasons: for the regeneration of the sorbent for its multiple reuse and for the potential recovery of the sorbed material. In this work desorption has been studied under dynamic conditions. Using 0.1 mol L^{-1} hydrochloric acid a 100% yield recovery has been found for both metals. However, using perchloric acid only 50% recovery has been obtained. These results can be explained based on metal chloride complexation. In these experimental conditions the sorbent is not damaged and might be reused again.

Acknowledgements: This work was supported by the Ministerio de Educación y Ciencia, Madrid, projects CTM2005-07342-CO2-01 i CTM2005-07342-CO2-02

INFLUENCE OF REACTIVE BLACK 5 ON THE ADSORPTION OF PARAQUAT ONTO ALGINATE GEL BEADS

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The removal of hazardous organics materials from wastewater is one of the most important environmental problems concerning modern agriculture today. Organic pesticide residues have been reported in drinking water, agricultural water and groundwater [1]. In order to avoid problems related to intoxications, in recent patents, commercialized formulations and adjuvant technologies added to the product claim that the newly commercialized products are safer to use or that they improve their application characteristics. In agricultural applications, paraquat was frequently used as an herbicide on a wide range of crops. Paraquat (1,1'-dimetil-4,4'-dipyridium chloride), was recently unauthorized within the European Union due its high toxicity but it is still used in a large number of countries [2].

A new paraquat formulation that exhibits less oral toxicity is based on the addition of alginate [3]. Alginate is a seaweed extract of non-toxic carbohydrates commonly used in food and the pharmaceutical industry. This formulation also contains both emetic and cathartic agents to further reduce paraquat adsorption and in order to prevent the confusion with cola, black coffee or other drinks, a blue dye, as a colouring agent, was added to the commercial paraquat [4].

In this study we have evaluated the capacity of adsorption of paraquat onto calcium alginate gel beads as well as the effect of the presence of RB5 on paraquat adsorption. In addition, the rate of agitation and the variation of paraquat concentration on adsorption have also been evaluated.

The applicability of the Langmuir and Freundlich isotherms for the present system was evaluated. Pseudo-first-order and pseudo-second-order models were applied using experimental data to predict the adsorption rate constant and the equilibrium adsorption capacity. The results show that the calcium alginate gel beads effectively remove paraquat from an aqueous solution. The adsorption of paraquat on calcium alginate gel beads was influenced by the pH. Adsorption increases as the pH increases. Sorption capacities as high as 140-171 mg.g-1 were obtained for high paraquat concentrations in aqueous solution. RB5 reduces adsorption of paraquat onto alginate gel beads. The results show a reduction of 20% or 24% in the maximum capacity of adsorption when 50 mg/L or 100 mg/L of RB5 are added, respectively. The Langmuir equation best fits the sorption isotherms. The rate of adsorption was influenced by the presence of the dye. The results obtained suggest that the pseudo-second-order adsorption model is predominant and that the overall rate of paraquat adsorption appears to be controlled by the chemical process.

[1] Tsai, W.T. ; Lai, C.W. (2005). Adsorption of herbicide paraquat by clay mineral regenerated from spent bleaching earth. *Journal of Hazardous Materials*, 134(1-3): 144-148.
[2] The Court of First Instance European Communities. 11 July 2007. Pres release Nº 45/07.
[3] Heylings, J.R.; Farnworth, M. J.; Swain, C. M.; Clapp, M.J.; Elliott, B. M. (2007). Identification of an alginate-based formulation of paraquat to reduce the exposure of the herbicide following oral ingestion. *Toxicology*, 241(1-2): 1-10.
[4] Green, J. M..; Beestman, G. (2007). Recently patented and commercialized formulation and adjuvant technology. *Crop Protection*, 26(3): 320-327.

LEAD CONTAMINATION OF AN AGRICULTURAL SOIL IN THE VICINITY OF A SHOOTING RANGE.

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This work evaluated the effect of a shooting range on lead (Pb) contamination of adjacent agricultural soils and the associated environmental risks. The shooting range has been operational for 30 years and has served as a training facility for trapshooting using Pb pellets as ammunition. For this purpose, coupled Pb concentration/Pb isotope data were used. Lead was mainly concentrated in the arable layer of the contaminated agricultural soils at total concentrations ranging from 573 to 694 mg kg^{-1}. Isotopic analyses ($^{206}Pb/^{207}Pb$) proved that Pb originated predominantly from the currently used pellets. Chemical fractionation analyses showed that Pb was mainly associated with the reducible fraction of the contaminated soil, which is in accordance with its predominant soil phases (PbO, $PbCO_3$). The 0.05 M EDTA extraction showed that up to 62% of total Pb from the contaminated site is potentially mobilisable. Furthermore, Pb concentrations obtained from the SPLP (Synthetic Precipitation Leaching Procedure) extraction exceeded the regulatory limit set by the USEPA for drinking water. Ion exchange resin bags showed to be inefficient for determining the vertical distribution of free Pb2+ throughout the soil profile. Increased Pb concentrations were found in the biomass of spring barley (Hordeum vulgare L.) sampled at the studied site and two possible pathways of Pb uptake have been identified: (i) through passive diffusion-driven uptake by roots
and (ii) especially through atmospheric deposition, which was also proved by analyses of a bioindicator species (bryophyte Hypnum cupressiforme Hedw.). This study showed that shooting ranges can present an important source of Pb contamination of agricultural soils located in their close vicinity.

Acknowledgements
The presented study was supported by the research projects MSM 6007665806 and MSM 293 6046070901 (Ministry of Education of the Czech Republic).

OXIDATIVE DEGRADATION OF 2,4- AND 2,6-DINITROPHENOLS WITH VARIOUS OXIDATIVE SYSTEMS

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Oxidative degradation is a widespread technique for detoxification of persistent ecopollutants. A choice of oxidative reagent is crucial: it is necessary to compare efficiency, toxicity of the very reagent and a price of it as well.

Dinitrophenols are appropriate model compounds to simulate behaviour of a representative group of substituted aromatic ecopollutants. The objective of the study was a comparison of various oxidative systems as reagents for mineralization of 2,4- and 2,6-dinitrophenols. Spectrophotometric and conductometric methods have been employed to control the oxidation process.

Radical oxidation was chosen as a main path of the mineralization, hydrodegen peroxide being the source of the radicals. Cations of transition metals were used to cause radical destruction of hydrogen peroxide.

The capacity of Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Mn^{2+} ions for peroxide destruction has been estimated. Average conversion of dinitrophenol in water solutions of these cations was shown to be about 5% in 11 hours; in 24 hours it is only in systems containing copper ions (II) that 100% conversion takes place.

It has been found out, however, that 2,4- and 2,6 –dinitrophenols can be oxidized at room temperature and normal atmospheric pressure with the help of iron (III)-catalysed hydrogen peroxide, which is known as Ruff's reagent. In this case a complete degradation of substrates in the systems under study takes place during 4-6 hours. Rate of dinitrophenol oxidation depends on concentration of both hydrogen peroxide and ferric ions. We have to acknowledge that iron ions have unique properties, which are difficult to account for. A possible explanation could be a profound hydrolysis causing a decrease of solution pH. The initial pH value is a major factor for process optimization in the given systems. Most effective oxidation of a majority of organic compounds takes place at pH ≈ 3. At the same time acidifying the solution alone is unlikely to increase the process efficiency so significantly.

Similar research has been conducted with few iron complexes, namely: Fe^{3+}- EDTA and Fe^{3+}-lignohumate. However, replacement of hydrated iron ions by a stable complex of iron with EDTA decreased the dinitrophenol decomposition rate. The mixture of sodium and iron humates also demonstrated small efficiency of the process.

The study revealed an increase of electroconductivity of the solutions during dinitrophenol destruction. This fact could be an additional evidence of dinitrophenol desnruction.

Oxidative degradation of dinitrophenols with iron-catalysed hydrogen peroxide can be recommended to deactivate any kind of nitrophenol-based pollutants.

REGRESSION MODEL APPROACH APPLIED TO IMPROVE THE ALUMINIUM EXTRUSION DIES CLEANING

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Extrusion is the most important technique to produce unfinished products of aluminium ant its alloys. This process is carried out employing extrusion dies (steel blocks of a complex geometry that give a particular shape to the extruded piece). The metal, previously heated up to at least 500 ºC, is forced to flow through the shape in the end portion of the die. At the end of the production cycle, it is necessary to clear all the cavities, filled with aluminium, to reuse the dies.
The ordinary cleaning process consists in the immersion of the extrusion dies into a hot solution of sodium hydroxide for at least four hours in order to dissolve or remove the aluminium left inside followed by a water soak. The main problems related to this cleaning operation are the high consumption of sodium hydroxide (6 kg NaOH/extrusion die) and water, the loss of aluminium (600 - 1000 g/extrusion die) in the spent bath as aluminate dissolved and the disposal and treatment of the exhausted alkaline solution (4500 L/day).

The aim of this work was to set a range of conditions for the cleaning process, mainly, concentration of sodium hydroxide, temperature and time of permanence in order to enhance the bath life, reduce the loss of aluminium and the costs of treatment.

The regression model approach has been used to illustrate the relationship between the response (dissolved aluminium concentration in the spent bath (g/L) and the process parameters (design factors) which affect it. The purpose of this regression model is to predict the response for different combinations of process parameters as initial concentration of sodium hydroxide (%), temperature (ºC) and time of permanence (minutes) at several levels based on the conditions found in the extrusion companies. The effects of each factor and the interactions within them have been also studied by experimental design. Data analysis has been performed using the statistical package Minitab.

The use of the regression model could help the aluminium companies to control and to improve the extrusion dies cleaning process. It would offer some advantages such as sodium hydroxide savings and a reduction of hazardous waste production and treatment.

REMOVAL OF Cd, Co, Sr AND Zn FROM AQUEOUS SOLUTIONS BY MOSS *Rhytidiadelphus squarrosus.* I. EFFECT OF pH AND CHEMICAL SPECIATION§

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Background: Water resources of the world are being polluted through various anthropogenic activities such as metal mining and metal processing activities. Removal of these contaminants from industrial effluents has become an important priority that is reflected in a tightening and enforcement of environmental regulations. The requirement for readily available low-cost adsorbents has led to research into biological materials.

Aim: The objective of this work was to describe the effect of pH and chemical speciation on Cd, Co, Sr and Zn removal from aqueous solutions by dried moss biomass *Rhytidiadelphus squarrosus.*

Methods: Cd, Co, Sr and Zn biosorption by dried moss biomass from aqueous $CdCl_2$, $CoCl_2$, $SrCl_2$ and $ZnCl_2$ solutions spiked with ^{109}Cd, ^{60}Co, ^{85}Sr and ^{65}Zn was studied by gamma spectrometry. Chemical speciation of these metals in experimental solutions at defined conditions (pH, T) was calculated by the Visual Minteq software, ver. 2.53.

Results and discussion: Biosorption of Zn^{2+}, Co^{2+} and Cd^{2+} ions by moss biomass is a rapid process and equilibrium was reached within 20 min. The process can be well described by pseudo second-order kinetics model in non-linear form ($R^2 = 0.995$ for Zn, $R^2 = 0.999$ for Co, $R^2 = 0.997$ for Cd). In the case of Sr, equilibrium with the maximum reached in the first rapid phase lasting 20 min was slowly diminished during the next few hours, what suggests the formation of new concentration equilibrium. The pH of solution significantly influences Cd, Co, Sr and Zn biosorption. Maximum uptake was reached at pH 4-6 and negligible biosorption was observed at pH 2. Obtained experimental data were fitted to the adsorption isotherms. The Langmuir, Redlich-Peterson and Langmuir-Freundlich isotherms were found to represent the measured sorption data well. The maximum sorption capacities of moss biomass from single metal solutions at the initial metal concentration 0.1 to 4.0 mmol/dm^3 calculated by Langmuir equation at both pH 4.0 and pH 6.0 decreased in the order Zn > Cd > Sr > Co. Metal sorption is also strongly affected by the existing chemical speciation given by pH values and concentration ratios. As can be calculated by the Visual Minteq software, under described experimental conditions, Zn, Sr and Co were present mainly in fully ionized biosorbable forms: Zn^{2+} (>98.5%), Sr^{2+} (>99.2%) and Co^{2+} (>99.9%). On the contrary, cadmium at the highest studied concentration 4.0 mmol/dm^3 is present by 70% in Cd^{2+} form and by 30% in less biosorbable $CdCl^+$ form.

Conclusion: Obtained biosorption characteristics of *R. squarrosus* can serve for behaviour study of bivalent toxic metals in contact with terrestrial mosses and their utilization as biosorbents for toxic metal removal from contaminated waters.

§ Part II: See Pipiska et al., this Book of abstracts.

REMOVAL OF Cd, Co, Sr AND Zn IONS FROM AQUEOUS SOLUTIONS BY MOSS *Rhytidiadelphus squarrosus.* II. COMPETITIVE ADSORPTION[§]

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Background: The majority of biosorption studies have focused on single metal solution. However, when more than one metal at a time is present in a sorption system, evaluation and interpretation of biosorption results become much more complicated. Even though it is important to understand the behaviour of metal mixture in solution and characterize the effect of the concentration of one metal on the uptake of other metals. Modelling of sorption equilibrium using mathematical models is a useful tool for investigating such systems.

Aim: The aim of present study was to describe the process of competitive sorption removal of Cd^{2+}, Co^{2+}, Sr^{2+} and Zn^{2+} ions from binary systems $CdCl_2$-$CoCl_2$, $CdCl_2$-$ZnCl_2$ and $CoCl_2$-$SrCl_2$ using dried moss biomass of *Rhytidiadelphus squarrosus*.

Methods: Sorption process was monitored by ^{109}Cd, ^{60}Co, ^{85}Sr and ^{65}Zn as radioactive tracers, measured both in biomass and solution samples by gamma spectrometry. To calculate the maximum sorption capacity values (Q_{max}) and corresponding parameters of binary competitive Langmuir model, non-linear regression analysis was performed by program OriginPro 8.

Results: Simple isotherm curves were not suitable for evaluation the Cd-Zn, Co-Cd and Co-Sr sorption systems and have been replaced by three-dimensional sorption isotherm surfaces. Binary competitive Langmuir type equations were found to exhibit good fit to the experimental data from binary systems. Obtained Langmuir parameters Q_{max}, b_{Me1} and b_{Me2} quantitatively describe each system. Results revealed that *R. squarrosus* exhibited preferential uptake of cobalt (Q_{maxCo} = 131 ± 3 μmol/g; b_{Co} = 0.018 L/μmol) from binary system Co-Sr and the uptake of Sr was greatly affected by the presence of cobalt ions in solution. Preferential uptake of cadmium (Q_{maxCd} = 170 ± 4 μmol/g; b_{Cd} = 0.032 L/μmol) from binary system Cd-Co was observed and the presence of Cd caused decrease of Co uptake by *R. squarrosus*. In binary system Cd-Zn both Cd (Q_{maxCd} = 167 ± 4 μmol/g; b_{Cd} = 0.009 L/μmol) and Zn (Q_{maxZn} = 186 ± 5 μmol/g; b_{Zn} = 0.012 L/μmol) were sorbed by biomass with comparable efficiency.

