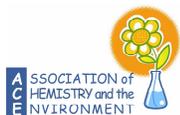


a conference co-organised by
the **University of Geneva** and
the **Swiss Federal Institute of Technology, Lausanne**
under the aegis of
the **European Association of Chemistry and the Environment**

BOOK OF ABSTRACTS



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PREVIOUS AND FORTHCOMING EDITIONS OF EMEC

PREVIOUS CONFERENCES

The CD-ROMs of the first and second editions of EMEC can be purchased via the ACE web site at <http://www.u-bourgogne.fr/ACE>

2000 - 1st EUROPEAN MEETING ON ENVIRONMENTAL CHEMISTRY

Nancy, France
38 oral presentations, 142 posters

Main sessions topics:

- Fossil Fuels
- Pesticides, Chlorinated Pollutants
- Toxic Metals
- Greenhouse Gases
- Water and Air Pollution
- Environmental Analytical Chemistry
- Stable Isotopes

2001 - 2nd EUROPEAN MEETING ON ENVIRONMENTAL CHEMISTRY

Dijon, France
74 oral presentations, 161 posters

Main sessions topics:

- Green Chemistry
- Air Pollution - Organic Pollutants, Toxic Metals
- Water and Food Pollution - Organic Pollutants, Toxic Metals
- Soil and Sediment Pollution - Organic Pollutants, Toxic Metals
- Stable Isotopes for Environmental Science
- Ecotoxicology
- Environmental Analytical Chemistry

FORTHCOMING CONFERENCES

2003 - 4th EUROPEAN MEETING ON ENVIRONMENTAL CHEMISTRY

December 10-13, 2003
Plymouth, United Kingdom

Contact:

Dr Mark Fitzsimons
Department of Environmental Sciences, University of Plymouth, Plymouth PL4 8AA, United Kingdom
mfitzsimons@plymouth.ac.uk
<http://www.science.plym.ac.uk/departments/environmental/>

2004 - 5th EUROPEAN MEETING ON ENVIRONMENTAL CHEMISTRY

December 2004
Bari, Italy

Contact:

Dr Michele Aresta
METEA Research Center, University of Bari, via Celso Ulpiani 27, 70126 Bari, Italy
aresta@metea.uniba.it

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Jan Schwarzbauer Aachen University of Technology, Germany

PROGRAMME

Wednesday, December 11

-
- 17:00- **Registration**
Welcome reception at Uni Dufour (24, rue du Général Dufour)
-

Thursday, December 12

-
- 07:45- **Registration; Poster set-up**
-
- 08:00- **Conference opening**
Welcome allocation by Robert Cramer, Minister of the environment, Geneva
-
- 08:30- **Boutron C.F.** **Invited Lecture: Heavy metals in snow and ice cores dated from the antiquity, the post industrial revolution period and the last climatic cycles**

ORAL SESSION 1 TRACKING POLLUTION ORIGIN AND SOURCES

Chaired by C.F. Boutron (University Joseph Fournier, France) and E. Lichtfouse (University of Burgundy, France)

-
- 09:10- **Belt S.T.** Characterisation of unusual hydrocarbon biomarkers from diatoms
-
- 09:30- **Macias-Zamora J.V.** Potential use of LAB's specific compound's isotopic ratios (¹³C/¹²C) to trace point sources of municipal wastewater in SCB
-
- 09:50- **Kronimus A.** Organic containments as anthropogenic marker compounds in sediments of the Lippe River, Germany
-
- 10:10- **Lebedev A.T.** Pollution of the North Caspian Sea with organic compounds

-
- 10:30- **Coffee-break in the poster and commercial exhibition hall**

ORAL SESSION 2 BEHAVING AFTER POLLUTION: SITE REMEDIATION

Chaired by W. Giger (EAWAG, Switzerland) and R. Helmer (WHO/OMS, Switzerland)

-
- 11:00- **Tarr M.A.** Enhanced Fenton based remediation using ternary pollutant-cyclodextrin-iron complexes
-
- 11:20- **Safi N.M.D.** Biodegradation of polycyclic aromatic petroleum compounds by cyanobacterial mats in mesocosm experiments in Gaza (Palestine)
-
- 11:40- **Chan M.S.M.** Photocatalytic degradation of aqueous MTBE in a supported-catalyst reactor
-
- 12:00- **Karg F.P.M.** Microbial & biochemical techniques to evaluate and to implement in-situ biodegradation potential and activity at sites contaminated with aromatic and chlorinated hydrocarbons
-
- 12:20- **Al-Najar H.** Techniques to enhance phytoextraction of thallium from a contaminated soil
-
- 12:40- **Mameri N.** Economic study of groundwater defluoridation of the North African Sahara

-
- 13:00- **Lunch on own; Poster session; Commercial exhibition**

ORAL SESSION 3 ECOTOXICOLOGY

Chaired by M. Koudelka (University of Neuchâtel, Switzerland) and C. Mougín (INRA, France)

-
- 15:00- **Odzak N.** Bioavailability of trace metals in saline waters: field experiments
-
- 15:20- **Meylan S.** Intracellularly accumulated and adsorbed metals on a natural biofilm
-
- 15:40- **Gourlay C.** The influence of non-humic dissolved organic matters and their biodegradation by-products on the bioavailability of benzo[a]pyrene
-
- 16:00- **Kawano T.** Effect of a sulfonylureic herbicide and reactive oxygen species on euglenoid movements in *Euglena gracilis*
-
- 16:20- **Coffee-break in the poster and commercial exhibition hall**
-
- 16:50- **Mougín C.** Fungal laccases: From structure-activity studies to environmental applications
-

17:10-	Gu M.B.	Stress specific functional cDNA microarray of Japanese Medaka fish for environmental stress analysis
17:30-	Temussi F.	Photochemical and eco-toxicological studies on corticosteroids
17:50-	Feidt C.	Milk, urine, and faeces excretion kinetics of phenanthrene and its metabolites in lactating goats after oral administration
18:10-	Dickey C.A.	Routes of trichloroacetic acid uptake by Sitka spruce trees

WORKSHOP TEACHING ENVIRONMENTAL CHEMISTRY

Convened by M. Filella (University of Geneva, Switzerland)

18:30-	Filella M.	Introduction
18:40-	Steinmann P.	Introducing geochemical and environmental modelling using "macro-assisted" spreadsheet calculation
18:55- -19:30	Informal discussion	

Friday, December 13

08:00-	Hassler C.S.	ACE Award: Non applicability of the BLM and the FIAM on zinc bioaccumulation by a green alga
08:30-	Davison B.	Invited Lecture: In situ measurements of metals in soils, sediments and waters: challenges and solutions

ORAL SESSION 4 CHARACTERISATION OF SORPTION PROCESSES

Chaired by B. Davison (University of Lancaster, U.K.) and J. Dominik (University of Geneva, Switzerland)

09:10-	Garnier C.	Modelling of natural organic matter's complexing and competing properties versus trace metals and proton
09:30-	Totsche K.U.	Sorption of hydrophobic organic contaminants to soil minerals and subsurface soil horizons
09:50-	Knicker H.	2D-solid-state ¹⁵ N- ¹³ C NMR spectroscopic studies on the immobilization of TNT
10:10-	Combourieu B.	Solid-aqueous interface revisited by HR MAS NMR spectroscopy: application to the adsorption of pesticides
10:30-	Coffee-break in the poster and commercial exhibition hall	

ORAL SESSION 5 TRACE ELEMENTS IN THE ENVIRONMENT

Chaired by M.F. Fitzsimons (University of Plymouth, U.K.) and W. Haerdi (University of Geneva, Switzerland)

11:00-	Chon H.T.	Enrichment and migration of selenium and associated elements in rock-soil-plant system in the area covered with black shales in Korea
11:20-	Rippey B.	Chemical models for Pb in lakes
11:40-	Braungardt C.B.	In-situ monitoring of dissolved Cd in the Fal estuary, southwest England
12:00-	Davranche M.	Impact of organic speciation on redox kinetics: The case of cerium
12:20-	Hunger S.	Solid-state speciation of phosphorus in natural and chemically amended poultry litter
12:40-	Tusseau-Vuillemin M.-H.	Estimating the impact of natural dissolved organic matter on copper toxicity with the DGT with constrained gel technique
13:00-	Lunch on own; Poster session; Commercial exhibition	

ORAL SESSION 6 ORGANIC POLLUTANTS IN THE ENVIRONMENT

Chaired by J. Schwarzbauer (Aachen University of Technology, Germany) and K. Becker (EPFL, Switzerland)

15:00-	Booth A.M.	An environmental assessment of the biodegradability and solubility of aromatic fractions from a biodegraded crude oil
15:20-	Jovančičević B.S.	Transformation of oil-type pollutants in surface soils, alluvial sediments and groundwaters affected by microorganisms

15:40-	Grötzschel S.	Organic pollutants on hypersaline microbial mats: Degradation and physiological implications
16:00-	Eggen T.	DDT degradation in fresh water sediment- effect of elementary iron and temperature
16:20-	Coffee-break in the poster and commercial exhibition hall	
16:40-	Mostafa A. E.-D. R.	Composition, distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in sediments of the Western Harbour of Alexandria, Egypt
17:00-	Schwarzbauer J.	Structure elucidation and quantitation of novel anthropogenic contaminants in riverine systems
17:20-	Ravelet C.	K_{doc} determinations by semi permeable membrane device to evaluate influence of dissolved organic matter on the PAH bioavailability
17:40-	Caslavsky J.	Environmental sampling of persistent organic pollutants by semipermeable membrane devices (SPMDs)
18:00-	Hohenblum P.	Pharmaceuticals in the Austrian environment – Analytical results
20:00-	Conference dinner	

Saturday, December 14

ORAL SESSION 7 BEHAVING PRIOR TO POLLUTION: GREEN CHEMISTRY

Chaired by D. Robert (University of Metz, France) and I. Tommasi (University of Bari, Italy)

08:00-	Kardos N.	Sonochemistry of carbohydrates: New improved eco-friendly acetalization of monosaccharides under hydrodynamic or acoustic cavitation
08:20-	Nogier J.P.	New TiO_2 - SiO_2 SBA mesoporous solids: characterization and application to the catalytic selective epoxidation of alkenes
08:40-	Tommasi I.	Abatement of polyphenols in industrial waste-water: identification of new demethylating enzymes and their potential use in synthetic chemistry

ORAL SESSION 8 BEHAVING DURING POLLUTION: WASTE TREATMENT

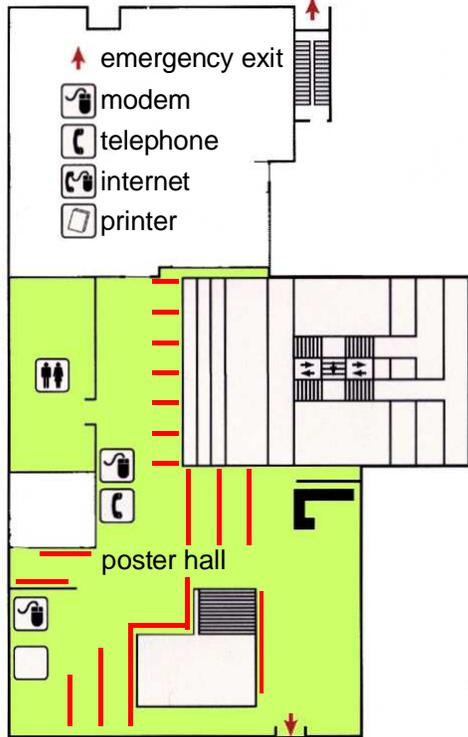
Chaired by D. Perret (EPFL, Switzerland) and I. Tommasi (University of Bari, Italy)

09:00-	Bremner D.H.	Green Fenton chemistry for removal of toxic organics from process wastewater
09:20-	Guivarch E.	Removal of organophosphorus pesticides from water by electrogenerated Fenton's reagent
09:40-	Hurtado Gimeno C.	Ozone wastewater treatment enhancement with ultrasound
10:00-	Coffee-break in the poster hall	
10:20-	Sauvignet P.	Application of high rate ballasted flocculation technology for storm flow treatment
10:40-	Kohli R.	Innovative methods for treatment of hazardous waste
11:00-	Kanno S.	Catalytic decomposition of perfluorocompounds (PFCs)
11:20-	Vasilyeva G.	Biodegradation of chemicals in soil at presence of natural adsorbents
11:40-	Zahir M.H.	Zinc aluminogallate spinel catalysts for NO reduction by hydrocarbon under oxygen-rich conditions
12:00-	Brändli R.	The fate of six polycyclic musk compounds and one metabolite thereof in a representative Swiss waste water treatment plant
12:30-	ACE Environmental Chemistry Poster Award Presentation of EMEC4 and EMEC5 Conference closing	

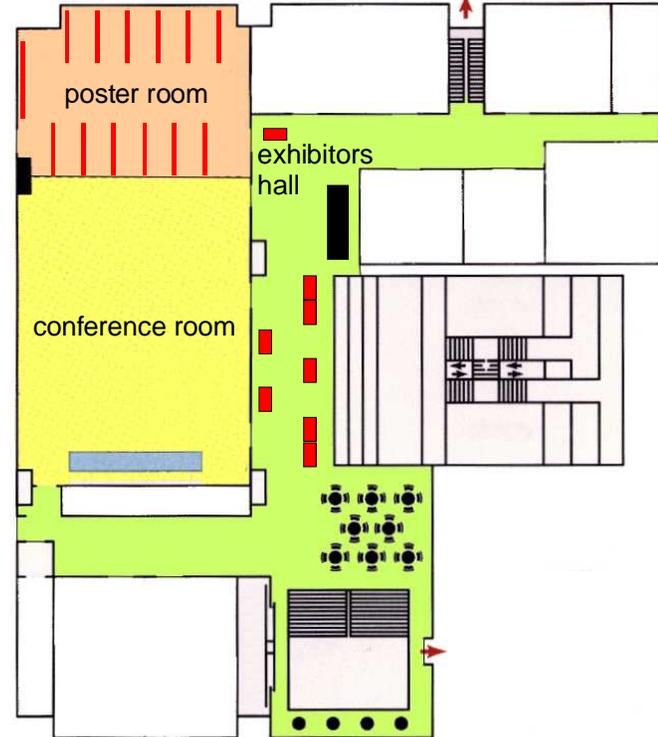
MAP OF THE CONFERENCE CENTER

IATA CONFERENCE CENTRE 33, route de l'Aéroport
registration, conference sessions, poster sessions, commercial exhibitions

level 4



level 5



OTHER INFORMATION

LUNCHES

For those participants who booked their lunch when registering (18 € per lunch), meal vouchers will be distributed at the reception desk for the Restaurant *Le Panoramique*. This restaurant is located in the Conference area. The lunch includes a salad, a main course, mineral water and coffee.

Alternatively, a number of excellent bars and restaurants, as well as shopping arcades, are located at walking distance in the nearby airport and railway station.

L'ESCALADE

The 3rd European Meeting on Environmental Chemistry takes place in Geneva at the same time as the celebration of the 400th anniversary of a famous battle for the city: L'Escalade (<http://www.compagniede1602.ch>).

For the people of Geneva the Escalade is the symbol of their independence. The Escalade (literally: "scaling the walls") marks the final attempt in a series of assaults mounted throughout the 16th century by Savoy which wanted to annex Geneva as its capital north of the Alps.

In 1602 Geneva was attacked by the Duke of Savoy who caught the town off guard during the night of 11 to 12 December. The entire population turned out to fight alongside the town militia and the full-time guard. The Duke's plan was to blow up the Porte Neuve gate, thus opening up the town to his 2000 soldiers. But this plan was thwarted thanks to the quick action of a soldier who had the wit to drop the portcullis. Seeing this, and realising that the attack had failed, the duke's troops swiftly retreated to their camps before daybreak.

Today, the event is still celebrated by a historical procession and a chocolate kettle filled with marzipan vegetables. These little confections symbolise a woman, the Mère Royaume (<http://www.resto.ch/ge/royaume/histoire.html>), who killed one of the invaders by pouring a pot of hot soup from her window onto his head. On this occasion the local population of Geneva sing the official hymn of the City of Geneva, the "Cé qué laino" (<http://hypo.ge-dip.etat-ge.ch/www/athena/helvetia/cqlaino.html>).

CERN VISIT

A visit to CERN for EMEC3 participants has been organised for the afternoon of Saturday 14 December.

As you all know, the CERN is the European Organization for Nuclear Research, the world's largest particle physics centre. Some 6500 scientists, half of the world's particle physicists, come to CERN for their research. They represent 500 universities and over 80 nationalities. A visit to the centre is a very rich and unforgettable experience.

The visit will start at 2 p.m., lasting for 3 hours and commentary will be in English.

CERN is on the border between France and Switzerland, just outside Geneva, and very close to the conference venue.

The visit to CERN is free and the number of participants is STRICTLY limited to 20. Pre-registration by e-mail (montserrat.filella@cabe.unige.ch) is essential and participants will be eligible on a first-come, first-served basis. Because the number of participants is limited, we kindly ask that you only book if you are certain to attend. Thanks for your understanding.