Conclusions: Obtained data confirmed that modelling studies of biosorption processes especially in multi-metalic systems can be used as a tool for prediction of toxic metals behaviour in complex environmental systems such as contaminated surface waters and liquid industrial wastes.

[§]Part I see Hornik et al., this book of abstracts.

REMOVAL OF Cr (III) IN A FIXED BED COLUMN AND BATCH REACTOR USING LEONARDITE AS SORBENT

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Heavy metals are common pollutants found in many industrial effluents. The use of sorption technologies, based on both ion exchange and chemical sorption for the removal of these pollutants from waste water, is especially promising. Low rank coals contain large amounts of humic acids with carboxylic and hydroxyl functional groups which can interact with metal ions. These natural materials, which are available in large quantities, may have potential as inexpensive metal sorbents.

The aim of this study was to investigate the behavior of chromium (III) sorption onto a low rank coal (leonardite) in a series of both batch and continuous experiments. Kinetics batch studies were carried out and the results were fitted to different well-established models in order to determine the kinetics steps that govern the adsorption process.

Different kinetic models: pseudo first-order and pseudo second-order equations, parabolic diffusion model**,** Elovich, Potential function and Urano-Tachikawa models were used to fit the experimental batch data (experimental sorption load vs time). Results showed that pseudo first-order equation fits well the kinetic results for the entire range of pollutant loading concentration, with correlation coefficients of 0,99. Potential function, Elovich, and Urano-Tachikawa models, also had a very good adjustment with experimental data (r^2 = 0,99, 0,97 and 0,98 respectively). Models fitting were used for the calculation of the diffusion coefficient value which determines the mass transfer rate for the pollutant to the sorbent. In this study a diffusion coefficient value of $4{,}11 \times 10^{-10}$ m^2/s was obtained, being in the same order of magnitude than when using activated carbons as sorbent.

Continuous experiments were performed in PET columns. A peristaltic pump was used for the synthetic polluted solution transport across the column, and a fraction collector was fitted to the column outlet for the sampling process. In order to obtain breakthrough curves and adsorption isotherms a wide range of Cr(III) concentrations were used (from 2 to 150 ppm). Results were adjusted according to Langmuir and Freundlich isotherms. Column results showed that under the specific conditions of this study, the complete saturation of the column occurs after 200 minutes for high load conditions. Column usage time is enhanced in great extent when using the lowest concentrations. From the Langmuir isotherm equation, the maximum sorption capacity obtained was 26,04 mg Cr (III)/g leonardite.

RISK ASSESMENT OF BTEX AND OZONE IN PRINTING INDUSTRY IN NOVI SAD

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Air pollution events are not limited to outdoor but can also affect indoor environment. Volatile Organic Compounds (VOCs) such as benzene, toluene and xylene, abbreviated BTEX, are widely used in printing and paint manufacturing units, and generally they are parts of the composition of the raw material. Because of the toxicity related to their physico-chemical properties, many VOCs are classified as suspected lung cancer substances. Also, they exert serious adverse effects on environmental air quality. The presence of Volatile Organic Compounds (VOCs) in ambient and indoor air is widely recognized as precursors of serious risk to human health. Air samples were collected and analyzed at the working place during working time (8 hr) using portable ambient air analyzer (Voyager) and colorimetric method. The measured concentrations of toluene and xylene showed levels below the recommended maximum level set by Serbian law.

Ozone is a pollutant of concern because it can affect both plants and human health. High ozone levels in urban and sub-urban areas during pollution episodes are able to affect human health. Ozone formation is a complex non-linear photochemical reaction driven by two major classes of precursors: nitrogen oxides (NO_x) and volatile organic compounds (VOCs). Emissions of both ozone and VOCs from printing plant were investigated in Experimental Laboratory for Environmental Engineering of the Faculty of Technical Sciences in Novi Sad.

Ozone concentration remained below 0.03 ppm, over two months of measurement campaign, and therefore it is not much lower than the Serbian standard (0.07 ppm). The observed low concentration of ozone is probably due to low concentrations of the three VOCs associated to low light intensity in the printing facility.

In this study, the concentrations of BTEX and ozone were measured in a printing facility during working hours, in order to investigate the level of exposure of the workers to these compounds in printing industry in Novi Sad, and to identify potential relationship between ozone and BTEX in this indoor environment.

Key words: BTEX, Volatile Organic Compounds (VOCs), Ozone, Printing industry

SEASONAL VARIATIONS OF PARTICULATE POLYCYCLIC AROMATIC HYDROCARBONS AND HEAVY METALS IN REMOTE AND URBAN AREAS IN SLOVENIA

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Polycyclic aromatic hydrocarbons (PAH) and heavy metals in airborne particles were measured in three sampling sites across Slovenia representing different sources of pollution. Variations in seasonal composition and concentration range of PAH and heavy metals at the three sampling locations were compared and discussed.

Sampling of PM_{10} was performed by a low volume sampler (Leckel, LVS3) on 24 hour basis using pre-combusted quartz filters (Whatmann, 47 mm). For PAH analysis, filters were spiked with perdeuterated surrogates and extracted with hexane:acetone (1:1) using microwave oven. Extracts were then cleaned on SPE Si columns and finally analyzed by GC/MS for seven PAH, i.e. benzo(a)anthracene, benzo(b,j,k)fluoranthenes, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene and dibenzo(a,h)anthracene that are mainly present in particulate phase and have carcinogenic and mutagenic potential. For analysis of heavy metals, filters were digested with a mixture of nitric acid:hydrogen peroxide (4:1) in a microwave oven. Subsequently, digestates were diluted with Milli-Q water and centrifuged. Analysis of four heavy metals (i.e., arsenic, cadmium, lead and nickel) was performed by ICP-MS. Iskrba (S Slovenia) was chosen as a remote background location, while Ljubljana (central Slovenia) and Maribor (E Slovenia) represented urban background and polluted urban location, respectively.

Throughout the year, the highest total PAH (i.e., the sum of seven analyzed PAH) and heavy metal concentrations were observed in Maribor, while in remote Iskrba the concentrations were the lowest. The sampling site in Maribor is located at a busy road, while the site in Ljubljana is located in a quiet urban area thus explaining higher concentrations at the former urban location. In winter, the total PAH concentrations at all locations were approximately one order of magnitude higher than in summer. On the other hand, a comparison among the locations in January showed that the total PAH concentrations in Maribor were approximately 4-fold higher than in Iskrba (16 vs. 4 ng/m^3). However, the difference diminished in the warmer period of the year. In June, the difference between Maribor and Iskrba was thus less than 2-fold (1.2 vs. 0.7 ng/m^3). In contrast, heavy metal concentrations were more uniform than the total PAH concentrations. The winter concentrations were up to 2-fold higher than the summer concentrations. Regarding composition of pollutants, the composition of PAH was very similar at all sites. Benzofluoranthenes (b, j and k isomers) were the most abundant PAH throughout the year accounting for 40-55% of the total PAH concentrations. On the other hand, dibenzo(ah)anthracene had the lowest abundance contributing only around 5% to the total PAH concentration. Among heavy metals, lead concentrations were the highest amounting up to 22 ng/m^3. On the other hand, arsenic and cadmium concentrations were the lowest being generally below 1 ng/m^3.

At all locations, concentrations of heavy metals were well below their respective target values. Benzo(a)pyrene concentrations in Iskrba and Ljubljana were also below the target value, while in Maribor the target value was exceeded in winter months.

SOLVENT EXTRACTION STUDIES OF ZINC FROM WASTE CELL ELECTROLYTES

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Hydrometallurgical waste material recovery operations are becoming interesting approaches in future clean technologies because of its various application advantages. Solvent extraction and stripping are some of the main unit operations used in hydrometallurgy for metal separation and recovery processes. In this study liquid-liquid solvent extraction of zinc from alkaline and zinc-carbon cell electrolyte leaching solutions and striping from these extractant solvents are investigated. Extraction studies were carried out with di (2-ethylhexyl) phosphoric acid and bis (2,4,4-trimethylpentyl) phosphinic acid as extractants and atomic absorption spectrophotometer was used for analysis of the samples. Initially the average compositions of the cells were determined by using at least 5 different types and brands of waste cells. The solution concentrations achieved by stoechiometric leaching were around 2.65-3.42 g Zinc/100 g solution. Solvent extraction experiments are carried out with both using leached and synthetically prepared solutions. Keeping the solution/solvent ratio around 1/1-1/6 for individual extractions a 50% yield was determined at pH 1.50. However multistage extraction studies at pH 2.00 showed that it is possible to achieve a total 97% yield by four stage extraction and it is possible to obtain a total 92% stripping yield by three stage operation.

SORPTION CHARACTERISATION OF PACKING MATERIALS IN THE BIOFILTRATION OF TOLUENE

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The effects of adsorption on biofilter performance are complex, depending on the medium, contaminant and microorganisms. The adsorption capacity of the medium tends to smooth changes in concentrations and to reduce stress on the microbial population.

The main objective of this study is to characterise the sorption capacities of packing materials commonly used in biofiltration according to different isotherm models for gas adsorption in porous materials as two-parameter isotherms (Langmuir, Freundlich and Dubinin) three-parameter isotherms (Toth, Redlich-Peterson, Radke and Dubinin-Radushkevitch) or a combination of them.

Toluene adsorption is determined for both dry and wet materials to obtain information regarding to the interactions nature between the contaminant, packing materials and the aqueous phase. Adsorption capacities for dry materials are evaluated to describe the behaviour on the non-colonized patches in an operated biofilter or to characterize the use of the materials as a buffer to adsorb intermittent pollutant loads using the material prior to the inlet of a biofilter. Adsorption capacities of wet material describe the ability to absorb intermittent pollutant loads when the media supports are used in steady conditions.

Sorption capacities are evaluated by a frontal analysis method based on toluene measurement at the inlet and outlet of a fixed-bed according to the staircase method. Isotherms are determined from the breakthrough times of step changes in the feed concentration.

The experimental quantities of the toluene adsorbed have been fitted to the different isotherm by non-linear regression according to the value of the objective function defined as the norm of the difference between experimental data and model predictions. Moreover, a confidence interval has been determined in the estimation of model parameters according to the Fisher information matrix method as function of the quantity and quality of experimental data.

The thermodynamic and kinetic interpretation of isotherm parameters reveal that materials with high surface area show a high capacity and affinity with the contaminant, eg. compost or sludge-based carbon. However, all packing materials decrease the sorption capacity at low levels when they are wet under the typical operating conditions in a biofilter. The water film on materials represents a high resistance for the mass transfer for a hydrophobic compound as toluene and, in addition water compete for adsorptive sites.

STATE OF KNOWLEDGE OF ROAD TRAFFIC POLLUTANTS EFFECTS ON AGRICULTURAL LANDS AT THE EDGE OF ROADS

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Road traffic is one of the most important sources of air pollution due the emission of components whose compositions are relatively well known. Particles (metallic particles, diesel, dusts…) differ from gases (carbon monoxide, nitrogen oxides, polycyclic aromatic hydrocarbons, volatile organic compounds…). These road traffic exhaust emissions are dispersed through the atmosphere and are partly settled at the vicinity of the road axes. They constitute a proximity chronic pollution on the lands at the edge of roads. The persistence of these pollutants in the natural environment has been the cause of much concern about the risk of contamination and the consequence for food safety. Indeed these compounds can have noxious effects on living beings health (phytotoxic, carcinogenic, mutagenic). Research interests for these pollutants have raised for a couple of years with the realization of studies which aim to determine the emissions/dispersions of automobile exhausts on various media (air, soil, biomonitoring methods with mosses, mushrooms, plants, animals, crops, …). Furthermore we observe a diversification of pollutant profiles to emerging pollutants, in particular the platinium group elements (Pt, Pd, Rh) produced by the abrasion and the deterioration of catalytic converters, which are obligatory in a range of developed countries to reduce the most toxic components of fumes (carbon monoxyde, incomplete organic matter combustion, nitrogen oxides).

This synthesis aims to evaluate the situation of current research concerning the effects of road traffic pollutants on agricultural lands at the edge of roads. Indeed, farmed lands are often very close to road axes and, as a consequence, crops are potentially exposed to toxic motor exhausts inducing a risk of contamination in the food chain by the direct intake of edible products (vegetables, cereals, fruits) or indirectly by the ingestion of animal products (milk). Some crops, in particular leafy vegetables can be more exposed than other plants because, in general, a wider foliar surface is exposed to air which aids to the pollutants retention (in particular through rough, waffled, waxy or hairy surfaces). In a first part, we will report the current knowledge on studied crops, impact distances for pollutants and risks spaces. Then, we will analyse the results, based on current studies, on the concentration of pollutants for cultivated plants by connecting these results to the factors of variation of emission and dispersion. This inventory and report of knowledge will allow opening new research perspectives, following the concern of some actors of the supply chain, concerned about the food safety of agricultural products.

Key words: road traffic; proximity pollution; agriculture; food safety; edible crops; contamination of food chain.

THE INFLUENCE OF REACTION CONDITIONS ON MECHANISM AND KINETICS OF AQUATIC CHLORINATION OF ANISOLE

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Chlorination is an effective method of water disinfection. Nevertheless chlorination of drinking water is known to lead to disinfection by-products that have been associated with adverse health effects. Formation of various organochlorines including carcinogenic trihalomethanes occurs in drinking water due to reactions of active chlorine species with dissolved organic matter. More toxic bromo- and iodo- containing analogues are also formed as by-products. Thus the mechanisms of aqueous chlorination should be carefully studied. The present report summarizes the results on concentration effects leading to the dramatic changes in the ratio of chloro- and bromo-derivatives in the reaction of aquatic chlorination of anisole. Temperature, pH effects and additions of bromide and iodide anions is also discussed. The kinetic parameters of the reaction at various pH values are obtained. The nature of the reactive particle is discussed.