Heavy metals in snow and ice cores dated from the antiquity, the post industrial revolution period and the last climatic cycles

Claude F. Boutron^{1,2}

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 2. Observatoire des Sciences de l'Univers et Unité de Formation et de Recherche de Physique, Université Joseph Fourier de Grenoble (Institut Universitaire de France), B.P. 53, 38041 Grenoble, France
- e-mail: boutron@glaciog.ujf-grenoble.fr

Dated snow and ice cores from Greenland, Antarctica and the Alps are very valuable archives of the history of atmospheric heavy metals pollution since the Antiquity, and past natural changes in atmospheric heavy metals during the successive climatic cycles. Deciphering these archives has however proved to be a real challenge. This is especially because heavy metals concentrations to be measured are exceedingly low, down to the sub pg/g level. Fully reliable data can then be obtained only if sophisticated ultraclean and ultrasensitive analytical procedures are used (Anal. Chim. Acta 450, 193-205, 2001; Anal. Chim. Acta 453, 1-12, 2002; Spectrochim. Acta 52B, 1535-1544, 1997; Anal. Chem. 65, 2510-2515, 1993).

Amongst the most interesting results obtained so far are: 1) Greenland ice evidence of an early large scale pollution of the Northern Hemisphere for Pb and Cu during Greek and Roman times (Science 265, 1841-1843, 1994; Science 272, 246-249, 1996; Environ. Sci. Tech. 31, 3413-3416, 1997); 2) Antarctic snow evidence of a pollution of the most remote areas of the Southern Hemisphere for Cr, Cu, Zn, Ag, Pb, Bi and U during the twentieth century (Earth Planet. Sci. Lett. 200, 207-222, 2002); for Pb, this pollution started as early as the end of the nineteenth century, long before the conquest of the geographic South Pole by Amundsen and Scot; 3) the evidence of a pronounced large scale pollution of the Northern Hemisphere for Pt, Pd and Rh; for Pt and Rh, a large fraction of this pollution originates from automobile catalytic converters which are backfiring in the environment (Environ. Sci. Tech. 35, 835-839, 2001); 4) the evidence of post World War II changes in uranium concentrations in Mont-Blanc ice and snow because of tropospheric transport of dust emitted in uranium mines in former Eastern Germany (Environ. Sci. Tech. 35, 4026-4030, 2001); 5) the reconstruction of past natural changes of various heavy metals in Antarctic and Greenland ice as a function of climate during the last climatic cycles (Nature 323, 222-225, 1986; Nature 362, 621-623, 1993; Earth Planet. Sci. Lett. 143, 233-244, 1996).

Oral: Thursday/8:30

Characterisation of unusual hydrocarbon biomarkers from diatoms

**S.T. Belt¹, G. Massé¹, G. Allard¹,
S.J. Rowland¹, S.G. Wakeham²**

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2. Skidaway Institute, University of Georgia, USA
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During the past few years, our investigations into the sources and structures of organic biological marker compounds has led to significant advances in the field. In particular, we have reported on the sources, structures and environmental controls of the so-called C25 and C30 highly branched isoprenoid (HBI) alkenes from diatoms. We have also modelled the early diagenesis of these compounds in laboratory simulations and shown that while some alkenes undergo simple isomerisation reactions, others undergo cyclisations. In our most recent studies of the ubiquitous planktonic diatom *Rhizosolenia setigera*, we have discovered some 'complementary' cyclic species which are biosynthesised directly by this organism as an alternative lipid group. Unlike the acyclic isoprenoids, these unusual biomarkers are only formed during selected phases of the diatom's life cycle which makes their biological role intriguing. Despite their limited formation, they would appear to make significant contributions to sedimentary organic input from *R. setigera*. Preliminary water column and sediment studies from as far afield as the Arabian Sea, the Peru Upwelling region and North America demonstrate that they are almost certainly more stable than the related HBI alkenes. Such observations could prove significant when evaluating e.g. global diatom inputs to sediments.

Oral: Thursday/9:10

Potential use of LAB's specific compound's isotopic ratios (¹³C/¹²C) to trace point sources of municipal wastewater in SCB

**J.V. Macías-Zamora,
N. Ramírez-Alvarez**

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Linear Alquilbenzene (LAB's) molecules represent a group of compounds being introduced into the Southern California Bight from numerous wastewater point sources. We are investigating the possible use of stable carbon isotope ratios of specific compounds to determine if these molecules can be useful in determining different sources of materials. Along the Bight, near the Mexico-USA border, several wastewater plants constantly discharge these and other pollutants. In our work, on Baja Californias coast, out of 67 stations collected, 66 showed LAB's concentrations above LOD's. These results proved the extensive contact of municipal wastewater discharges with the local marine ecosystem. It is expected that the primary hydrocarbon materials from different oil sources being used to manufacture the commercial detergent formulations would result in differences in $\delta^{13}\text{C}$. We have measured some US and Mexican detergents of common use and have found differences of $\delta^{13}\text{C}$ for some formulations. The most abundant isomers of LAB's were the n-C12 and n-C13. The average $\delta^{13}\text{C}$ for the tested US detergents was from -25.1 to -26.0 ‰. For some Mexican detergents went from -22.6 to as much as 28.7 ‰. We will present preliminary results on some of the local point source characterizations as well as results on a wide sample of local commercial detergents and how they are reflect in particular point sources.

Oral: Thursday/9:30

Organic contaminants as anthropogenic marker compounds in sediments of the Lippe River, Germany

A. Kronimus, J. Schwarzbauer,
R. Littke

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The composition of anthropogenic organic compounds in riverine sediments is characterized by numerous substances released from industrial, municipal and agricultural sources. Source-specific Xenobiotics in natural systems can act as anthropogenic molecular markers. Besides the source specificity, molecular markers are defined by massive and widespread uses as well as environmental persistence. Sediments of the Lippe River (Germany) were investigated for a wide range of anthropogenic organic substances by GC-MS-analysis. The obtained structural informations were verified by comparison with specific analytical data of synthetic reference substances. Molecular markers from three different industrial sources were identified, furthermore numerous molecular markers from municipal and agricultural sources were found. The qualitative and quantitative analytical data were interpreted to visualize the anthropogenic contamination of the Lippe River including spatial distribution, input effects and time depend occurrence of the contaminants.

Oral: Thursday/9:50

Pollution of the North Caspian Sea with organic compounds

A.T. Lebedev, O.V. Poliakova,
M.N. Repina, M.L. Khrushcheva,
N.S. Sokolov

Moscow State University, Moscow, Russia

e-mail: lebedev@org.chem.msu.su

The Caspian Sea is known to be the largest inland reservoir of salted water in the world. The square of the sea is 378000 km². According to the old USSR data hydrocarbons, phenols, surfactants, organochlorine pesticides and PCB were pollutants of special concern. Seventy one samples of sediments were collected in October 2001 in the North part of the sea. GC-MS was used to analyze organic pollutants in the samples. Although the presence of all types of hazardous chemicals was detected, petroleum hydrocarbons and sulfur were the major ingredients. Geo-informational system approach was used to estimate the pollution of the sediments in the various regions of the sea. The data of sputnik altimetry (water and surface) were used as the map basement. The covering of the sea and surface was elaborated using shaded relief technology with the eastern lightning. To develop the maps of pollution with various chemicals on the prepared basement the program media Surfer and Adobe Photoshop were used. The constructed map of the sea pollution clearly revealed the sources of the sea pollution with various chemicals.

Oral: Thursday/10:10

Enhanced Fenton based remediation using ternary pollutant-cyclodextrin-iron complexes

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Fenton reagent (Fe(II) + hydrogen peroxide) has been applied for pollutant degradation and soil remediation. Such chemical methods can provide an excellent alternative to biological methods, which are limited by high concentrations and/or mixtures of contaminants. In-situ chemical oxidation technologies also have limitations, including interference from non-pollutant species and isolation of pollutants in hard to reach soil regions (e.g. pores, hydrophobic sites). Cyclodextrins (CDs) can significantly enhance Fenton oxidation processes by bringing a hydrophilic iron ion and a hydrophobic pollutant into close proximity. The iron catalyzes conversion of hydrogen peroxide to hydroxyl radical, which degrades the pollutant. Cyclodextrins (CDs) are non-toxic, biodegradable, natural products consisting of fused glucose rings. These torus shaped molecules have hydrophobic interiors and hydrophilic exteriors and can simultaneously bind both iron and a pollutant. In aqueous systems in the presence of dissolved natural organic matter, CDs enhance Fenton oxidation of pollutants such as PCBs, PAHs, chlorinated phenoxyacetic acids, and other aromatic hydrocarbons. For example, nearly 7-fold increases in TNT degradation rates were observed with CD added. Such findings indicate that the use of iron-cyclodextrin-peroxide systems may provide an improved and selective technology for degrading hydrophobic pollutants in aqueous and soil systems.