Reaction of aquatic chlorination of anisole starts with electrophilic substitution in the aromatic ring. Monochloro anisoles are the main products at neutral pH values. Acidic media increases the rate of the substitution reaction, while basic conditions slower the process. Dichloro and trichloro derivatives arise at low pH values. The aromatic ring remains intact. The presence of bromide-anions in water leads to the increase of the conversion rate of the organic substrate with formation of mainly organobromines. The presence of iodide-anions in water leads to slight acceleration of the chlorination reaction. Iodoanisole was detected only at very high level of iodine. Copper (2+) ions, metallic copper or iron do not influence notably on the aquatic chlorination of anisole.
The study of anisole reaction with sodium hypochlorite aquatic solution was carried out at substrate levels in the range from 10-4 to 10-6 μM, ratio of substrate to active chlorine in the range from 1:1 to 1:50, range of pH from 2 to 10, range of temperatures from 0 C to 40 C, and in the presence of various levels of bromides and iodides. Purge and trap technique with Agilent 5973 quadrupole instrument was used to identify volatile compounds. LECO Pegasus IV TOF instrument in GC-MS and GC-GC-MS mode was used to study semi volatile products. HPLC technique (Agilent 1100) was used for the accurate quantitative measurements.

TRENDS IN THE PHOSPHORUS VARIATIONS IN THE SURFACE WATER IN LAKE PEIPSI (EASTERN EUROPE)

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The submeridionally elongated Lake Peipsi is the fourth largest lake (surface 3555 km^2) in Europe with respect to the surface area, and the biggest transboundary lake in Europeand consists of three parts named from north to south: Lake Peipsi *sensu stricto (ss)*, Lake Lämmijärv and Lake Pskovskoe. The unbalanced P content in the lake ecosystem speaks about the essential role of P in sediments in its biogeochemical cycling within the lake. Despite a decrease in the external nutrient inputs, no corresponding improvement has been observed in the state of the Lake Peipsi. Many studies have been undertaken to measure the lake's water quality trends, but important questions remain unanswered, particularly about the role of internal and external phosphorus loading. The study was aimed to examine P seasonal variations in the surface water in Lake Peipsi *ss,* relationships among algal blooming, chlorophyll content, P internal load, and P in the outflow water to augment the understanding of P budget calculation. The distribution and variations of P, chlorophyll *a,* water fluctuation in surface water in Lake Peipsi *ss* are discussed. The P dynamics in the surface sediments of Lake Peipsi *ss* also are argued. The detailed monitoring data during 2000-2007 showed the typical seasonal variations in the content of P-total concentration in the Lake Peipsi *ss* water with minimum values in spring- early summer and maximum values in autumn which were in average four times higher compared to minimum. Our data showed that internal processes can largely compensate for year-to-year changes in the P balance. The quantity of P stored in sediments is great compared with P in the water column. Much of this phosphorus is thought to be released from cohesive sediments (silt) which are relatively unstable and their composition can change very easily. In Lake Peipsi *ss*, 70 % of the total bottom area is covered by such sediments, the rest being covered by sand and clayey sand. We found season-specific correlation of the dynamics of the total P concentration in Lake Peipsi *ss* and in outflow in the Narva River water. Year average P-total concentration in lake slightly responds to variations in the external load and varies relatively smoothly. The fluctuations of volume in relation to the annual average amount of water in Lake Peipsi have been in the amplitude from +11 % to –15%. It is natural to predict that such large variation of the water volume will have impact on the ecological state of the lake.

OPTIMIZATION OF THE GC-Py-AFS FOR ORGANIC MERCURY DETERMINATION

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Since mercury (Hg) become a proved cause of environmental concern due to its high neurotoxicity and widespread occurrence, its monitoring attracted special attention over the last decades. Particularly, methylmercury (MeHg), the most toxic mercury specie, can cause severe neurological damage to humans and wildlife. Hence, the accurate determination of the MeHg at low concentration levels in a variety of environmental matrixes is a current analytical challenge.

In this work, the main chromatographic parameters affecting to the organic mercury determination such as make-up and carrier gas flow rates and pyrolyzer temperature were optimized and their effect on the peak width and symmetry factors evaluated.

Accordingly, standards of MeHg and ethylmercury (EtHg) were propylated using aqueous $NaBPr_4$ and sampled by headspace SPME. Diisobutylmercury (iBu_2Hg) was used as internal standard. The GC determination was performed by using a Thermo Trace GC interfaced to a Tekran CVAFS detector via a pyrolyser. This system converts the different mercury species into Hg^0 by thermal decomposition. Optimum conditions were obtained at 2 mL/min of carrier, 6.75 mL/min of make-up flow and 750ºC of pyrolyser temperature. The repeatability was 9% (n=6) for MeHg and 11% (n=6) for EtHg. Furthermore, the reproducibility of the methodology was tested by analysing the standards on six different days, which yielded an RSD of 9% (n=6) and 16% (n=6) for MeHg and EtHg respectively.

Selected analytical conditions were applied to the determination of MeHg in complex biological matrixes such as eggs and feathers of *Ardea purpurea* showing the selectivity and sensitivity of the optimized analytical technique.

CADMIUM AND COPPER SORPTION ON PECTIN ENCAPSULATED IN CALCIUM ALGINATE BEADS

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Pectin is an acidic polysaccharide constituted by monomer units of galacturonic acid. It is a main component of peel fruits where is present as protopectin. Due to the presence of a high number of carboxylic binding sites in its structure, pectin (Pect) shows a good sequestering capacity towards metal ions [1]. Pectin has been proposed as a sorbent to remove metal ions from aqueous solutions. In this work the ability of pectin on solid phase to remove Cd(II) and Cu(II) from aqueous solutions has been evaluated. To this end, a powder of a commercial pectin, (esterified potassium salt from Citrus fruit) was encapsulated in a polymeric matrix of calcium alginate (CA) at different ratios of pectin to obtain spherical beads of calcium alginate.
The different ratio pect-CA, contact time, different number of beads on solution and different initial pH has been studied in order to obtain kinetic data of metal adsorption on the biosorbent. To better characterize the kinetic behavior the experimental data were fitted by Lagergren (pseudo-second order) equation.
Results showed that calcium alginate, used as blank, is able to remove cadmium and copper and the presence of pectin into the beads enhance the sorption capacity. The highest sorption rate was obtained with beads with the highest percentage of pectin (2%). The optimal contact time was found to be two hours and the most favourable initial pH is around 5.

References

[1] Kartel M. T., Kupchik L. A., Veisov B. K. *Chemosphere*. 1999, 38(11), 2591-2596.

Cr(VI) SORPTION ONTO GRAPE STALK WASTE : KINETICS MODEL

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The chromium present in industrial wastewaters is mainly in the hexavalent form as chromate and dichromate. Cr(VI) is much more toxic than Cr(III) and its discharge to surface water is regulated to below 0.05 mg L^{-1} by the US EPA. Reduction to its trivalent form is the first step of the generalized methods for hexavalent chromium removal. For Cr(VI) reduction to occur, a suitable redox couple having a compatible electron symmetry to allow electron exchange must be present. Biosorbents are potential electron donors and Cr(VI) has the potential of electron acceptor.

Grape stalks waste has been reported to be an efficient biosorbent for Cr(VI) removal and in a recent work, it has been postulated that Cr(VI) removal by this sorbent is due to two different mechanisms, adsorption and reduction to trivalent chromium. Nevertheless, the rate at which both processes take place, and the possible simultaneity of both processes, has not been yet investigated. Therefore, the aim of the present work is to investigate kinetics of Cr(VI) sorption onto grape stalk waste and propose a model that predict the overall process of metal removal.

First results obtained with the stirred reactor allowed to observe that the Cr(III) formed due to reduction is partially adsorbed onto grape stalk waste. Taking into account this observation reversible reaction adsorption-desorption of Cr(III) was introduced in the model formulation together with reduction reaction and Cr(VI) sorption-desorption. The rate constants values obtained from the model put into evidence that reduction is the main reaction, Cr(VI) is rapidly reduced to Cr(III) and the rest of the processes are affected by this fact. The proposed model fits adequately the obtained experimental data for Cr(VI) sorption onto grape stalk waste. Furthermore, this model would be helpful for researchers in the field of Cr(VI) biosorption to design and predict the performance of biosorption processes.

ACKNOWLEDGEMENTS
This research was funded by Ministerio de Educación y Ciencia (Spain), project CTM2005-07342-C02-01/TECNO. Thanks are due to Mª Àngels Morera for her help in the experimental work.

DEVELOPMENT OF A SEQUENTIAL INJECTION ANALYSIS SYSTEM TO MONITORIZE CHROMIUM POLLUTED EFFLUENTS

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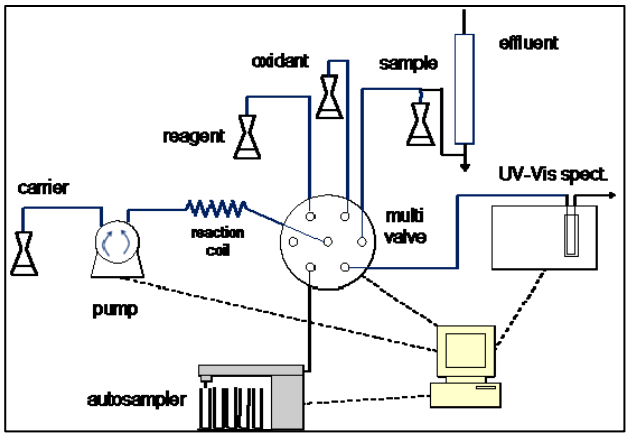
Recently, many studies are focused to improve the treatment of industrial effluents polluted with chromium and reduce the cost of the process. These studies require a huge amount of samples to obtain enough experimental data in order to calculate reliable decontamination parameters. Besides that, chromium is present in two oxidation states that must be quantified separately: Cr(VI) is directly determined by the colorimetric method of 1,5-diphenylcarbazide and Cr(III) is calculated by the difference between total chromium determined by Atomic Spectroscopy and Cr(VI). Therefore, the number of analysis duplicates and the sources of errors increase.

The development of Sequential Injection Analysis (SIA) systems for Cr(VI) and Cr(III) determination leads to the automation of all the analytical process and let to determine in "real time" the concentration of both species of Cr in one analysis.
This system requires a very small volume (less 1 mL) and the determination of both species can be completed in less than 5 minutes[1]. An autosampler will allow make automatically the required calibrations.



In this work, the development of an automatic SIA system for simultaneous determination of Cr(VI) and Cr(III) is presented. The system was developed following these phases:

1. Definition of the main tasks to be done by the SIA system.
2. Outline of the sequence to execute these tasks.
3. Development of the appropriate software.
4. Optimization of the procedure through the analysis of Cr(VI) and Cr(III) standard solutions.
5. Validation of the proposed SIA system [2]

Acknowledgment
This work has been supported by Ministerio de Educación y Ciencia, CTM2005-07342-C02-01/TECNO and "Càtedra de Processos Industrials Sostenibles" of Universitat de Girona.

[1] Mulaudzi, Ludwig V., Jacobus F. van Staden, and Raluca I. Stefan. **2002** Determination of chromium (III) and chromium (VI) by use of a spectrophotometric sequential injection system. Analytica Chimica Acta, 467(1-2):51-60.
[2] Fiol, N., I. Montero, F. De la Torre, and I. Villaescusa **2008** Development and Validation of a Spectrophotometric Method for Continuous Analysis of Cr(VI). Actes XIII Trobada Transfronterera sobre Sensor i BioSensors.

REMOVAL OF HEAVY METALS FROM WASTEWATERS BY ADSORPTION ON LOW-COST SUBSTRATES

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High concentrations of heavy metals in the environment represent a major concern due to their harmful effects on living being. Many industrial effluents contain high quantity of heavy metals and need to be treated before being discharged in natural water. Heavy metals can be removed from wastewaters by adsorption on different substrates. The efficiency of chromium removal from aqueous solutions by white, yellow and red sands from the United Arab Emirates (UAE), has been investigated. We found that white sand is the most efficient adsorbent of Cr(III). The minimum sand dosage required for complete removal of Cr(III) is *ca.* 20, 40 and 100 g/l for white, yellow and red sand, respectively. By contrast, the adsorption of Cr(VI) on all sand forms was very low (removal ≤ 10%). The optimum pH for adsorption was *ca.* 5.0 for Cr(III), 2.0 for Cr(VI) and the optimum adsorption time was *ca.* 3 hours. At pH 5.0 Cr(VI) was not adsorbed at all whereas Cr(III) was totally removed. Adsorption of Cr(III) by the three sand forms obeyed Lagregren first order kinetics and the Langmuir isotherm. At 25.0 ^{o}C, the maximum mass of Cr(III) removed per gram of sand (Q_{max}) was 62.5, 9.80 and 2.38 for white, yellow and red sand, respectively. Adsorption of other heavy metals, such as Cu(II), Cd(II), Ni(II), Hg(II) and Pb(II) is now being studied in our laboratory as a function of pH, temperature, metal concentration and sand dosage.

EDTA LEACHING OF Cu CONTAMINATED SOIL USING ELECTROCHEMICAL TREATMENT OF THE WASHING SOLUTION

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The feasibility of a two-phase method for remediation of Cu contaminated vineyard soil (364±2 mg kg^{-1}) was evaluated. In the first phase we used EDTA for Cu leaching, while in the second phase we used an electrochemical advanced oxidation process (EAOP) for the treatment and reuse of the washing solution for soil rinsing (removal of soil-retained, chelant-mobilized Cu complexes) in a closed loop. In the EAOP, a boron-doped diamond anode was used for the generation of hydroxyl radicals and oxidative decomposition of EDTA-metal complexes at a constant current density (40 mA cm^{-2}). The released Cu was removed from the solution mostly as an electro-deposit on the cathode. Two consecutive additions of 10 mmol kg^{-1} EDTA removed 26% of Cu from the soil, mostly from carbonate and oxide soil fractions (58 and 40 % Cu reduction). The soil Cu oral availability (*in vitro* Physiologically Based Extraction Test) was reduced after remediation by 42 and 51% in the simulated stomach and intestinal phases. The discharge solution was clear, almost colorless, with pH 8.4 and 0.5 mg L^{-1} Cu and 0.07 mM EDTA. The novel method enables soil Cu availability stripping using small volumes of process waters, and no wastewater generation or other emissions into the environment.

HYDROPHOBIC FUNGICIDES SORPTION BY A PEAT SOIL.

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Sorption and desorption of non-ionic pesticides by soils are fundamental processes controlling fate and transport of these organic pollutants in surface and ground water. The predominant sorbent of hydrophobic organic contaminants in soils and sediments is the natural organic matter, as long as the total organic carbon content is higher than 0.1 % (Chefetz et al., 2004).

The study of the interaction between currently used pesticides and soil organic matter (SOM) is therefore important for assessing the risk of pesticide transport from agricultural fields into the broader environment. In this framework, we studied the adsorption-desorption processes of two hydrophobic fungicides (metalaxyl and penconazol) with a peat soil (95.9 % organic matter). Metalaxyl and penconazol are two systemic fungicides widely used in the specific wine-growing areas of NW-Spain (Galicia) that are very different as regards their hydrophobicity (Tomlin, 2000).

Adsorption isotherms for both fungicides with the peat soil were obtained by means of batch equilibration experiments and desorption was followed subsequently by withdraw-refill technique. Comparison between both fungicides, revealed that penconazol, the most hydrophobic, is retained by organic soil in greater magnitude than metalaxyl. Within the same added concentration range and under equal conditions (w/v ratio, pH and ionic strength), the amount of adsorbed metalaxyl ranged between 43 to 23 % whereas the percent of adsorbed penconazol represented between 100 to 93 %.

Desorption experiments also revealed different behaviour among pesticides: while the desorption of metalaxyl did not deviate significantly from adsorption isotherm, penconazol desorption seemed to be hysteretic.

Although we dealt with non-ionic pesticides, SOM is widely characterized by its polyelectrolyte nature produced by ionization of acidic functional groups, carboxylic and phenolic mainly. Because of this, we evaluated the effect of pH and ionic strength on metalaxyl adsorption. The resulted pH-edge revealed an inverse dependence between the adsorbed amount of metalaxyl and pH, however the magnitude of this effect accounts only for a 2 % decrease on the adsorbed pesticide per pH unit. Otherwise, the isotherms obtained at two different background electrolyte concentration (0.010 and 0.10 M KNO_3) showed little effect of the ionic strength, being the adsorption at the lower ionic strength about 4 % higher.

References:

Tomlin C., Ed. The pesticide manual; British Crop Protection Council Publications: Surrey, U.K. (2000)

Chefetz B., Bilkis Y.I., Polubesova T. Sorption-desorption behaviour of triazine and phenylurea herbicides in Kishon river sediments. *Water Res.*, **38**:4383-4394 (2004).

INFLUENCE OF MICROBIAL PRODUCTS ON THE STRUCTURE-CHEMISTRY AND CHEMODYNAMICS OF COVALENTLY IMMOBILISED RESIDUES OF XENOBIOTICS IN SOIL DERIVED ORGANO-CLAY COMPLEXES

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Organo-clay complexes in soil play a major role in immobilisation and the persistence of xenobitotics and their metabolites. This project will contribute to the understanding of the interactions in such complexes. We study the biogeochemical and chemodynamic behaviour of ^{13}C- and ^{14}C-labelled compounds, 4(3', 5'-dimethyl-3'-heptyl)-phenol (NP), (4-chloro-2-methylphenoxy)acetic acid (MCPA) and their metabolites during the formation, release and degradation of residues covalently bound to natural and model humics-coated clay.

Adsorption and binding of the xenobiotics to organo-clay complexes are investigated by separating humics-coated clay into fulvic acids, humic acids and humin. Fractionation is also favourable regarding ^{13}C-NMR anaylses due to the higher carbon concentration in these samples as compared to the complete soil containing additional mineral matter. The separation is also reasonable for subsequent chemical degradation and derivatisation experiments which yield products measurable by GC-MS.

For our research, we used two A-soils differing in particulate composition and content of humic matter, soil from Ultuna (Sweden) sand: 19%, silt: 48%, clay: 28%, C-org.: 4.2% and from Fuhrberg, (Germany) sand: 74%, silt: 17%, clay: 5%, C-org.: 8.2%. In a preliminary test with Ultuna soil, we optimized sample preparation and different analytical methods. After two days of incubation, both the assays with NP and those with MCPA showed characteristic distributions of radioactivity and also interactions of the compounds with the organo-clay fraction.

Based on these results we used ^{14}C- and ^{13}C-labelled NP in the first time course experiment with Fuhrberg soil, incubation periods up to 180 days were used. Soil was divided into sand, silt and clay; the clay-fraction was fractionated into fulvic acids (FA), humic acids (HA) and humin. Supplementary, we determined the mineralisation of NP to $^{14}CO_2$. The complete soil and the aqueous fraction occurring during sample preparation were analysed for their microbial activity (reductase) and carbon content (TOC). Samples derived from the ^{14}C assays were used to determine the ^{14}C distribution among several fractions and were analysed by DC and HPLC. For GC-MS and NMR spectroscopy, similar ^{13}C samples were prepared in order to obtain structural information of the residues. By combining the ^{14}C and ^{13}C methods, we are able to support information on the structure and binding of the covalently immobilised residues.

LITHOGENIC THALLIUM GEOCHEMISTRY IN SOILS WITH CONTRASTING LAND USE

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Thallium (Tl) is considered as a highly toxic trace metal by many authors. Nevertheless, its geochemical and consequent environmental fate in soils with naturally increased Tl contents has received quite little attention.
The aims of this study were (i) to understand the effect of contrasting land use on Tl geochemistry in soil, and (ii) to evaluate the influence of different land cover on lithogenic Tl uptake. For this purpose two forest and grassland soils developed on an identical Tl-rich substrate were examined.
A complex soil-plant investigation supplemented by mineralogical methods was performed. The modified BCR sequential extraction combined with X-ray diffraction analysis (XRD) and voltammetry of microparticles (VMP) was carried for a detailed insight on lithogenic Tl speciation and bioavailability in both contrasting soils.
It was revealed that soil forming processes like bioturbation and probably dust deposition may influence the increased input of lithogenic Tl into the forest floor. Thallium was predominantly bound within the residual fraction (up to 95%) corresponding to primary silicates (mainly orthoclase and muscovite) and probably secondary illite, which were detected by XRD in all studied horizons. Thus, stable silicates can be thought as the phases controlling the solubility of lithogenic Tl in both the forest and grassland soils. The highest portion (~ 5%) of "labile" Tl was found in the organic horizons of the forest soil indicating a distinct role of forest soil organic matter (SOM) on Tl mobilization and bioavailability. Thallium adsorption was dominated by an identified non-crystalline Mn(III,IV) oxide detected by VMP that proves the strong affinity of Tl for Mn oxides in mineral soils. On the contrary, Tl adsorption by more abundant Fe(III) oxides (goethite and ferrihydrite) was evaluated to be low. Organically bound Tl in the forest floor was found to be associated with primary SOM corresponding to the raw and partially decomposed litter of Norway spruce (*Picea abies* L.). Moreover, a relatively high Tl uptake was recorded by this species. In contrast, lithogenic Tl uptake by common grasses like red clover (*Trifolium pratense* L.) or timothy grass (*Phleum pratense* L.) seems to be very low.

Acknowledgements
This research was funded by the grant of Czech Science Foundation (GAČR 526/08/P428), the internal project from the Czech University of Life Sciences (No. 213115) and the projects of Ministry of Education of the Czech Republic MSM 6046070901 and MSM 6007665806.

FATE AND EVOLUTION OF TOXIC TRACE ELEMENTS IN SEDIMENTS OF THE NERBIOI-IBAIZABAL ESTUARY (BILBAO, BASQUE COUNTRY) IN THE PERIOD 2005-2008

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Trace elements from natural and anthropogenic sources continuously enter the aquatic ecosystem where they pose a serious threat because of their toxicity, long time persistence and bioaccumulation. To study this, the metallic content in sediments is an accepted and widely used indicator of anthropogenic pollution.
We focused the study in the sediment of the Nerbioi-Ibaizabal River (Bilbao, Basque Country) which is an area that has suffered an extreme industrial and mining pressure during the last century and it is located in one of the most important urban areas of the Cantabrian coast. Correct environmental policies started to be implemented in the 90's and they have led to a remarkable recovery of the ecosystem. Sediments from its bed, however, still show an important metallic content and remain not only as memory of historical pollution activities, also as sink of current activities.
Sediments were collected at eight different points of the estuary (four in tributary rivers, one in a closed dock, two in the main channel and another one in the mouth of the estuary), approximately every three months from 2005 to 2008, in order to quantify metallic pollution and to identify trends in space and time. After drying the sediments by lyophilisation and sieved through a 65 μm mesh, the concentration of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mg, Ni, Pb, Sn, V and Zn were measured in the acid extracts by inductively coupled plasma/mass spectrometry.
Searching of seasonal and spatial trends was performed by means of the Mann-Kendall test and correlation analysis (CA), using the whole data matrix obtained. The eight sampling locations can be grouped in three sets, according to different patterns of contamination. There are still areas in the estuary (mouth, the closed dock and two tributary rivers with industrial activity) with high metallic content. In these areas, the main trend indicates that concentrations are gradually decreasing. Otherwise, in areas with lower pollution the concentrations increase and, in addition, seasonal trends are observed (with maximum at the end of summer and minimum at winter). Whatever the metallic trend is, the CA of data revealed connections between the concentrations of several elements of natural origin (Al and Mg) or industrial use (e.g. Co and Ni).

Acknowledgemets: This work has been financially supported by the Basque Government through the ETORTEK BERRILUR II (IE06-179) project. S. Fdez-Ortiz de Vallejuelo, A. Gredilla, M. Astobieta are grateful to the UPV/EHU for thei pre-doctoral fellowship.

VARIATIONS OF RADON AND AIR-IONS CONCENTRATIONS IN INDOOR AIR

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Air-ions and radon are basic constituents of outdoor and indoor air the lower tropospheric air. Air-ions are composed of the central ion and 4–12 molecules of water around, depending on polarity. The structure of dominant air-ions in indoor air is determined by water, ammonia, nitrogen oxides and radical of nitric acid (NO_3). Their mobilities are ≥ 0.5 $cm^2V^{-1}s^{-1}$ and life time up to 100 *s*. Near the ground level, air-ions originate mostly by radon α-decay and cosmic radiation. In order to clarify relation between radon and air-ions, and their behaviour in indoor space, we performed series of measurements. The air-ions detector ″CDI-06″, made in the Institute of Physics, Belgrade, and with ″RAD7″ - Electronic Radon Monitor/Sniffer were utilized for measurements. Several representative indoor places were chosen to perform measurements: ground floor houses, different buildings and cellar. The results have shown that air-ions pair production rate is mostly caused by radon activity. Outdoor meteorological conditions and local geophysical properties of surrounding soil determining daily changes of radon emanation and consequently air-ions concentrations. Also, concentration of the air-ions have minimums and maximums with period of about 12 *hours* what are closely connected with measured changes of radon activity. Higher values of radon and consequently air-ions are about one hour before sunrise when they can reach values of few tenths above daily concentrations. Relation between air-ions expressed in the *ions/m*^{3} and radon activity in *Bq/m*^{3} for positive and negative air-ions are between 10-15 x 10^{-6} depending on humidity, air pollution and quantity of electrostatic surfaces in indoor area.

NEW APPROACH TO THE MONITORING OF HYDROPHOBIC PERSISTENT ORGANIC POLLUTANTS IN WATER USING THE SEMIPERMEABLE MEMBRANE DEVICES TECHNOLOGY. A CASE STUDY: PAH's IN THE URDAIBAI ESTUARY (BAY OF BISCAY, BASQUE COUNTRY)

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Oysters have been widely used to monitor pollution in aquatic systems. Passive sampling by SemiPermeable Membrane Devices (SPMDs) is emerging as an alternative to the use of biomonitoring organisms. SPMDs preconcentrate hydrophobic organic contaminants from the surrounding aquatic environment. They mimic the bioconcentration of organic pollutants in fatty tissues of organisms but they are unaffected by environmental stressors that affect biological sentinels, providing a simple matrix for a subsequent analysis.

The aim of this work is i) to quantify the PAH pollution in sediments, water and biota of the estuary, ii) to investigate the interchange of PAH in the sediment-water-biota interfaces and ii) to compare the effectiveness of oysters and SPMDs as indicators of polycyclic aromatic hydrocarbons (PAHs) pollution in estuarine waters.

Non-polluted oysters and SPMDs were deployed in selected points of the estuary of the Oka River (Urdaibai Reserve of the Biosphere, Bay of Biscay, Basque Country). Oysters and SPMDs were collected for chemical measurements two and four weeks after deploying, together with autochthonous oysters, water and sediments. Sampling campaigns were carried out in July, November 2007 and April 2008.

The concentrations of PAHs were measured in all the samples by gas chromatography with mass spectrometry detection (GC/MS) after extraction of the analytes to an appropriate solvent and a clean-up step when necessary. The results obtained show a high positive correlation between concentration in oyster (both autochthonous and transplanted ones) and amount of analyte uptaken by the membrane. The concentrations found are similar to thoseof other similar environments.

In some campaigns, a negative correlation between concentration in sediment and analyte preconcentrated in oysters and membranes was also observed. This results suggest that, in certain seasons, sediments of the estuary may act as a secondary pollution source to the sorrounding water.

Acknowledgements: This work has been financially supported by the Basque Government through the ETORTEK BERRILUR II (IE06-179) project and the UNESCO Chair on "sustainable development and environmental education" of the University of the Basque Country through the UNESCO 07/19 project. M. Astobieta is grateful to the UPV/EHU for his pre-doctoral fellowship

A WALK THROUGH NEW APPROACHES FOR SOLVING THE NATURAL ORGANIC MATTER CONUNDRUM

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The term "natural organic matter" (NOM) is normally used to designate all the organic matter in a reservoir or natural ecosystem other than living organisms and compounds of man-made origin. The NOM found in natural waters possesses a large variety of properties and is composed of an extremely complex mixture of compounds, most of which have not yet been identified. Past studies have focused mainly on the refractory fraction of NOM (often called humic substances), largely because of the key role that it plays in the fate of trace metals and organic micropollutants. Issues related to NOM degradation and turnover have traditionally been addressed in the frame of pollution abatement strategies and now have become an important part of studies associated with climate change. However, in spite of all these efforts, many problems remain unsolved and NOM is still largely perceived as a complex mixture of substances of relatively unpredictable properties. First results and ongoing projects where new approaches for the understanding of NOM are being applied will be discussed in this presentation. They concern:

- Clarification of the confusion surrounding the extensive terminology related to NOM used in freshwaters [1].
- Evaluation of the gap existing between basic and applied NOM-related research [1]. Presentation of a blog-based initiative (www.schema.lu).
- Development of methods for quantifying all types of NOM present in surface waters [2,3,4].
- Evaluation of the extent of NOM attachment to mineral colloids and particles in surface waters [5].
- Unbiased revision of existing models to describe trace element-NOM binding [6]. Development of a wiki (http://www.schema.lu/tiki/tiki-index.php).
- Presentation of a new IUPAC project devoted to the collection of all published data on binding of trace elements by humic substances [7].

[1] M. Filella (2008) Env. Chem. Lett., DOI 10.1007/s10311-008-0158-x.
[2] V. Chanudet, M. Filella and F. Quentel (2006) Anal Chim Acta, 596, 244-249.
[3] F. Quentel and M. Filella (2008) Anal. Bioanal. Chem., DOI 10.1007/s00216-008-2366-4.
[4] M. Filella, F. Quentel and V. Chanudet (2008) In: From Molecular Understanding to Innovative Applications of Humic Substances, Ed: I.V. Perminova, N.A. Kulikova, Humus Sapiens, Moscow, pp. 151-154.
[5] T. Schäfer, V. Chanudet, F. Claret and M. Filella (2007) Environ. Sci. Technol., 41, 7864-7869.
[6] M. Filella (2008) J. Mol. Liquids, 143, 42-51.
[7] IUPAC Analytical Chemistry Division Project, Humic-metal binding constants database (2009-2011).