Oral: Thursday/11:00

Biodegradation of polycyclic aromatic petroleum compounds by cyanobacterial mats in mesocosm experiments in Gaza (Palestine)

**N.M.D. Safi^{1,2}, J. Köster¹, J. Safi²,
Y. El-Nahal², J. Rullkotter¹**

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2. Environmental Protection and Research Institute, Gaza, Gaza Strip, Palestine

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Microbial mats can be found all over the world in a wide range of environments. They are a promising ecosystem for biodegradation studies because of their high internal turnover rates of carbon compounds, changing diurnally, their steep physicochemical gradients and the presence of many different physiological groups of microorganisms. Petroleum compounds are widespread environmental pollutants. Their biodegradation has been the subject of numerous investigations. We carried out experiments for biodegradation of hydrophobic petroleum model compounds (phenanthrene and dibenzothiophene) added to natural microbial mats from Wadi Gaza. In nature the mats are exposed to variable levels of pollution, mainly by diesel oil. They thrive under fluctuating salinity due to seasonal sea water intrusion and fresh water run-off. Montmorillonite with a chemically altered, hydrophobic surface was used as carrier material, forming an organo-clay complex (OCC) with the petroleum model compounds. The experiments were carried out in an outdoor experimental pond in natural climate at Gaza, Palestine. A mixture of 2 mg OCC/cm² mat surface (containing c. 50 µg/mg of each compound) was applied to pieces of cyanobacterial mat. The degradation experiment was performed for one hundred days. It showed that phenanthrene and dibenzothiophene were efficiently biodegraded.

Oral: Thursday/11:20

Photocatalytic degradation of aqueous MTBE in a supported-catalyst reactor

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e-mail: msmc3@eng.cam.ac.uk

Contamination of groundwater by MTBE poses serious environmental problems and economical losses to water companies. Remediation methods of MTBE, such as air-stripping and biodegradation, have been proven inefficient. Photocatalysis is an advanced technology for remediation of many organics. This paper investigates the feasibility of using a supported-catalyst reactor for photocatalytic degradation of MTBE in water. The reactor is designed to obtain a uniform light intensity on catalyst surface. The effects of light intensity and different sizes of cylindrical reactors and oxygen content on degradation efficiency have been investigated. It was found that photocatalytic degradation of MTBE follows first-order kinetics. The reaction rate constant is proportional to the light intensity but decreases with the ratio of reactor volume to catalyst area. The reactors of smaller diameters are more efficient in degradation than reactors of larger diameters under the same light intensity. As much as 99% of degradation of MTBE was achieved in 40 hr with a UVA light intensity input of 6 mW/cm². Complete degradation of MTBE was found with excess supply of air (oxygen). However, intermediates are observed in degradation at low oxygen content.

Oral: Thursday/11:40

Microbial and biochemical techniques to evaluate and to implement in-situ biodegradation potential and activity at sites contaminated with aromatic and chlorinated hydrocarbons

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Intrinsic bioremediation harnesses the ability of indigenous microorganisms to degrade contaminants that are present in soil and groundwater. Over the past decade many environmental regulatory agencies especially in Europe have come to recognize the importance of these natural processes in contaminant attenuation. In order to use in-situ bioremediation to clean up a site successfully it is necessary to investigate the indigenous microbial population and its potential activity to degrade the contaminants of concern (COCs). The evaluation of naturally-occurring degradative activity in initial screening of soil and groundwater samples using recently developed molecular and microbial methods may allow for the implementation of a contaminant reduction and management program without the need for fully engineered remediation intervention. Limited engineering approaches (nutrient delivery etc.) can be implemented to support naturally-occurring bioremediation processes to achieve a controlled, dynamic attenuation of COCs. Techniques for monitoring pollutant-degrading microorganisms were previously limited to standard culturing techniques. More recently, techniques based upon detection of genetic elements and metabolic activities have been developed in collaboration with university partners Europe, especially in France. The modern techniques are more sensitive for monitoring microbial populations, metabolic activity and the genetic potential to degrade the COCs, and avoid the need for cultivation of microbes under artificial conditions in the laboratory.

Oral: Thursday/12:00

Techniques to enhance phytoextraction of thallium from a contaminated soil

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In pot experiments the effect of the chemical and spatial (root growth and morphology) availability in soils on enhancing thallium (Tl) phytoextraction by kale genotype (*Brassica oleracea acephala* L. c.v. Winterbor F1) were investigated. Chemical availability was investigated by lowering rhizosphere soil pH by applying different N fertilizer forms. While spatial availability were influenced by applying different amounts of N fertilizer to kale grown in pots of different sizes. The relationship between Tl uptake and root growth was studied by intermediate harvests. As a result of rhizosphere acidification kale fertilized with NH₄ in addition to a nitrification inhibitor showed a slightly higher total Tl uptake than those plants fertilized with NO₃. While direct acidification of the soil with diluted sulphuric acid doubled Tl uptake. The increase of the total Tl uptake was higher in the treatments with less N fertilization compared with the treatments with high N fertilization as an influence of root morphology. In conclusion, chemical and spatial availability play an essential role for the success of Tl phytoextraction.

Oral: Thursday/12:20

Economic study of groundwater defluoridation of the North African Sahara

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Economic evaluation of defluoridation of Sahara ground waters is presented for three processes: electro dialysis, reverse osmosis and the electrochemical bipolar reactor. The economic study was accomplished for drinking water unit production of 100 m³/h. It was found that the costs per m³ of treated water obtained with different processes would not excessively high for the states of the North African region. The results also indicate that the most efficient process uses the electrochemical bipolar reactor, followed by the electro dialysis process. However, the water produced by the first process does have the required quality for drinking water, it may nevertheless be utilised for agricultural purposes. On the other hand, the electro dialysis unit produces high quality drinking water and appears to be an interesting solution to the fluorosis disease.

Oral: Thursday/12:40

Bioavailability of trace metals in saline waters: field experiments

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Aquatic organisms may take up trace metals mainly from solution and from food. Mussels, as filter feeders, effectively filter particulate matter out of a suspension. Suspended matter, therefore, may be a source of trace metals if ingested by mussels. Obviously, trace metal concentrations in the water column (dissolved and particulate), environmental and biological conditions are the parameters determining metal accumulation in marine organisms. To study bioavailability of trace metals, three age groups of marine mussel *Mytilus galloprovincialis* were transferred from the clean area (Mali Ston Bay, Middle Adriatic coast, Croatia) to the experimental station in relatively polluted area (Kastela Bay, Croatia). The experiments were conducted in summer (21 June – 27 July 2001) and in winter (23 January – 07 March 2002). During each of those two experimental periods, the mussels, suspended matter (sediment traps) and biofouling organisms (plexiglass plates) were sampled six times. The same trace metals like in the mussels (Hg, Cd, Pb, Cu, Zn, Cr, Mn) and organic matter concentrations were measured in the particulate matter deposited in the sediment traps. Diffusive gradients in thin-films (DGT) was used to measure trace metal concentrations in the saline water. This technique provides an in situ means of quantitatively measuring labile metal species in aqueous systems and could help in better understanding of trace metal bioavailability to the marine organisms.

Oral: Thursday/15:00

Intracellularly accumulated and adsorbed metals on a natural biofilm

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The determination of the intracellularly accumulated metal concentration has always been controversially discussed. The simple acidic digestion of a biofilm followed by the measurement of the metal concentration indicates the intracellular as well as the extracellularly adsorbed metals. Indeed, metals are partly found adsorbed on the cell walls or incorporated in the natural biofilm in iron or manganese oxides. To measure the real bioaccumulation, the external metals need to be discriminated. Experiments using a 4mM solution of EDTA to wash a natural biofilm (periphytic community) showed that a 10 minutes exposure was appropriate to desorb the metals without inducing cell-breakage or extracting the intracellularly accumulated metals. These experiments were performed over a 60 minutes period and the emphasis was given to the behavior of copper and zinc, both essential metals. In natural water containing background concentrations of metals, 89 to 96 % of total cellular Cu and 94 to 96 % of Zn were found to be intracellularly accumulated. In metal polluted waters, the proportion of metal adsorbed on the biofilm increased and the proportion of intracellularly accumulated metal obtained was 75 % of Cu and 82 % of Zn.