APPLICATION OF ICP-MS TO DETERMINE TOXIC METAL IONS IN HUMAN TISSUES

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The metal intoxications can be due to acute and chronic metal poisoning due to general pollution or occupational causes.
Human intoxication by different metal ions can be treated by administration of proper chelating agents, that generally act by mobilisation of the toxic metal ions and successive excretion. The chelating agents can also reduce the toxicity by shielding metals from their biological targets.
The knowledge of the metal concentration in tissues, which can be determined on agobiopsies, can be required in order to modulate the chelation therapy. The use of a proper technique and of proper analytical method is required in order to obtain reliable results.
ICP-MS can be considered one of the most advanced among the different nowadays available techniques. The detection limits of ICP-MS are significatively lower than those of optical and electrochemical instruments. This technique moreover presents high precision and accuracy, relatively fast determinations and it allows to quantify separately all the isotopes of the detectable elements.
A wide number of recent publications report methods for the treatment of biological tissues; we optimised [1] an analytical procedure for the analysis of metal ion content in human tissues, pointing out that an optimal procedure consists in drying the crude sample in oven at 110°C and dissolving by digestion with nitric acid.
In this work we present a check of the analytical procedure to determine copper, zinc, iron and aluminium by ICP-MS, operating on NIST 1577b bovine liver. The calibration curves were prepared using standard ion solutions for ICP-MS. Fresh working standards were obtained by diluting the commercial standards with double distilled water containing the same nitric acid concentration as in the samples. The working ranges of each element was chosen according to its expected concentrations in the samples and was covered with nine solutions of evenly spaced concentrations. The results obtained as a mean of thirteen different samples prepared from different amounts of NBS bovine liver, were compared with the NBS certified values finding a good agreement for all the elements, in the limits of experimental error.

[1] G. Crisponi, V.M. Nurchi, R. Silvagni, G. Lubinu, R. Ambu, A. Marras, G. Parodo, G. Faa, *Atomic Spectroscopy*, 73-78 (1995)

CHARACTERISATION OF ATMOSPHERIC AND BIOLOGICAL DEGRADATIONS ON MODERN CONSTRUCTION MATERIALS BY MEANS OF ULTRAMOBILE RAMAN SPECTROSCOPY

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Mineral construction materials are susceptible to suffer from the attack of different environmental stressors. Appart from the physical weathering, biodeterioration is as important as the chemical decaying sources. Civil buildings located in polluted urban/industrial areas are substantially deteriorated not only apparently (black crusts, cracks, material losses…) but also compositionally (carbonation of concrete, formation of soluble salts…) due to the impact of combustion and greenhouse acid gases (mainly SO_x, CO_2, and NO_x). Different micro-organisms can cause alterations on stone materials as well as in modern concrete and cement mortars during their colonization process.
Degradation products and original composition of construction materials (concrete and calcareous stones) used in buildings erected in the first half of XX century, located in polluted and non-polluted areas near Bilbao (Bay of Biscay), were analysed in situ by means of ultramobile Raman spectroscopy with the purpose of characterising the chemical and biological degradations on such modern materials.
The acid gases, in atmospheres with high humidity levels, neutralise the alkalinity of concrete and promote the decarbonation of calcareous stony materials. The side reaction of the solubilised cations, from the original materials, with the anions of the acid gases promote the formation of the corresponding sulphate and nitrate salts. Some examples, identified with the Raman device will be discussed.
One of the main alteration processes induced by lichens is due to the excretion of organic acids on the surfaces of the colonised materials. Some of them give an extra acidity to that promoted by the atmospheric acid gases, increasing the deterioration through acidification; that is the situation with the usnic acid, identified in this work on a degraded concrete sample. But others, when neutralised give anions, like oxalate, that form new mineral phases; in this work, the results obtained in the surrounding (scale of microns) of several recent lichen colonies, growing on carbonate based stones, have been used to propose a model for such oxalate formation:
The analysed round colonies presented a systematic distribution of compounds. The centrum was white and shown only whewellite ($CaC_2O_4.H_2O$). Then coloured rings (from yellow to orange) appear showing different carotenoid substances. The most outer ring is generally green (chlorophyll) but in its border another calcium oxalate, weddellite ($CaC_2O_4.2H_2O$), appears always without any trace of whewellite. That means, weddellite seems to be formed at the beginning (oxalic acid reacting with $CaCO_3$) and then dehydrate to whewellite in areas left by the living colony.

Acknowledgements: This work has been funded through the project IMDICOGU (ref. BIA2008-09267, Spanish MICINN). I. Ibarrondo and N. Goienaga acknowledge her Ph.D. grants from the EHU/UPV

DETERMINATION AND QUANTIFICATION OF LAS-ISOMERS USING GC-MS AND GC-FID

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Linear alkylbenzene sulfonates (LAS) are the most widely used anionic surfactants in detergents [1]. They possess an acute aquatic toxicity to micro organisms, algae and fish. The quantification of LAS in wastewater, sediments and sewage sludge is carried out in routine practise by reversed phase liquid chromatography using different types of detectors like fluorescence detection or mass selective detection with electrospray ionisation. For quantification in most of the cases calibrations are done with technical products with a purity of about 80%. These technical products comprise LAS homologs ranges from 10 to 14 carbon atoms in their aliphatic chain. Each homologous species has a variety of isomers. The so called inner isomers having substitution positions close to the center of the alkyl chain, whereas isomers having positions of substitution close to the terminal carbon atom are referred to as external isomers. For purity assessment 26 different LAS-species have to be quantified and characterized. For each homologous LAS-species a synthetic analogon was prepared. Therefore 1-alkylbenzenes with defined chain lengths (C_{10} - C_{14}) and known purity are synthesized. In order to use the separation efficiency of the gas chromatography for the separation of the complex mixture of isomers a new method for the derivatisation of LAS was attempted. Using different alkylation reagents like trialkyl orthoformates [2] a capable methodology was established and validated. The synthetic LAS analogons were derivertized as well and were used as internal standards for the accurate quantification of the separated structural isomers. The alkylated LAS-analogons are now available as calibration standards for the exact quantification of LAS in different environmental compartments like wastewater or sewage sludge.

Literature:

[1] HERA, 2007, Version 3.0, URL: http://www.heraproject.com/files/4-F-HERA_LASFinalReport2007 revision10_07.pdf

[2] A.A. Padmapriya, G. Just, N.G. Lewis, Synthethic Communications, 1985, 15, 1057-1062

DETERMINATION OF AMMONIUM BY THERMAL LENS SPECTROMETRY

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Ammonia is produced in large amounts by reductive chemical reactions and by microbiological processes under anaerobic conditions, and a considerable fraction of it is released into the air. It contribuites significantly to various atmosferic processes and to water pollution. Furthermore, ammonium in drinking water can be converted to nitrate that is toxic for humans. Ammonium in waters can be determinated by various methods such as flow injection analysis (FIA), ion chromatography (IC), enzymatic methods, and gas chromatoghraphy-mass spectrometry (GC-MS). But most frequently, various spectrophotometric methods are applied for this purpose, despite the time consuming colouring reactions, which can last up to 24h at room temperature.

In this work we to improve the sensitivity of the existing indophenol blue spectrophotometric method by utilizing thermal lens spectrometry (TLS) as a detection method. This should in principle result in an increased sample throughput of the method.

The indophenol method is based on the Berthelot colorimentric reaction, where a blue coloration with the absorption maximum at 640 nm is developed after mixing solutions of ammonium, phenol or less toxic salicylic acid, and hypochlorite. Manganese sulfate is used as catalyst and potassium sodium tartrate as complexing agent. For the purpose of TLS detection we built a dual beam TLS system consisting of a He-Ne exitation laser (35mW) operating at 632.8 nm, and a He-Ne probe laser operating at 543.5 nm (5 mW). This is the first known TLS system utilizing a green probe laser beam, and according to theory, the sensitivity of TLS method should increase as the ratio of the wavelengths increases (632.8/543.5).

To further enhance the TLS signal we performed the measurements in mixtures of ethanol/water (1:1) and acetonitrile/water (1:1) since organic solvents provide enhancements of TLS signals of up to 40 times compared to water, due to more favorable thermo-optical properties (lower thermal conductivity, higher temperature coefficient of refractive index).

The LODs obtained with TLS as detection unit were significantly lower compared to the LODs on a spectophotometer (160 ng/mL) and were 13 ng/mL in ethanol/water and 8 ng/mL in acetonitrile/water. Preliminary results also show that in the mixture acetonitrile/water the formation of indophenol is about three times faster compared to water or other solvents. As a result, the descibed TLS method enables determination of ammonium with sample througputs higher than 1/h while mainaining LODs comparable to existing methods.

Our current work is focused on the incorporation of the novel TLS detection system into a FIA manifold, which is expected to result in further improvement of sample throughput and reliability of amonnium determination.

DETERMINATION OF Co(II) IN PLANT TISSUE BY ION CHROMATOGRAPHY COUPLED WITH LUMINOL/PERBORATE OR LUMINOL/PERCARBONATE CHEMILUMINISCENCE DETECTION.

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Cobalt is a heavy metal that naturally occurs in some serpentine or calcareous soils, but this metal may enter to the agricultural soils trough the application of sewage sludge, farming practices, mining, combustion of fossil fuels and metal working industries. The Co(II), which is essential for the symbiotic N_2 fixation by leguminous plants, is a component of several enzymes and coenzymes that affect the plants growth and metabolism and its quantification is of particular importance for plant scientists and environmentalists. Many analytical procedures such as atomic absorption spectroscopy, inductively coupled plasma, atomic emission spectroscopy or amperometric techniques are available for the determination of Co (II) at trace or ultra trace levels in plant tissues, but these methods require of sophisticated and high cost equipments.

This work proposes a simple, fast, accurate and inexpensive method for the quantification of Co(II) in plant tissue. The method comprises two steps; firstly, 100 mg of the plant material are digested with 2 mL of a nitric acid-hydrogen peroxide solution, using a microwave oven to irradiate during 20 seconds, the resulting clear solution is filtered into a 50 mL volumetric flask. The quantification step was based in the catalytic effect of Co(II) in the oxidation of luminol promoted by sodium perborate or sodium percarbonate, producing the 3-aminophtalate in an electronic excited state which returns to the ground state emitting light at 430 nm. An aliquot of 250 µL of the digested solution is injected to a simplified ionic chromatographic system and the separation of Co(II) from interferences such as Cu(II) or other oxidant species is made using a Dionex CS5A column and oxalic acid as the eluent. A chemiluminiscence (CL) detector connected to a computer was employed to acquire and to process the data by using specific software to integrate the chromatographic peaks of Co(II) at a retention time of 6.1 min.

Two parameters were measured, the peak area and the peak height as indicators for the total and the maximum CL signal respectively. The optimum experimental conditions for the chromatographic separation were 40 mM oxalic acid and an eluent flow rate of 1.5 mL min^{-1}. The concentration and pH of post column reagents also affected the CL emission, obtaining optimum concentrations of 5 mM for oxidant and luminol, this last dissolved in a 0.1 M borate buffer at pH 12. Calibration curves following linear models were obtained in the working range of 0.9 to 6.3 ng mL^{-1}, with detection limits between 0.6 and 1.4 ng mL^{-1}; depending on the type of oxidant and on the CL response employed. Recoveries close to 100 % were obtained in the analysis of the certified reference material GBW 07602. With this method a complete analysis of a plant sample requires less than ten minutes, from the mineralization until the quantification of the heavy metal; also, lesser amounts of the acid mixture for the digestion is needed in relation to the usual digestion techniques, constituting a significant reduction of the environmental impact.

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN REAL SOIL SAMPLES

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Polycyclic aromatic hydrocarbons (PAHs) represent an important group of environmental pollutants with carcinogenic/mutagenic potential of some representatives. These environmental PAHs occurring in atmosphere represent main source of soil contamination.
Microwave extraction is based on microwave action which heats extraction agent surrounding the sample. Microwave energy is nonionising radiation with frequency 300 – 300 000 MHz causing molecular motion by migration of ions and rotation of dipoles. In the electric field the dipoles are coordinated; positive poles are charged in the direction of electric lines of force. In the consequence of these rotations the heat energy is released. The most commonly used extraction agents are organic solvents. The efficiency of extraction depends especially on the temperature and the nature of extraction agent.
The main objective of the presented study was the determination of PAHs levels in soil in the southern Moravia (Czech Republic) representing an important production area. Real samples of soil were sampled by soil pit from six different localities (A, B, C, D, E and F). These samples originated from different regions, e.g. one was sampled directly near frequented road, other came from the outcrop of soil during the construction of a new road; different level of contamination was supposed at these samples.
Soil samples were adjusted by quartation. Before analysis each soil sample was dried for 42 hours at room temperature. Always approx. 1 g of soil was weighed for the experiment. Microwave extraction of soil was performed in the microwave extraction system Multiwave 3000 Solv (Anton Paar, USA) at the following conditions: temperature 120 °C, input 1200 W, extraction time 25 minutes, the ventilator was set to the level one. The extraction agent was the mixture hexane : acetone (1 : 1; 20 ml). The extracts obtained by isolation procedure were always cleaned using column chromatography on silica. The measurement of PAH was performed by high pressure liquid chromatograph using Agilent 1100 Series instrument with DAD and FLD detectors; linear gradient elution was used (0 min: 60 % water and 40 % acetonitrile; 30 min: 100 % acetonitrile; 40 min: 100 % acetonitrile).
The individual PAH content in soil was ranged: A (3.6 – 225.3 mg/kg); B (0.05 – 0.25 mg/kg); C (0.02 – 0.26 mg/kg); D (0.04 – 0.40 mg/kg); E (0.04 – 0.40); F (0.03 – 0.49 mg/kg).

Acknowledgement
This study was supported by the grant given by Ministry of Education, Youth and Sports of the Czech Republic no. MSM 6215712402.

EFFECTS OF RAINWATER SAMPLE PRESERVATION ON DOM PROPERTIES, EVALUATED BY FLUORESCENCE SPECTROSCOPY

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Rain plays an important role in scavenging compounds from the atmosphere where natural organic matter is a significant fraction. The bulk chemical characterization of the dissolved organic matter (DOM) in rainwater in different areas with distinct climate patterns and different levels of contamination is of relevance since rain is the predominant source of all the freshwater and may affect both the terrestrial and aquatic ecosystems. The chromophoric organic constituents are an important subset of rainwater DOM, because they may react with metals and organic pollutants, as well as they may interact with incoming solar radiation, affecting the amount of solar radiation absorbed by the planet and thus affect climate. Molecular fluorescence spectroscopy is an excellent tool for tracing the origin and characterizing the nature of chromophoric DOM and the fluorescence properties of DOM may reveal important features about rainwater composition.

The aim of this work was to evaluate the effects of refrigeration and freezing of rainwater samples on the preservation of DOM original fluorescence characteristics. The effect of temperature during the analysis of fluorescence of rainwater samples was also evaluated. The results showed that the preservation of water samples may affect its fluorescent properties, mainly when labile compounds are present.

ELECTROPHORETIC METHODS (CE AND CEC) FOR THE TRACE ANALYSIS OF BIOLOGICAL SUBSTANCES (STEROIDS AND PROTEINS) IN HUMAN FLUIDS (SERUM, URINE)

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One of the important field of toxicology is the application of capillary electrophoresis (CE) in drug testing (such as anabolic steroids, proteins) of humane samples. CE combines high efficiency, minimum consumption of both reagents and samples, ability to analyze ionic and neutral substances. The disadvantages of CE are unsufficient selectivity and poor concentration sensitivity of UV- detectors, which are the most popular among CE detectors.

To solve the first problem the method of capillary electrochromatography (CEC) with polymethacrylate monolithic capillary column in this work was examined. CEC combines the advantages of CE and HPLC. Porous monolithic support is functionalized (with n-ethylbutylamine) in situ in order to attach ionogenic functions and chromatographic binding sites to the surface. The resulting column was demonstrated in the CEC of proteins (albumin, lisozyme, insulin) at low pH (*e.g.*, pH 2.5). To improve the sensitivity for the trace analysis of steroids and proteins in biological fluids by CE with UV detection was used the on-line preconcentration approaches. The performance of five different on-line preconcentration techniques under acidic conditions, namely normal stacking, stacking with reversed migration micelles, stacking with high conductivity matrix, enhanced sample injection - reversed migration micelles and sweeping for model mixture of steroids by MEKC was examined in terms of their sensitivity enhancement and reproducibility for a group of steroids. Sweeping, using SDS with urea in buffer and neutral β-cyclodextrin (β-CD) in the sample matrix resulted in optimal resolution and focusing in over a 120-fold enhancement in concentration sensitivity (Fig.). Complementary five on-line preconcentration strategies in CZE were investigated for analyzing of albumin in urine by CZE with UV-absorption (214 nm).

With use of the selective on-line focusing strategies in CE have been developed the determination of steroids in biological fluids (serum and urine) by MEKC with on-line concentration (sweeping) with detection limit for about 3 ng/ml (S/N=3) and method for the analysis of proteins in urine using CZE (LOD 10 μg/ml).

This work is supported by grant of Russian foundation for basic research no. 07-03-01001a

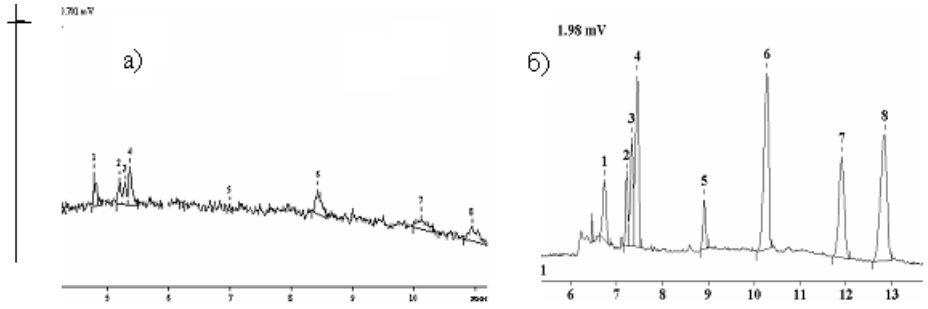

Рис. 2. Electropherograms of MEKC analysis of eight steroids (2,5 μg/ml). Sample matrix: H_3PO_4 with conductivity equal with back ground electrolyte with addition of 5 mM β-CD. Sample injection: (a) 60 mbar·s, (b) 3000 mbar·s. Separation buffer: 25 mM phosphoric acid (pH 2.5), 10 mM SDS, 4.5 M urea; separation field strength: - 25kV.

LIGAND-EXCHANGE CAPILLARY ELECTROPHORESIS POSSIBILITIES FOR ENVIROMENTAL AND FOOD CONTROL

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The possibilities of the ligand-exchange capillary electrophoresis (LECE) method with direct UV-detection for the determination of biologically active compounds, such as sugars (glucose, fructose, sucrose), polyphenols (catechins, gallic acid), biogenic amines (putrescine, cadaverine, sperimidine, spermine), amino acids (alanine, valine etc.), in plants and food products are discussed.

It was shown that the LECE method had the advantages for determination of many natural compounds because it can solve the problem appearing when analytes don't absorb at UV-light (sugars, some amino acids and biogenic amines), decrease the detection limits of compounds with weak chromophoric groups and increase the separation and detection selectivities in analysis of complex natural samples (fruits, tea, honey etc.).

To realize LECE mode salts of transition metals (Cu(II), Ni(II), Co(II) etc.) and NH_3 were added into running electrolyte. Sugars (glucose, fructose, sucrose) which are capable to form absorbing complexes with ions Cu^{2+} became detectable by UV-detector (245 nm).

The migration behavior of an analyte in dynamic complexation CE is determined by the mobility and capacity factor of analyte. The separation mechanism in LECE is based on the interchange between analyte molecules (sugars) and ligand ones (NH_3) in the coordination sphere of a central ion (Cu^{2+}). Resolution is achieved due to the difference in complex stability constants for different analytes with Cu^{2+}.

The advantages of the complex forming processes usage for decreasing of the detection limits of the main plant polyphenols discussed as well.

The results obtained in this report should prove useful in studying the binding procedures of biomolecules in natural samples.

A capillary electrophoresis system "CAPEL 105" ("Lumex" Ltd, St-Petersburg) equipped with a UV-detector was used to separate analytes.

MODELLING OF LIQUID-LIQUID EXTRACTION AND LIQUID MEMBRANE SEPARATION OF ARSENIC SPECIES IN ENVRONMENTAL MATRICES

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Arsenic is a naturally occurring metalloid that has become problematic in many areas in the world. Besides its natural sources, arsenic is introduced into water through anthropogenic activities such as dissolution of mineral ores. Industrial effluents, agricultural activities and atmospheric pollution are other sources responsible for arsenic pollution.

Arsenic is present in a variety of inorganic and organic chemical species in the environment, being the inorganic forms of arsenate [As(V)] and arsenite [As(III)] the most common encountered in groundwater. Due to the long-term toxicological and carcinogenic effects of arsenic, its analytical monitoring represents an important challenge. Moreover, arsenic speciation is of great interest due to the much higher toxicity of As(III).

Liquid extraction in two-phase or three-phase systems is a separation technique that has traditionally been used for separation and preconcentration of analytes for analytical and hydrometallurgical purposes. In this work we have studied the liquid-liquid extraction of inorganic As(III) and As(V) species using an organic phase containing the quaternary ammonium salt Aliquat 336 dissolved in a mixture of dodecane:dodecanol. The efficiency of the system has been evaluated at different pH of the aqueous phase and best results were obtained at pH 13 for both arsenate and arsenite. Extraction has been studied at different arsenic and Aliquat 336 concentrations (ionic strength 0.02 M adjusted with NaCl) and these data have been used for the modelling of the extraction system by both graphical and numerical (LETAGROP) methods. Models which take into account the formation of complexes with 1:2 and 1:3 (arsenic:Aliquat 336) stoichiometry provide the best fit for both As(V) and As(III),.

The implementation of the system in a supported liquid membrane in flat-sheet (FSSLM) configuration has also been tested. The experiments carried out demonstrated that arsenate can be transported through an Aliquat-336-liquid membrane system from an aqueous solutions at pH=13 using HCl 0.1M as acceptor phase The permeability value increased with the carrier concentration until reaching a plateau at an Aliquat-336 concentration of 0.3 M. The influence of the aqueous matrix has been studied using spiked tap water and river water and good results have been obtained in both cases. Experiments undertaken with As(III) solution under similar experimental conditions failed to achieve arsenic transport. In this way As(V) was selectively separated from As(III) when mixtures of both species were used in FSSLM experiments.

Moreover, the designed separation system has been implemented in hollow fifer (HF) configuration. HFSLM are one of the tools which are well suited for both separation and preconcentration purposes. In preliminary experiments, a 6-fold preconcentration of As(V) was obtained.

MODELLING THE ION EXCHANGE OF Fe(III) IN CHLORIDE MEDIA AS THE BASIS TO DESING THE CLEANING OF A FLOOD IMPACTED CHALK ALTARPIECE

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The referred altarpiece is belived to be the original from the North of the transept of Santa María de Orduña church (Biscay, North of Spain). The altarpiece is sculpted over a whitish stone that corresponds to Albula Alba chalk (as revealed by Raman and IR analysis), it was polychromed but nowadays it is fragmented into 9 pieces after ecclesiastical authorities removed it from the original location, at the beginning of the XX century, and stored in the cellar of a Museum located in the Old Town of Bilbao. Since then, the artwork suffered at least two floods that affected to the whole town for several days (the last in 1983). Raman and X-Ray Fluorescence analysis of the altarpiece revealed a poor conservation state; apart from the original pigments detected as scarce remains (namely vermillion, yellow ochre, carbon black, lead white and gold and silver leafts), some kind of contamination was also detected with both solid phases (mainly gypsum as a result of dry/wet acid deposition from CO_2 and SO_x), and soluble species (mainly Cl^-, Fe^{3+}, Na^+ and K^+).

In an attempt to find a soft cleaning procedure to remove the soluble ions, anion exchange was considered because the amount of Chloride in the altarpiece is greater than four times that of Iron. Among different commercially available exchangers, the Dowex M41 anion exchanger (Cl^- form) was experimentally selected, being $FeCl_4^-$ the species responsible for the Fe(III) retention, with an exchange equilibrium constant of $k_{FeCl4-/Cl-}$=269±20.

This information was used to construct a chemical model in terms of components and species (solid and soluble) formed as a consequence of competing heterogeneous equilibria among components. To account for changes in ionic strength, the model uses the Modified Bromley's Methodology (MBM) to estimate activity coefficients and solve the mass balance equations. Thus, simulation of the cleaning processes was accomplished by changing the total concentrations of components trying to find the maximum retention of Fe^{3+} in the anion exchanger.

Once selected, confirmation tests were conducted in the back of three of the 9 current fragments of the altarpiece by applying poultices of 5 cm diameter with the anion exchanger over Japanese paper for restoration. The results showed the quantitative extraction of Fe^{3+} after the application of three poultices. The possibilities of the tested cleaning methodology, first modelling followed by experimental confirmation on selected spots, will be discussed.

Acknowledgements: This work has been funded through the projects PIETRA (ref. UE05-A09, EJ-Basque Government) and INGAPROX (ref. DIPE06/12, Biscay County Government-BFA)

PERSISTENT ORGANIC POLLUTANTS IN WASTE WATERS

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Human activities have negative impact on all environmental compartments including hydrosphere. The main way the pollutants get into the water is through wastewaters. Purity of surface water is influenced by developed industry and agriculture and it cannot be no longer used as water for technical purposes. Moreover polluted surface waters are able to affect sources of drinking water. Apart from surface water, even waster water is very polluted which can threaten the quality treatment before its discharge into rivers. Among significant producers of polluted wastewater belong the industry and agricultural primary production. According to the levels of pollutants, industrial water can be divided into two main groups: waste water predominantly contaminated with organic compounds and waste water predominantly contaminated with inorganic compounds. In the first case (e.g. waste water from food industry) biological purification in an independent industrial waste water treatment plant may be taken into account.

Organochlorine compounds such as polychlorinated biphenyls (PCBs) or selected chlorinated pesticides belong to the persistent organic pollutants (POPs). Despite the fact they were banned from production or strongly restricted in use many years ago these POPs still continue to be found in various samples from the environment.

Tri- (major congener 28), *tetra-* (47), *penta-* (99, 100), *hexa-* (153, 154), *hepta-* (183) and *deka-*(209) are the most commonly used PBDE compounds which also occur most frequently in the environment. PBDEs are lipophilic and persistent substances that show low solubility in water. Because of their high resistance against acids, bases, heat, light, and redox reactions, they pose a marked risk to the environment. When they enter the environment, they remain there for a prolonged period of time due to their properties. The octanol/water distribution coefficient (log K_{ow}) is another important characteristic of these compounds. The values of their log K_{ow} vary in a range of 5.98 (28) – 9.97 (209), which indicates that the substances are highly hydrophobic.

Some polycyclic aromatic hydrocarbons (PAHs), particularly those with a high molecular weight, have been classified as probably carcinogens to humans by the International Agency for Research on Cancer (IARC). Were detected in waste water, too.

For determination of these analytes separation methods were used, GC/MS, GC/ECD and HPLC/DAD. Most of organochlorine compounds, PBDE and PAHs were determined in waste water from the Waste Water Treatment Plant at University of Veterinary Medicine and Pharmaceutical Science Brno.

Acknowledgement: This study was supported by the Project OC-83, COST Action 636 and by the grant given by Ministry of Education, Youth and Sports of the Czech Republic no. MSM 6215712402

POLYCYCLIC AROMATIC HYDROCARBONS IN SMOKED SALAMI "POLIČAN"

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Some polycyclic aromatic hydrocarbons (PAHs), particularly those with higher molecular weight, have been classified as probably carcinogens to humans by the International Agency for Research on Cancer (IARC). The significance of the determination of PAHs is reflected by the special attention of the European Union, which is paying to regulate the maximum allowed levels of PAHs in foodstuffs such as smoked foods. The maximum levels have been recently set by European Commission on B[*a*] P for smoked meat products on 5 μg kg^{-1}.

Our study was focused on the monitoring of PAH levels in smoked salami. Samples were taken from company KMOTR-Masna Kroměříž a.s. The production of dry fermented sausages (Poličan, Paprikáš) consists of several steps. The last step is smoking and ripening in conditioned smoke rooms under controlled conditions (temperature, humidity, wind speed) during one month. In the production facility three types of smoking rooms are available. At the beginning of ripening period passive samplers of SPMD type were placed in one of each type of smoke rooms. Salamis of "Poličan" type were sampled at the beginning, after one week and one month after the end of smoking (before expedition of the finished product). 160 of salami samples were taken within this study, 40 SPMDs were exposed.

Homogenized salami samples were dried by sodium sulphate anhydride and extracted using Soxtec extractor for 6 hours with n-hexane. Approx. 0.5 g of extracted fat was dissolved in $CHCl_3$ and cleaned-up by GPC on Bio-Beads S-X3. PAHs fraction was solvent-exchanged using keeper to acetonitrile (for HPLC) or n-hexane (for GC/MS).
Exposed SPMDs were dialyzed in n-hexane (2 x 24 h), dialysate was concentrated using rotary evaporator. The concentrate was treated by the same method as the extracted lipid.