Oral: Thursday/15:20

The influence of non-humic dissolved organic matters and their biodegradation by-products on the bioavailability of benzo[a]pyrene

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Anthropized aquatic ecosystems may receive high levels of persistent organic pollutants (POPs). They also usually contain high amounts of allochthonous and autochthonous dissolved organic matters (DOM), originating from domestic and industrial effluents or phytoplanktonic degradation. Some types of DOM (particularly hydrophobic humic substances) have been proved to greatly reduce the bioavailability of POPs. However, little is known about other types of DOM, specially the highly non-humic and biodegradable ones. Two models of DOM (an artificial substrate miming a domestic effluent and algae extracts) were tested for their influence on the bioavailability of benzo(a)pyrene. This influence was also monitored along with the biodegradation of the DOM, as more and more refractory matter was produced. The biodegradation of DOM was monitored in a reactor using respirometric analysis. Aromaticity was followed with UV absorbance. At fixed times, crustaceans (*Daphnia magna*) were exposed to a synthetic water solution spiked with benzo[a]pyrene and various concentrations of DOM from the reactor. The bioaccumulation of benzo(a)pyrene in *Daphnia* was compared versus the concentration and the biodegradation stage of DOM. Results showed that DOM always significantly reduced the bioaccumulation. Moreover, the more degraded the organic matter, the more aromatic and the more affected the bioaccumulation was.

Oral: Thursday/15:40

Effect of a sulfonylureic herbicide and reactive oxygen species on euglenoid movements in *Euglena gracilis*

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The euglenoid flagellates in aqueous environments are able to change their shape rapidly in response to a variety of stimuli such as strong light. In this phenomenon so called "euglenoid movement", two extremes of shape can be identified: the relaxed form is cylindrical and the contracted form is round. We found that the euglenoid movement is a sensitive indicator for cellular responses to environmental oxidative status and the presence of a herbicide in *Euglena gracilis*. Here, a commercial sulfonylureic herbicide containing, methyl 3-[[[4-methoxy-6-methyl-1,3,5-triazin-2-yl]carbonyl]sulfamoyl]-2-thiophenecarboxylate (known as thifensulfuron methyl, 75 % purity, w/w) was added to the culture of *E. gracilis* at various concentrations ranging from 0.01 to 1000 mg/L. Euglenoid movements were assayed in the presence and absence of hydrogen peroxide and herbicide, by using a flow cytometer. Data indicated that the treatments with the herbicide and hydrogen peroxide resulted in the extreme elongation (1.5-2.0 times longer than the normal relaxed form) and contraction of the cells, respectively. We present the data as a groundwork providing useful primary knowledge for assessing the impact of the environmental chemical levels in the aqueous micro-ecosystem.

Oral: Thursday/16:00

Fungal laccases: from structure-activity studies to environmental applications

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Fungal laccases are multi-copper oxidases that catalyze the oxidation of a wide range of compounds of environmental interest, including pesticides and polycyclic aromatic hydrocarbons. Nevertheless, their activity needs to be optimized (in terms of activity, efficiency or substrate specificity) for environmental applications such as tools for bioremediation or biomarkers to assess the impact of chemicals. We present here the structure-activity studies intended to allow a better knowledge of the laccases of the white rot fungus *Trametes versicolor*, including structural, catalytic and molecular features. In a first time, the crystal structure of laccase of the fungus has been solved. Two charged or polar residues interact with 2,5-xylydine, a weak substrate. These results allow developing a strategy for the directed evolution of the enzyme. The gene of the laccase has been cloned in *Escherichia coli*, then expressed in the yeast *Yarrowia lipolytica*. Other studies have been performed to assess the molecular basis for enzyme production. Finally, we describe two environmental applications involving natural or recombinant enzymes.

Oral: Thursday/16:50

Stress specific functional cDNA microarray of Japanese Medaka fish for environmental stress analysis

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In this study, we have developed a novel cDNA microarray for analyzing stress specific responses and seeking distinct biomarkers in Japanese Medaka Fish. More than 23 different genes including estrogenic, cytotoxic, and carcinogenic responsive genes from Medaka fish were selected and cloned to design and fabricate this functional DNA chip. This newly developed DNA chip has been tested and confirmed with RT-PCR and real time RT-PCR tools. Chemicals including nonylphenol, bisphenol A, phenol, and diazinon as representatives of EDCs and cytotoxic chemicals have been tested to analyze their effect on Fish. This DNA chip can be utilized to analyze the stress responses and seek potential biomarkers for environmental biosensors. All the details in the features of DNA chip fabrication and analysis data will be presented. This work was supported by the National Research Laboratory (2001 NRL) program of Korea Institute of Science and Technology Evaluation and Planning (M10104000094-01J000004100). Authors are grateful for their support.

Oral: Thursday/17:10

Photochemical and ecotoxicological studies on corticosteroids

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During the last years many studies of the impact of chemical pollution have focused on pharmaceuticals since most of these chemicals have been found in the environment. Prednisone, one of the most widely prescribed medical substances in the United States during the last five years, is a corticosteroid used for many conditions of human health. Pharmacokinetics studies in man have proved that about 10% of prednisone is metabolized to prednisolone. High levels of both drugs are excreted through urine and carried by sewage effluent into surface waters, where they may be subjected to modifications by sunlight. The photochemical behavior of prednisone and prednisolone in water was studied by irradiation of aqueous suspensions by a solar simulator. The several photoproducts obtained have been isolated by chromatographic techniques and identified on the basis of their physical features. All chemicals have been tested to evaluate their effects on freshwater organisms from different trophic levels. Toxicity tests have been performed on the bacterium *Escherichia coli*, the alga *Selenastrum capricornutum*, the rotifer *Brachionus calyciflorus*, the cladoceran *Daphnia pulex* and the anostracan *Thamnocephalus platyurus*.

Oral: Thursday/17:30

Milk, urine and faeces excretion kinetics of phenanthrene and its metabolites in lactating goats after oral administration

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The aim of this study was to characterize the differential transfer of phenanthrene and its metabolites to milk, urine and faeces in lactating goats after a single oral ingestion of phenanthrene (200 mg). Four Alpine goats were used for this experiment. Blood, milk, urine and faeces samples were collected twice a day (at 8 am and 5 pm) during five days. Phenanthrene and its metabolites from contaminated samples were extracted by a liquid-liquid extraction (cyclohexane and ethyl acetate (v:v - 50:50) and purified by using ENVI Chrom P columns. The determination of phenanthrene and its metabolites was conducted on a GC/MS. Three hours after ingestion concentrations of metabolites in blood were at their highest levels, indicating a very fast absorption and metabolisation of the molecule. Concerning milk excretion route, the highest phenanthrene and sum metabolite levels were detected 7 h after the oral ingestion of the compound (17.5 and 157.4 ng/ml). 3 OH-phenanthrene was mainly detected and the total metabolites concentration appeared 10 fold higher than the native compound. Regarding the other excretion sources, phenanthrene was mainly detected in faeces contrary to its metabolites which were highest in milk and urine.

Oral: Thursday/17:50

Routes of trichloroacetic acid uptake by Sitka spruce trees

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Trichloroacetic acid (TCA: CCl₃COOH) is known to be present in the atmospheric aqueous phase. TCA is also present in conifer needles, and studies have suggested a link with forest decline. The questions are by what route does TCA enter the tree, particularly given the lipophilic surfaces of needles, and how fast? In a fully balanced experimental design, we exposed 120 Sitka spruce seedlings (stratified by height) to foliage-only or soil-only application of TCA solution at three concentrations (0, 10 and 100 ppb). At the end of the growing season TCA concentrations in needles of 100 ppb-dosed seedlings were significantly elevated for both foliage and soil applications, demonstrating that TCA uptake occurs via both foliage and roots. Total foliage TCA is < 10% of total TCA applied over the season, yet soil concentration is not elevated. Increased activity of detoxification enzymes in needles suggests that uptake via foliage causes greater stress. In a separate experiment, we applied a single dose of TCA (200 µg) to foliage and roots of seedlings. Bi-weekly analyses showed rapid uptake of TCA into needles, with greater amounts via the soil application route. Needle concentrations began to decline after 30 days from which uptake and elimination rates can be derived.

Oral: Thursday/18:10

Introducing geochemical and environmental modelling using "macro-assisted" spreadsheet calculation

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Geochemical and environmental modelling can adequately be introduced using "macro-assisted" spreadsheet calculation (e.g. Excel). A variety of problems can be solved ranging from equilibrium determination in a carbonate system, to reaction path calculations (of feldspar weathering, e.g.), to more involved coupled advection/diffusion/reaction models. Very similar approaches, however, can also be used for non-chemical models. The spreadsheet approach is flexible and easily incorporates different kinds of processes. A further advantage is that only a minimal mathematical background is required to formulate the models. Also, the students will be easily convinced that the obtained results have to be viewed critically and verification (e.g. checks against benchmark cases) are mandatory. I will present a geochemical model of microbial methane production accounting for kinetic reactions, advection, diffusion, bubble formation and speciation reaction (according to a predefined pH gradient). This model is solved using a more generally applicable "macro-assisted" Excel worksheet.