The obtained results enabled to estimate the influence of various types of smoke rooms on the content of PAHs in the final product.

Acknowledgement:
This study was supported by the grant given by Ministry of Education, Youth and Sports of the Czech Republic no. MSM 6215712402.

PROPOSAL OF A SIMPLE SCREENING METHOD FOR A RAPID EVALUATION OF METALS MOBILITY IN CONTAMINATED SOILS

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The environmental impact of the contamination of soils by toxicologically relevant metals not only depends on the total concentration, but mostly on the form in which metals occur, their mobility and, consequently, bioavailability. Risks become relevant in the following cases:
- medium/high levels of concentration and high mobility; but also
- very high levels of concentration and moderate mobility.

Many extraction procedures have been developed to evaluate "heavy metals" mobility in contaminated soils, but they are generally time consuming (especially the sequential extraction procedures-SEP) and, consequently, applicable on a limited number of samples. The proposal of a simple in-field screening method is based on the foregoing considerations. This method was developed and applied on soil samples collected from rural, urban and mining areas and representing different situation of soil contamination.

A buffer solution of trisodium citrate and hydroxylamine hydrochloride was used as extractant for a single-step leaching test. The choice of this buffered solution was strictly related to the possibility of directly determining, via titration with dithizone, the content of Zn, Cu, Pb and Cd, which are among the most representative contaminants in highly mineralised soils. Moreover the extraction solution is similar, unless for the pH value, to the one used in the BCR SEP second step. However, the effect of several parameters (pH of the extractant, L/S ratio, time…) was studied.

The analysis of bivalents ions through dithizone titration was exploited in order to further simplify and quicken the whole procedure. The proposed method measures, in few minutes, generically the concentration of total "heavy metals" expressed as mol/L without distinguishing between elements: 1mL of Dithizone ≈ 3 nmol of M^{++}(Zn, Cd, Cu and Pb).

The "analytical performance" obtainable by dithizone titration was tested operating a leaching test and measuring the metal concentrations (sum of Zn, Cu, Pb and Cd) in the leachates both with dithizone titration and ICP-OES. Results were in good agreement.

The proposed rapid in-field screening method gave a useful information, in substantial agreement with the analyses of the total concentration of the metals and the BCR procedure.

Moreover, the kinetical approach evidenced that it can be possible to have a useful preliminary evaluation of "heavy metals" mobility in almost 30 minutes, suggesting a possible application of this screening method for in-field tests.

QUICK ASSESSMENT FOR METAL CONTAMINATION IN FORMER VINEYARD SOILS USING PORTABLE X-RAY FLUORESCENCE AND SINGLE EXTRACTION PROCEDURES.

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Repeated cooper-based fungicides application (Bourdeaux mixture) to former vineyards creates an important pollution source that requires a quick assessment in terms of available copper content in many soils of the Mediterranean region. Despite agricultural practices were abandoned 28 years ago, noticeable amounts of copper (70-128 $mg \cdot kg^{-1}$), arsenic (10-24 $mg \cdot kg^{-1}$), lead (20-70 $mg \cdot kg^{-1}$) and zinc (64-111 $mg \cdot kg^{-1}$) are observed in a former vineyard area in Catalunya, NE, Spain, rising above regional governmental limits for soil ecosystem protection. An initial estimation suggests a continuous application, up to 3 to 5 times each year of 3 to 5 kg ha^{-1} of Cu for each Bordeaux treatment, depending on the rainfall regime and plants infection degree. Portable X-ray fluorescence combined with single leaching test, using HCl, were applied to soil samples to provide first hand information useful for fast and detailed risk assessment, in terms of mobility and possible bioavailability of pollutants.

In this study, 48 soil cores regularly distributed were collected at 0-5 cm depth in a former vineyard area of 3000 m^2. Adittionally, 3 background samples were collected at a depth profile of 60 and 80 cm depth. This soil was developed on a calcareous, non consolidated, sediments. About 0.35 kg of each soil sample was collected and mixed thoroughly, being stored in a sealed coded plastic bag in order to transfer them to the laboratory and determine soil parameters, such as organic matter and moisture content as well leaching tests. Samples were dried at 105ºC during 24 h and were passed through a 2 mm stainless steel sieve to remove coarse particles and homogenised by quartering with a riffler. The resulting subsamples were grinded and sieved below 100 μm. Three different measurements batches using FP-XRF were performed, in-situ, after drying, and finally after sieving and grinding the samples, in order to evaluate the moisture and particle size effect.

Furthermore, complementary reliable information was obtained by considering the variation of metals concentration within the different geological substrates. In this sense, an evaluation by concentration enrichment ratios (CERs) using both, total and available copper concentrations let to better establish anthropogenic contribution to the site contamination. CERs were calculated considering the concentration of a given element, in both target and background sample, normalized with respect to a lithogenic conservative element such as, Ti or Zr. The selected lithogenic element was characterized by an accurate and precise determination, a reduced anthropogenic contribution compared with its natural occurrence as well its resistance to the weathering processes.

SIMPLE AND LOW-COST ATOMIC ABSORPTION SPECTROMETRY METHODS FOR DETERMINATION OF SOME PRIORITY SUBSTANCES IN SEA WATER

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The European Water Framework Directive (WFD) 2000/60/EC [1] is probably the most significant international legislative measure to be introduced in the field of water for many years. The Directive aims to achieve and ensure "good quality" status of all water bodies throughout Europe by 2015. The European Parliament and Council adopted Decision No. 2455/2001/EC [2] establishing the list of priority substances that present a significant risk to the aquatic environment. For this reason, analytical methods are required for the routine determination of a large number of such compounds in trace concentrations in water samples.

In this study some of these substances (total Chromium, Chromium VI, Lead, Nichel, Mercury, Cadmium) were determined in sea water, with simple and low-cost atomic absorption spectrometry methods. Because of complexity of matrix and low concentrations of contaminants, separation and preconcentration was necessary for the trace metal analyses.

There are several techniques, including co-precipitation, chelate solvent extraction, chelating ion exchange resins and electrolysis for the preconcentration of trace metals. Solvent extraction is of great value in the trace metal preconcentration as it is simple, rapid, easy to manipulate, eliminates matrix effects and provides matrix normalisation for samples.

The proposed method for Cr VI, Pb, Ni, Hg and Cd used ammonium pyrrolidinedithiocarbamate (APDC) as chelating agent; total Cr determination was made with oxidation of Cr III to Cr VI by $Fe(OH)_2$ and successive instrumental detection. All metals were determinated with GF-AAS, only mercury was determinated with Direct Mercury Analyzer (DMA-80).

The precision of the whole procedure was evaluated by repeating three analysis per day, in three different consecutive days . Analysis of variance (ANOVA) of the results indicates the within-day and the between day precision are statistically comparable ($F_{calculated} < F_{critical}$) for all samples.

LOQ were always lower than the values prescribed by the Proposal (Brussels, 21 September 2007) for the Directive on environmental quality standards in the field of water policy and emending Directive 2000/60/EC [3].

[1] European Commission, Off. J. Eur. Commun. L327 (2000) 1.
[2] European Commission, Off. J. Eur. Commun. L331 (2001) 1.
[3] ENV 473, CODEC 966

TRACE ELEMENTS IN MOSS BAGS: INFLUENCE OF EXPOSURE TIME ON MOSS ACCUMULATION CAPACITY

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Samples of the moss *Sphagnum girgensohnii* Rusow were exposed in bags for 15 days to 5 months in the urban area of Belgrade (Serbia) from July to November, 2007. Different treatments, with and without irrigation, were applied to the exposed moss. The concentrations of 66 trace elements were determined by ICP-MS and the accumulation capacity of the elements during exposure in the wet and dry moss bags was compared during 15-day periods. The contents of some elements increased with time in both dry and wet moss bags, *i.e.* Al, V, Cr, Fe, Ni, Cu, Zn, As, Se, Sr, Pb, Sm, whereas Na, Cl, K, Mn, Rb, Cs, and Ta were depleted. Irrigation of moss resulted in higher accumulation capacity for most of the elements, especially for Cr, Ni, Cu, Zn, As, Se, Br, Sr, and Sb. Principal Component Analysis with Varimax rotation was performed on the dataset of element concentrations in wet and dry moss bags for source identification. The factor arrangement for both indicators was similar but not identical due to the differences in element accumulation mechanisms. Five rotated factor loadings with eigenvalues >1 explained about 70% of total variance for dry and wet moss bags. The first factor, explaining most of the variance (about 40%), can be attributed to mixed urban aerosol mostly representing road dust resuspension, which includes soil dust mixed with traffic related particles. Some other factors can be related to local pollution sources.

VIRTUAL INSTRUMENT FOR THE MONITORING OF METAL BIOSORPTION PROCESSES

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Aim of our research is the valorization of vegetable residues coming from industrial processes as biosorbents for metal ion elimination. Different vegetable wastes as grape stalks coming from the wine production have been used for the elimination and recovery of divalent metals as well as chromium in their trivalent and hexavalent forms present in aqueous solutions. These studies have been carried out at laboratory scale, in continuous methodology, by using packed columns filled with the biomaterial and being the aqueous metal solution pumped upward through the column. Up to now, samples were collected from the column outlet during days or weeks and metal concentration was analyzed at the end of the experiment by FAAS. Frequently, this procedure resulted in not-completed or over-time experiments and not-well defined breakthrough curves. For this reason, a real-time automatic monitoring system based on potentiometric chemical sensors is proposed in the present work.

The automatic system for the biosorption on-line monitoring is formed by a PC, a data acquisition card, a signal conditioning interface, the chemical sensors, peristaltic pumps, solenoid valves, connecting tubes and the Virtual Instrument. Sensors are connected to the analog input of the acquisition card through a high-impedance front-end interface, allowing for the use of up to sixteen sensors. Virtual Instrumentation is the use of customizable software and modular data acquisition hardware to create tailored measurement systems according to the user interest. Virtual Instrumentation manages PC hardware and other devices (i.e multifunction DAQ cards, instruments) by means of the computer bus (serial RS-232, GPIB, parallel, USB ports, etc.), performing measurements like a real instrument.

In this work, we present a family of three Virtual Instruments, developed under the LabVIEW environment. The first one is for study and characterization of Ion Selective Electrodes and permits multicalibration of chemical sensors to be used in the on-line monitoring system. Two other Virtual Instruments are for different control options: one permits the manual control of all the components (valves, pumps, sensor channels ...) and the other, for long-term experiments, controls all the components automatically in a pre-set order fixed by the user. Moreover, the developed Virtual Instruments let to store, process and analyze the information, displaying on the screen the user's preferences. In conclusion, Virtual Instrumentation is an integrated choice for the automatic monitoring of biosorption processes, resulting in a single, user-friendly, reliable and expandable instrument.

Acknowledgements: This work was supported by the Ministerio de Educación y Ciencia, Spain, project CTM2005-07342-CO2-02.

APPROACH TO THE CHEMICAL SPECIATION OF CD, CU, PB AND ZN IN AN ANIONIC SURFACTANT-SOIL SYSTEM WITH GEOCHEM.

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At present, it is widely recognized that the distribution, mobility and bioavailability of heavy metals in soil depend not only on their total content but also on the sequestered metals solid phase, on the kind and strength of the bond and on the properties of the solution in contact with the solid particles. Concerning the last aspect, surfactants, that may reach the soil-water systems due to several sources (i.e. pesticides formulations, wastewater irrigation, sewage sludge disposal), cause some variations of the chemical properties of the soil solution modifiying to some extent the release of metals to groundwater, thus causing contamination. Previous studies confirmed that anionic ones, particularly Aerosol 22, can solubilise soil metals increasing their environmental risk. Knowledge of metal speciation in soil pore waters is important in addressing metal bioavailability and risk assessment of contaminated soils.

The aim of this work was, therefore, to describe and predict the chemical forms of Cd, Cu, Pb and Zn in soils treated with Aerosol 22 (named A22). Batch assays were carried out with a contaminated soil and aqueous solutions of A22 in a range of concentrations 5-40 mM at solution:soil ratio of 10 L/kg. Enhance of concentration in solution was observed for the four metals assayed with increasing surfactant concentrations, up to ten times for Zn. The equilibrium speciation program GEOCHEM was applied to predict the speciation of Cd, Cu, Zn, Pb in presence of A22. Speciation here refers to chemical fractionation (organic complexes, inorganic complexes, free metal ions) Oxalate was chosen as a representative ligand for A22, because of its more adequate resemblance with the dicarboxy-ethyl group of the cited surfactant.

Results of the speciation approximation pointed out to main role of A22 as a metal complexing-ligand. Cadmium, Cu and Zn in solution are complexated with the surfactant up to 90% at any A22 concentration, while in control solution (MQ water) they were mainly as free ions (Cd, Zn) or hidroxides (Cu). Despite that the presence of surfactant increased also the concentration of Pb in solution, GEOCHEM predicted around 75% of Pb^{2+} and the rest of $Pb(OH)^{-}$ as in control assays. These preliminary results suggested that metal fractions sequestred by A22 will probably mobilise from soil. Additionally, other processes, such as solubilization of organic matter together with metals bound to it, may be also responsible for the increasing extracted metal provided by A22.

COMPOSITIONAL VARIATIONS OF OIL POLLUTANT IN SHORT DISTANCE VERTICAL AND LATERAL PROFILE OF ALLUVIAL SEDIMENTS

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The composition of an oil pollutant in alluvial sediments is a result of combined effects of physical weathering, biodegradation and migrational fractionation. It is well known that these processes over large distances can result in significant compositional changes of oil pollutants.
The objectives of this study were to evaluate compositional variations of an oil pollutant in short distance vertical and lateral profile of alluvial sediments.
Sediment samples from the alluvial formation of the Danube River were investigated. The samples were taken at different depths (from 1.10 to 3.5 m) from six boreholes at regular distance of 10 m within the Pančevo Oil Refinery, Northern Serbia.
Conventional ***Soxhlet extraction*** was applied to ***extract*** organic substance from the ***sediment samples. The extracts were fractionated by column chromatography into*** saturated, aromatic and NSO fractions. Gas chromatography-mass spectrometry was used to analyze n-alkanes (m/z = 71), isoprenoids (m/z = 183), terpanes (m/z = 191) and steranes and diasteranes (m/z = 217).
As expected, the shallowest samples from all boreholes contained a similar mixture of an oil pollutant and native organic matter.
In the vertical profile investigated the most irregular alteration was observed in the fraction of *n*-alkanes and isoprenoids, resulting in significant lateral variations in distribution of these compounds. Some boreholes were characterized by gradual lost of longer homologues with increasing depth and, at same time, by an increase in the relative abundance of shorter ones. In one borehole gradual lost of shorter homologues and an increase in the relative abundance of longer ones with increasing depth were observed. In other boreholes *n*-alkanes were completely lost at the depth of 3 m.
Small and irregular differences in the sterane distributions in samples from different depths were observed. GC-MS analysis revealed that vertical distance as short as 1-2 meters could result in significant increase in relative abundances of C_{23} and C_{24} tricyclic terpanes relative to pentacyclic terpanes while distributions of pentacyclic terpanes were almost unchanged.
According to these results it can be concluded that short distance (vertical and lateral) in alluvial sediments can result in significant compositional difference of oil pollutant. The most prominent differences could be observed in the distribution of *n*-alkanes and isoprenoids. On the other hand, distribution of pentacyclic terpanes remained almost unchanged, making them the most reliable parameters in characterization of oil pollutant over short distances in alluvial sediments.