Oral: Thursday/18:40

THE ACE YOUNG RESEARCHER OF THE YEAR AWARD

This Award is aimed at recognising the achievements of young researchers who have made an outstanding contribution to our scientific understanding of Environmental processes. The award will be presented annually to a young European-based researcher M.Sc., Ph.D. or post-doctoral researcher; first post-doctoral position within three years of their Ph.D. award. The award will be for research excellence, e.g. a published paper in a highly rated journal, in the field of Environmental Chemistry. This award consists of 500 Euros and of a free registration for the meeting. The Award recipient will be invited to give a paper at the meeting.

The European Young Researcher Award is presented in the memory of Dr Gareth Rieley (1969-1998). Gareth, himself an exceptionally bright and committed young researcher, with an already successful career aimed at understanding the factors which control the isotopic fractionations at the molecular level in organic components of biological and environmental significance. Gareth studied at the Organic Geochemistry Unit, University of Bristol, United Kingdom, obtaining his Ph.D. in 1993 in "Molecular and Isotopic Studies of Natural Environments; Distributions and Stable Carbon Isotopic Compositions of Individual Lipids".

Non applicability of the BLM and the FIAM on zinc bioaccumulation by a green alga

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Chlorella kesslerii was adapted to three $[Zn^{2+}]$ (10^{-11} , 10^{-9} and 10^{-6} M). The adaptation media affected both growth and bioaccumulation of zinc. Algae grew slower in the presence of high and low $[Zn^{2+}]$ but had an identical final biomass, suggesting that no toxicological effects were apparent. Zinc bioaccumulation was studied over a large range of $[Zn^{2+}]$ in order to ensure that both environmental conditions was respected and saturation of the uptake system was attained. Compared to algae grown with 10^{-9} M $[Zn^{2+}]$, bioaccumulation was not influenced by preconditioning with 10^{-6} M $[Zn^{2+}]$ whereas much higher internalisation fluxes were observed for 10^{-11} M $[Zn^{2+}]$. This observation was attributed to the synthesis of high affinity transporters. In none of the growth conditions used, was a first order uptake flux or adsorption, as predicted by the FIAM and the BLM models, observed. This was due to the occurrence of a primary active transport. Several hypotheses were analysed in order to explain the usefulness of $[Zn^{2+}]$ in solution and adsorbed $[Zn]$ as predictors of biological effects. These results should have a broad impact if it is considered that the European community is reconsidering their water assessment criterion by measuring the free ion instead of total and dissolved metal concentrations.

Oral: Friday/8:00

In situ measurements of metals in soils, sediments and waters: Challenges and solutions

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Traditionally environmental analytical chemists have striven to measure metals in what they consider to be defined compartments. For example in waters the focus has been on solution versus particulate (*filtration*), whereas in soils and sediments it has been on solution (pore waters) versus the total metal. Further division into smaller compartments is exemplified by chemical speciation in solution and the various models that aim to predict the distribution of species under equilibrium conditions. In soils and sediments a series of reagents with specific properties are used to classify operational fractions. These approaches have significantly advanced our knowledge and understanding of environmental systems, but they have limitations. Firstly they seldom provide direct information about the kinetics of chemical supply and transformation, yet many environmental processes are controlled by such rates. Secondly they usually demand measurements on bulk samples. As soils and sediments are heterogeneous systems, where processes controlling chemical change may operate at the scale of the grain size (*dissolution/desorption*) or organism (*microbial mediation or electron supply*), the averaged information obtained from a bulk sample may not be applicable to the individual process.

The emerging technique of DGT (*diffusive gradients in thin-films*) can be used in-situ to obtain kinetic information relevant to solution speciation and solid phase - solution interactions in soils and sediments. It binds metals at a resin after they have diffused through a layer of gel. The resin perturbs the system (*removes metal from solution*), while the combination of a resin with a defined diffusion pathway in the form of a gel allows quantitative measurement of metal supply. In solution DGT can be used to measure the rates of dissociation of complexes. In sediments and soils it can be used to measure the rates of release of metals from solid phase to solution. Examples of such measurements will be given, along with an outline of the underlying principles. Their relevance to biological uptake will be demonstrated with data for metal uptake by plants. A further feature of DGT is the ability to make measurements in sediments and soils in two dimensions at a spatial resolution of 100 microns. The resulting highly structured distribution of metals in pore waters appears to be related to biological supply processes.

New developments in biogeochemical understanding are demanding measurements that can operate on a range of temporal and spatial scales and provide information that is not restricted to concentrations in compartments. The challenge will be to both make the measurements and to interpret the environmental significance of the novel information.

Oral: Friday/8:30

Modelling of natural organic matter's complexing and competing properties versus trace metals and proton

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This work focused on NOM's characterisation by complexing properties, versus trace metals (Cd, Pb) and proton, which can be directly used in a contaminant's transport model. In order to determine the largest ligands distribution on NOM (0.1nM - 5µM of total metal) different techniques are used (electrochemistry, potentiometry). To increase precision for this determination, a metal logarithmic scale titration have been used. In the same way, a new software for optimisation and chemical speciation's calculation (PROSECE) have been developed. It is based on mass balance equation for speciation resolution and use a simplex for binding parameters' optimisation. Different experiments have been done on a Suwannee River Fulvic Acid. Results obtained, shown that NOM's complexing with and competing between trace metals and proton, can be modelled by a set of virtual entities, only defined by some complexing properties versus metal and proton, named "quasi-particles" (Sposito, 1981). Three types of "quasi-particles" have been used for experimental data modelling. Binding parameters optimised are "quasi-thermodynamical" ones since they take account of metal competing and they aren't pH dependent. Use of this determination's process for natural waters, within the framework of the french SeineAval2 program, improve the knowledge of NOM's role on trace metal's speciation.

Oral: Friday/9:10

Sorption of hydrophobic organic contaminants to soil minerals and subsurface soil horizons

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In subsurface soil horizons, the sorption of hydrophobic organic contaminants may primarily be controlled by the composition and the properties of the soil minerals. Therefore this study aimed to elucidate the properties and mechanisms which control the sorption and the sorption kinetics of hydrophobic organic contaminants to different inorganic soil constituents and subsurface soil horizons. Batch sorption experiments are conducted with three polycyclic aromatic hydrocarbons (PAHs: phenanthrene, pyrene and benzo(a)pyrene), with three model minerals, and five B and C horizons of different soils. Batch experiments show a considerable sorption of PAHs to all soil minerals except for the sorption of phenanthrene to quartz sand. The sorption process is rapid and seems to be completed after 4 hours of contact time. Sorption capacity is higher for clay minerals and iron oxides than for quartz sand. In contrast, the sorption of pyrene to subsurface soil horizons is rate-limited. Increasing rate-limiting processes correspond with increasing OC content of the soil material. Sorption isotherms of PAHs to soil minerals are best described by a nonlinear isotherm. However, more linear sorption isotherms of pyrene to subsurface soils are observed.

Oral: Friday/9:30

2D-solid-state ^{15}N - ^{13}C NMR spectroscopic studies on the immobilization of TNT

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TNT-contaminated soils from activities of munitions and defense industries have become a subject of environmental concern. One suggested strategy for the clean-up of soils contaminated with such compounds represents the irreversible immobilization of their transformation products into soil organic material by humification processes. To test the efficiency of this strategy, ^{15}N -TNT was incubated with soil material and the humification process was followed by solid-state ^{15}N NMR spectroscopy. High addition of secondary energy sources, lead to an almost complete reduction of nitro groups. Considerable ^{15}N -intensity was assignable to condensation products of TNT-metabolites, giving a first indication that TNT degradation products can covalently bind to soil organic matter. To confirm this conclusion, ^{15}N -TNT was incubated with ^{13}C -enriched plant material (*Lolium perenne*) and the immobilization was followed by 2D ^{13}C - ^{15}N double cross polarization MAS NMR spectroscopy. In such spectra, only the ^{15}N -labeled nitrogen groups of TNT and its transformation products bound to ^{13}C -labeled group of humified plant material show cross peaks. Applying this technique, it was revealed that the covalent immobilization occurs via amide-bonds, possibly resulting from acetylation or formylation reactions. The obtained results further demonstrated 2D solid-state ^{15}N NMR spectroscopy as a valuable tool for characterizing the humification process of nitrogen containing bound residues in soils.

Oral: Friday/9:50

Solid-aqueous interface revisited by HR MAS NMR spectroscopy: application to the adsorption of pesticides

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Weak interactions are usually difficult to analyze. Especially, few analytical methods are available to study adsorption-desorption mechanisms at the solid-aqueous interface. Quantification of such phenomena would allow to appreciate the "bioavailability" of a pollutant in soil or at least in a solid matrix. We recently demonstrated the potential of the ^1H HR-MAS NMR technique to study such interactions in situ (Combourieu et al., Chem. Commun., 2001, 21, 2214). By using a well-characterized model of soil it was possible to distinguish unambiguously the mobile and immobile pesticide. In the present communication new molecular insights into surface adsorption of pesticides through different MAS NMR approaches will be presented. Particularly, comparison between adsorption capacity of some synthetic anionic clays and functional diversity of several organic pollutants will be evaluated. The scope and limits of HR-MAS NMR spectroscopy in this field will also be discussed

Oral: Friday/10:10

Enrichment and migration of selenium and associated elements in rock-soil-plant system in the area covered with black shales in Korea

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The purpose of this study is to investigate the enrichment level and dispersion patterns of Se and associated elements in rock, soil, and crops which were collected in the Dukpyung (DP) and the Chubu (CB) areas covered with black shales of the Okchon Group in Korea. The mean value of Se in rocks of DP and CB areas is 2.0 mg/kg and 17.7 mg/kg, respectively. Soil pH ranges from 5 to 6 and LOI is in the range of 3 to 7 %. Mean concentration of Se in mountain, farmland and paddy soils overlain black shales are 4.4 mg/kg, 1.8 mg/kg, and 1.5 mg/kg, respectively. Maximum level of Se is up to 72.6 mg/kg in mountain soils. Distribution patterns of Se show very similar trend with uranium. Selenium has significant correlations with Ag, As, Mo, U, V, and Zn. Mean concentrations of Se in rice grains, rice stalks and Chinese cabbage from the Dukpyung area is 0.4 mg/kg, 2.2 mg/kg and 5.0 mg/kg, respectively. Relationship between Se in soils and crop plants shows good correlation ($r=0.99$). The BAC (Biological Absorption Coefficient) of Se, As and Mo increases in the order of rice grain < rice stalk < Chinese cabbage.

Oral: Friday/11:00

Chemical models for Pb in lakes

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Two chemical models that lead to an almost constant Pb concentration in the sediment of lakes in a region that receives contamination from the atmosphere were investigated. Realistic values for the distribution coefficient (K_d , 100 to 2000 l/gDS), particle concentration in lake water (C_p , 0.001 to 0.01 gDS/l) and adsorbed metal concentration on particles in lake water (SOM, 10^{-7} to 1.2×10^{-6} mol/g), equivalent to 20 to 250 $\mu\text{gPb/gDS}$) were used. For a simple distribution coefficient model, there are two options. Either K_d is large (>1000 l/gDS) and C_p low (1 mgDS/l) or K_d is between 150 and 2000 l/gDS, with a corresponding C_p value between 1 and 8 mgDS/l. Whatever the conditions, SOM varies least from lake to lake either if C_p is low and constant or if C_p is higher. For the total particle flux model, it is more difficult to produce an almost constant SOM when the total particle flux and hydraulic load varies between lakes, unless there is relationship between these two lake characteristics. We conclude that constant SOM is likely to be due to an almost constant C_p rather than almost constant total particle flux.

Oral: Friday/11:20

In-situ monitoring of dissolved Cd in the Fal estuary, southwest England

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Research has shown that the biological impact of pollutants is related to their physico-chemical speciation in aquatic systems. In-situ speciation measurements offer several advantages over a discrete sampling approach, including a minimised risk of speciation changes and of sample contamination prior to analysis. We have used the Voltammetric in-situ Probe (VIP) to monitor the labile fraction of dissolved Cd in dynamic coastal systems. The Fal estuary in the southwest of England lies in a mineralised area that has been mined for metals (e.g. Cu, As, Sn) until the late 1990s. Metal monitoring was carried out over full tidal cycles, with a temporal resolution of 30 - 40 minutes. Maximum total and labile Cd concentrations (1.5 and 3.6 nM, respectively) were observed at low water, while lower concentrations (0.15 and 0.67 nM) were measured when mixing with more pristine seawater was evident at higher salinities ($S > 34$). The proportion of labile Cd formed between 27 and 99% of the total dissolved concentration. Together with auxiliary data (pH, conductivity, temperature, dissolved organic carbon and nutrient concentrations) and total dissolved metal data, the VIP has a significant potential for contributing to biogeochemical studies in coastal systems.

Oral: Friday/11:40

Impact of organic speciation on redox kinetics: The case of cerium

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The coherent geochemical properties of the rare earth elements (REE) can be used to study the behaviour of trace metals (particularly the trivalent actinides) during interaction of aqueous solution with metal oxides. Among trivalent REE, Ce can be oxidized into Ce(IV) through an oxidative scavenging reaction on Mn oxides, a process which is thought to be responsible for the development of negative Ce anomalies in many natural oxidizing waters. However, some oxidizing, organic-rich waters show no Ce anomaly, suggesting that the reaction could depend on the presence of organic matter. We have tested this possibility in two ways. First, thermodynamical calculations at equilibrium were performed using the geochemical model CHESS to investigate the speciation of REE in natural organic-rich waters showing no Ce anomaly. Second, laboratory experiments of REE adsorption and Ce oxidation by commercially available Mn oxides were performed with, and without organic ligands (humic acid). The results show that the kinetic of the reaction is strongly slowed down: one month was necessary to create a negative Ce anomaly under organic conditions, while it happened only after 10 hours when the REE speciation was purely inorganic. These results question the use of Ce anomalies in natural waters as proxies of redox conditions and evidence the influence of organic matter on the cycle of trace metals in the environment.

Oral: Friday/12:00

Solid-state speciation of phosphorus in natural and chemically amended poultry litter

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Eutrophication of surface water with nutrients, especially phosphorus (P) run-off from agricultural soils is a problem world-wide. Over-application of synthetic fertilizers, animal manures and biosolids has been suggested to be responsible for an increased P loss from soils. The mobility and bioavailability of P in animal wastes and in soils that have received them is determined by its chemical form. In the past, chemical analysis of biosolids and animal wastes has been limited to the determination of the total P content and of different soluble fractions by chemical extraction. The scope of spectroscopic methods in the investigation of P-speciation in animal wastes is limited and they have only recently been employed. In our research, P speciation has been studied in natural and in alum-amended poultry litter using solid-state ^{31}P -NMR spectroscopy, thermo-gravimetric analysis and x-ray diffraction, in order to gain insight in the P reactions involved and to predict P losses from the litter and from soils amended with the litter. Results indicate that the P speciation in natural poultry litter is dominated by calcium phosphate and a complex mixture of organic phosphate esters, in the alum-amended litter by orthophosphate complexed with an amorphous aluminum hydroxide.

Oral: Friday/12:10

Estimating the impact of natural dissolved organic matter on copper toxicity with the DGT with constrained gel technique

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Natural dissolved organic matters greatly reduce the bioavailability of most metals, due to their complexing capacity. The Diffusion Gradient in Thin films technique recently emerged as a convenient way of in situ exploring the speciation of trace metals. By using various types of gel, the metal complexes can theoretically be discriminated upon their chemical lability and their physical properties, provided that the diffusion characteristics of the complexes are known. Natural organic matter contains however a wide variety of potential ligands that are still poorly documented. In order to evaluate the potentialities of DGT for estimating in situ bioavailable copper concentrations, we performed simultaneously total copper measurements, DGT measurements with different gels (restricted or not) and toxicity biotests on mineral water solutions spiked with copper and dissolved organic matters representative of natural surface waters (Humic and Fulvic Acids, phytoplanktonic residues). Our results confirm that DGT with restricted gel do not fix the HA and FA copper complexes and allows a good estimation of copper toxicity in such mixtures. However, the dissolved organic matter of phytoplanktonic origin appears to form copper complexes that are partly labile and measured even with constrained DGT, whereas they significantly decrease the toxicity of the metal.