Acknowledgments We thank Dr Hermann Wehner (retired professor at Federal Institute for Geosciences and Natural Resources, Hannover, Germany) for conducted GC-MS analyses, and the Alexander von Humboldt Foundation and the Ministry of Science and Technological Development of the Republic of Serbia for supporting this research.

POISONOUS METALS IN VEGETABLES GREW IN URBAN AREAS

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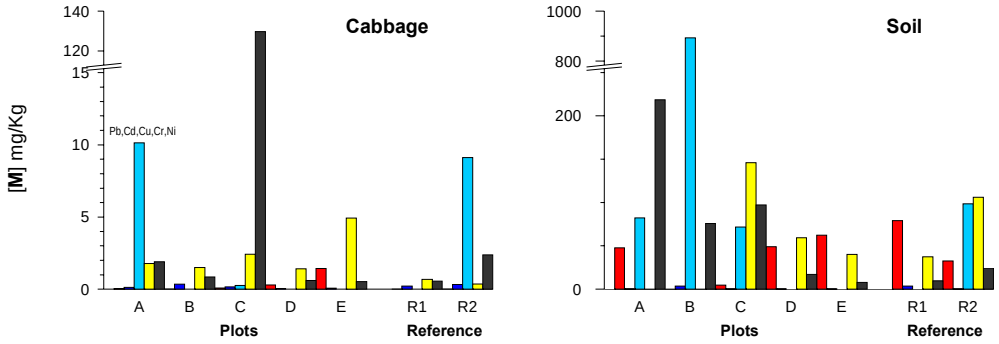
Nowadays in Lisbon city is frequent to verify the existence of small areas of agricultural exploration (vegetable gardens) in the shelving of roads with high automobile traffic intensity. In these small vegetable gardens a significant variety of species is cultivated for consuming and is usually explored by population with weak economical resources, namelly emigrants and aged retired people. These people think they are consuming healthy products, free from any chemical agents, when in reality the levels of poisonous metals and other pollutants can represent a risk [1,2]. Same countries like Portugal, Spain, UK, France, Nederlands have official programs of social vegetable gardens in several cities. The main objectives of these programs are to increment the consume of vegetables by the population whereas helplessness terrains are used.
In this work we analize the most comun vegetable present in the vegetable plots in Lisbon: the gallician cabbage (*brassica oleracea*). Wa have analised five plots near the principal traffic routes of access to Lisbon and in each plot we have grab, from 25 diferent plants, the major leaf of each. In the same plot the soils are also analysed. For the gathering of three samples of soil in each plot, and in a random way, a plastic tube with 4 cm of diameter and 25 cm deep are used. The samples after proper treatment were digested with *Suprapur* acids from Merck in a microwave digestion system from CEM. The contend of metals in the samples were determined by GFAAS (Graphite Furnace Atomic Absorption Spectrometry) using a spectrometer Thermo, model Solaar.
The results of metal contend in cabbage and soils are shown in the figure below.



The values obtained are below the maximum defined in the Codex Alimentarius but some are much closed to the recommended maximum. Therefore the exploration of vegetable gardens in urban areas, near roads with intensive car traffic [3], needs to be controlled periodically to preserve the health of their consumers.

[1] K. Ravindra, L. Bencs, R.V. Grieken - *Sci. Total Environ.* **318** (2004) 1.
[2] R. Nataf, C. Skorupka, L. Amet, A. Lam, A. Springbett, R. Lathe - *Toxicol. Appl. Pharm.* **214** (2006) 99.
[3] G. Mercier, J. Duchesne, A.C. Gibergues - *Environ. Pollution* **118** (2002) 285

CONTROLLED-RELEASE FORMULATIONS OF CHLORIDAZON-LIGNIN MATRIX COATED WITH ETHYLCELLULOSE

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The aims of controlled release (CR) formulations of pesticides are to protect the supply of agents, to allow the release of these agents to the target at a controlled rate, and to maintain its concentration in the system within the optimum limits, over a specified period of time, thereby providing great specificity and persistence. In this research lignin (L), a low-cost waste product in the paper pulp manufacturing, and ethylcellulose (EC), one of the most widely-used polymers in film coating have been used for the preparation of CR formulations of chloridazon (CH). The lignin matrixes were prepared by mixing technical grade chloridazon with kraft lignin (CHL) under melting conditions. They were also crushed and sieved to obtain granules of size between 0-0.2mm, 0.2-0.5mm, 0.5-1mm, 1-2mm and 2-3mm. The coated chloridazon-lignin granules were produced in a Wurster-type fluidized-bed equipment, using an ethanolic solution of EC on two different polymer levels. That of the highest level in EC was modified by the addition of dibutyl sebacate (DBS) as a plasticizer.

Having researched encapsulation efficiency and the homogeneity of the CR formulations, kinetic-release experiments were therefore carried out in water. A high encapsulation efficiency was reached, it oscillated between 94.84% for the 0,2mm<d<1mm CHL system and nearly 100% for the system coated with 20% of EC plus DBS. The rate of chloridazon release from CR granules diminished in all cases in relation to non-formulated chloridazon, being the latter completely dissolved in less than 10 h, but it took at least 62 days to release approximately the 82% of chloridazon from the EC coated formulation modified with DBS.

Using an empirical equation, the time taken for 50% of the active ingredient to be released in water (T_{50}) was calculated. From the analysis of T_{50} values, we can deduce that the release rate of chloridazon can be controlled by selecting the granule size for lignin CR systems and changing the thickness of the coating film and using a plasticizer as well for EC coated granules.

GEOCHEMICAL INVESTIGATION OF RECENT ALLUVIAL SEDIMENT

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The research area, the Makiš plain near Belgrade, is a part of the Sava river alluvion of Quaternary age. Makiš alluvion has a rather complex lithologic structure, showing frequent changes of lithologic members (sandy, silty and clay sediments) with depth. Generally, sandy and clay sediments have many differing physical and chemical characteristics, and consequently represent widely different environments in a geo- and eco-chemical sense. These differences are reflected by their permeability to water and gases, sorption and ion exchange characteristics, redox potential and microbial activity. All this causes a certain degree of selectivity in accumulation and transformation of organic and inorganic substances, which arrive to such environments.
Eighteen samples (9 clays and 9 sands) from different depths of 7 research boreholes were investigated.
The aim of this paper was to investigate the origin, accumulation and transformation of dissolved organic matter and inorganic component in analysed sediments. Inorganic part were investigated by granulometrical and mineralogical analysis, dissolved organic matter by gas chromatography/mass spectroscopy analysis.
The results obtained demonstrated presence of ancient organic substance, unusually for recent sediments. The total hydrocarbon concentrations, as well as abundance and distributions of *n*-alkanes, steranes, terpanes and the other evaluation indices suggest that some samples contain the mixture of ancient and recent organic matter. Anthropogenic hydrocarbons are not related to distance of sampling sites from potential pollution sources (freight-train station and surrounding agricultural fields). Their presence was found to be depended of physical and mineralogical structures of the analysed sediments.

NATURAL PHOSPHATE IN CATALYTIC OXIDATION OF ALCOHOLS WITH MOLECULAR OXYGEN

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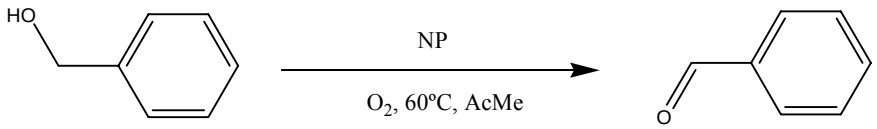
Natural phosphate such as Ca10(PO4)6-x(CO3)x(OH, F)2+x (0,39 □x□1,36), denoted NP, have found many applications in catalysis [1].The natural phosphate (NP) has advantages in that it is cheap, readily available, nontoxic, not pollutant, easily recovered and repeatedly used.
Oxidation of alcohols to the corresponding aldehydes and ketones is a fundamental transformation and widely used in organic synthesis. Traditionally, stoichiometric inorganic oxidants represented by Cr(VI) reagents and DMSO oxidations have been successfully applied for this reaction [2]. However, these methods are unavoidably associated with unpleasant waste materials, which limits their synthetic value. From the viewpoints of environmentally benignity and atom-economy, catalytic methods utilizing clean oxidants such as molecular oxygen (O2) and hydrogen peroxide (H2O2) are highly desirable [3]. In particular, O2 is an ideal oxidant because it is ubiquitous and safe. It is further advantageous that the byproduct in oxidation with O2 is basically non-toxic H2O or H2O2.
In this work, we report on the synthetic utility of the reaction catalysed by robust oxidation-resistant compounds like NP, and present a general route for the selective oxidation of alcohols to the corresponding carbonyl compounds .
Using benzyl alcohol and NP as catalyst precursor, the reaction was carried out in acetonitrile at 60 °C.



The use of NP as heterogeneous catalyst was then applied successfully for the aerobic oxidation of various types of alcohols including cyclic alcohols and primary aliphatic alcohols.
The present study has proved that the oxidation of alcohols to carbonyl coumponds catalysed by natural phosphate and dioxygen could replace stoichiometric polluting reagents either for large-scale products or for fine chemicals synthesis.

[1] (a) Bazi, F.; El Badaoui, H.; Tamani, S.; Sokori, S.; Solhy, A.; Macquarrie, D.J.; Sebti, S. *Appl. Catal. A,* **2006**, 301, p211, (b) Dakkach, M.; Allouni Z.; Atlamsani, A.; Sebti, S..*Proceedings of Covaphos II*, **2006**, Vol 4, p59.
[2] (a) Ley, S.V.; Madin, A. In Comprehensive Organic Synthesis; Trost, B.M.; Fleming, I.; Ley, S.V.; Eds.; Pergamon Press:Oxford, **1992**, Vol. 7. p 251. (b) Lee, T.V. In Comprehensive Organic Synthesis; Trost, B.M.; Fleming, I.; Ley, S.V. Eds.; Pergamon Press: Oxford, **1992**, Oxidation, Vol. 7. p 291. (c) Procter, G. In Comprehensive Organic Synthesis; Trost, B.M.; Fleming, I.; Ley, S.V. Eds.; Pergamon Press: Oxford, **1992**, Vol. 7. p 305.
[3] Sheldon, R.A.; Arends, I.W.C.E. In Advances in Catalytic Activation of Dioxygen by Metal Complexes; Simandi, L.I. Ed.; Kluwer Academic Pub: Dordrecht, **2003**, p 123.

WO_x/ZrO_2 ACIDIC CATALYSTS FOR BIODIESEL PRODUCTION

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Biodiesel is a clean fuel source which is viewed as a viable alternative for dwindling petroleum-based diesel resources. It is made from renewable resources, is biodegradable and non-toxic and has a higher flash point than normal diesel. Though considerable literature exists on the esterification of simple aliphatic and aromatic acids by various solid acid catalysts such as zeolites and resins there are only a few reports on fatty acid esterification and even less using acid oxides.
For these reasons, in the present work, we studied the preparation and characterization of W-based oxide catalysts for the esterification and transesterification of free fatty acids.
One series of tungstated zirconia (WO_3/ZrO_2) has been prepared by a classical incipient wetness impregnation of sodium tungstate solution varying the tungsten oxide loading in the range 0.5-20 wt%. After the impregnation, the sample were dried at room temperature overnight and then calcined in flowing air for 4h at 450 °C.
The textural properties of samples have been characterized by nitrogen adsorption and desorption isotherms at 77 K in order to get the surface area and pore volume; X-ray powder diffraction (XRD) patterns to check any formation of WO_3 microcrystallites or WO_3-like phase and evaluate the dispersion and at what W loading a crystalline WO_3 phase will begin to appear and XPS for the proportion and oxidation state of the surface species. Temperature-programmed reduction (H_2-TPR) under 5% H_2/Ar flow in the range of temperature from 423 to 1273 K and further re-oxidation in 1 % O_2/He flow were used in order to measure the interaction between tungsten oxide species and supports (metal-support interaction).
The acid-base properties of the supports and catalysts have been evaluated by ammonia adsorption microcalorimetry, providing information on the number, strength and strength distribution of acidic sites (as reported in the figure).
A clear and valuable map of the supported tungsten oxide catalysts surface and molecular/electronic structure-surface acidity relationships were established. Moreover the activity for esterification reaction was tested and correlated with the surface data.

URBAN SURFACE RUNOFF POLLUTANTS AND THEIR IMPACT ON AQUATIC ENVIRONMENT

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In many countries urban surface runoff is proved to have a significant effect on aquatic systems, but in Finland research on its quality is still quite limited, especially studies on organic pollutants. Finnish law does not demand cleaning of the surface runoff and there are no limits set on its purity. Therefore, study on the runoff quality and fate is necessary in order to estimate how it impacts surrounding aquatic habitat and possibly link environmental pollutant concentrations to the urban sources.

Lahti is a middle-sized Finnish city and most of its surface runoff discharge is directed to adjacent Lake Vesijärvi. Main part of discharge is generated from few large urban watersheds (altogether approximately 350 ha), from where surface runoff water is collected with a sewer network. The outlets of two major watersheds are located in the bottom of sheltered bay. The other route to the Lake Vesijärvi is an urban stream, River Joutjoki (1200 ha catchment area), which collects both stormwater and runoff water from a snow dumping site. The objective of this study was to develop a fate model, which describes how organic pollutants in surface runoff from Lahti urban area are carried along to the Lake Vesijärvi and how they impact lake ecosystem.

For this purpose concentrations of organic pollutants (including PCB- and PAH-compounds) were determined in the runoff and lake sediment in the vicinity of urban surface runoff outlets. Gradient sampling methodology was implemented in order to trace the changes in pollutants' concentrations while they enter the lake, disperse in its body and are adsorbed to the sediment. Grab sediment samples were taken from different distances of stormwater drainage system outlet in Lake Vesijärvi. The samples were analyzed for PAHs and PCBs with GC-MS. Both PAH and PCB concentrations in sediments were found to be elevated near the urban shores, which might be due to the surface runoff impact.

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