Oral : Friday/12:40

An environmental assessment of the biodegradability and solubility of aromatic fractions from a biodegraded crude oil

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Despite the extensive global usage of crude oil, to date, the identification of most of the hydrocarbons in crude oil has not been achieved. Instead, when these complex mixtures of organic pollutants are analysed they produce so-called gas chromatographic UCMs (unresolved complex mixtures). We have previously demonstrated that the monoaromatic fraction of a crude oil is environmentally the most important, acting as a non-specific narcotic toxin to the mussel, *Mytilus edulis*. Recently, we have synthesised a variety of monoaromatic hydrocarbons, which appear to 'model' aromatic UCM behaviour, at least in terms of toxicity, aqueous solubility and biodegradability. Since bioresistance is a well-known property of many UCM hydrocarbons, we have compared the susceptibility of the synthetic 'models' and an isolated aromatic UCM to biodegradation by the aerobic bacterium, *Pseudomonas fluorescens*. The results confirm the candidacy of the synthetic compounds as analogues. Using a generator column technique we have investigated the solubility of aromatic fractions of heavily biodegraded crude oil. As oils are complex mixtures of hydrocarbons it is impossible to determine a single solubility value, however, we have been able to determine the most soluble fractions, and identified some of the compounds resolved using this technique.

Oral: Friday/15:00

Transformations of oil-type pollutants in surface soils, alluvial sediments and ground waters affected by microorganisms

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Extractable organic matter was investigated in the samples of alluvial sediments and ground waters (Danube, Pancevo Oil Refinery, Yugoslavia), and in the surface soil samples (fuel storage facilities in Nis, destroyed during the war activities in 1999). On the basis of the amount of extractable organic matter and its bulk composition and according to distribution and abundance of biological markers of sterane and triterpane type, the presence of oil-type pollutant in the samples was detected. On the other hand, on the basis of changes in distribution and abundance of n-alkanes and isoprenoids, pristane and phytane, it was monitored intensity of microbial degradation of oil-type pollutant during a distinct time period depending on depth and on the intensity of interaction with water. The obtained results have shown that degradation of n-alkanes in samples of soil (at the depth of 30cm), sediments (7m) and ground waters (4m) begins in a few days and that it finishes during the period of approximately two years. It is also proved that presence of water, i.e. intensity of interaction between oil pollutant and water, has an effect on intensity of biosynthesis of n-alkanes characterized by pronounced dominance of even-number homologues (C14-C30).

Oral: Friday/15:20

Organic pollutants on hypersaline microbial mats: degradation and physiological implications

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Selected petroleum model compounds (phenanthrene, pristane, n-octadecane and dibenzothiophene) applied on clay to form an organo-clay complex (OCC) were degraded by a submersed hypersaline microbial mat from Eilat (Israel). Within 18 weeks the aromatic compounds were preferentially degraded (phenanthrene (85 %), dibenzothiophene (87 %) compared to the alkanes (pristane (63%), n-octadecane (60%)). Changes in the physiological activity of the mat determined with electrochemical microsensors were not significant. Microbial mats from Guerrero Negro (Mexico) incubated with 20 mg/l of 2,4-Dichlorophenoxy acetic acid (2,4-D) degraded the herbicide within 13 days. The major removal process was microbial degradation in the light and in the dark, but also photochemical breakdown occurred. The phototrophic community of the mat was slightly, but constantly inhibited by the 2,4-D addition, the sulfate reduction in the entire mat and the respiration in the photic zone were inhibited to a larger extent but the effect was reversible as measured with microsensors. From both experiments we conclude that microbial mats possess a potential for pollutant degradation which strongly depends on substance characteristics

Oral: Friday/15:40

DDT degradation in fresh water sediment- effect of elementary iron and temperature

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We have investigated the effect of Fe⁰ and temperature, 9 and 22°C, on the DDT transformation in a contaminated lake sediment. Initially in the sediment the DDT, DDOH and DDD were the dominating compounds, 2.7 µM/g (974 mg/kg), 3.5 µM /g, and 1 µM /g, respectively, which indicate that reductive dechlorination of DDT has been the major degradation pathway in-situ. At both 9 and 22°C the addition of Fe⁰ had a significant effect on the transformation rate of all compounds. After 10 weeks incubation at 22°C the DDT concentration was reduced from 974 mg/kg to 346 mg/kg (64% degradation) and to 702 mg/kg (28% degradation) in samples with and without addition of iron, respectively. At 9°C without addition of Fe⁰, there was no significant transformation for none of the compounds, however addition of iron stimulated the transformation rates of both DDT and the metabolites in a similar transformation pattern as for sediment incubated at 22°C without Fe⁰. Most pronounced stimulation was obtained for degradation of DDT and DDOH, and formation of DDD. Half life time for DDT degradation at 22°C was decreased from 24 weeks to 8 weeks with addition Fe⁰. At 9°C half life time was 36 weeks.

Oral: Friday/16:00

Composition, distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in sediments of the Western Harbour of Alexandria, Egypt

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The composition, distribution and the source of polycyclic aromatic hydrocarbons (PAHs) in surficial sediments of the Western Harbour of Alexandria were investigated. To document the spatial PAH input, surficial sediment samples from 23 locations throughout the harbour were analysed. The total PAH load determined in the surficial sediment samples ranged from 7.9 to 131149 ng g⁻¹ dry wt. Generally, most of the samples having total concentrations of PAHs greater than 5000 ng g⁻¹ dry weight. The highest concentration of total PAHs was recorded in sediments of the inner harbour. Ratio values of specific compounds such as phenanthrene to anthracene, fluoranthrene to pyrene, methyl-phenanthrene to phenanthrene, methyl-dibenzothiophenes to dibenzothiophenes, alkylated to non-alkylated and high molecular weight to low molecular weight PAH, were calculated to evaluate the possible source of PAH contamination in the harbour sediments. However, chrysene and perylene were used as indicator of terrigenous input. Two main sources of PAH in the study area have been found: pyrolytic and petrogenic. Interferences of rather petrogenic and pyrolytic PAH contaminations were noticed for most samples. The dominant sources of PAH appear to be the combustion processes through run-off, industrial and sewage discharges, and atmospheric input. The concentrations of PAHs were generally above levels expected to cause adverse biological effects.

Oral: Friday/16:40

Structure elucidation and quantitation of novel anthropogenic contaminants in riverine systems

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The composition of organic substances in riverine systems reflect both the biogenic and geogenic input as well as anthropogenic contamination. Accordingly, many environmental studies investigate the fate of organic pollutants in riverine water and particulate matter. Of special importance is the knowledge on the molecular characteristics, because most of the natural transport and transformation processes depend on the physico-chemical properties and base therefore on the individual chemical structures. Structure elucidating analyses of organic contaminants in riverine systems are, however, hindered by the occurrence of complex mixtures with often low concentrations of the relevant substances. Therefore, postulated molecular structures revealed by GC/MS-analysis have to be verified, either by specific MS experiments or by comparison of specific analytical data with those of synthetic reference substances. Organic-geochemical analyses applied to samples from the Elbe, Mulde, Havel/Spree, Lippe and Rhine rivers (Germany) using a non-target-screening-approach revealed numerous novel xenobiotics, which were formerly not described as riverine contaminants. The presented talk introduced to the structure elucidation as well as to the environmental distribution of these novel substances (e.g. dinaphthylsulfones, brominated methylhydroxy-acetophenones, dichlorocarbazole). Next to GC and MS data also spectroscopic properties, syntheses as well as proposed emission pathways and technical applications are discussed.

Oral: Friday/17:00

K_{doc} determinations by Semi Permeable Membrane Device to evaluate influence of Dissolved Organic Matter on the PAH bioavailability

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Dissolved organic matter (DOM) has been shown to affect the environmental fate of many contaminants in aquatic environments. Hydrophobic organic contaminants (HOC) as polycyclic aromatic hydrocarbons (PAHs) are bounded by DOM in natural waters. The resulting complexes can potentially alter the fate of PAHs by making them less bioavailable and biodegradable by biological/chemical processes. Quantitative evaluations of the coefficient describing association of HOC with natural DOM (K_{doc}) are thus necessary. - Huckins, J. N. (1993). "Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water." *Environmental Science and Technology* 27: 2489-2496 The first objective was to measure the K_{doc} of fluoranthene, pyrene, benzo(e)pyrene, benzo(b)fluoranthene and benzo(a)pyrene to aquatic humic material from various sources using the Semi Permeable Membrane Device (SPMD). This method used for in situ experimentations to determine water quality (Huckins 1993) has been adapted and validated in our laboratory for this new application. The K_{doc} obtained by SPMD was compared with K_{doc} estimations from bioaccumulation experiments with *Daphnia magna* and with results from the literature. The second objective was to attempt to probe the DOM properties such as aromaticity, molecular weight, SUVA by studying PAH's relative binding intensity to a great number of aquatic DOM.

Oral: Friday/17:20

Environmental sampling of persistent organic pollutants by semipermeable membrane devices (SPMDs)

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The sampling of the persistent organic pollutants in the environment by standard active methods is quite often very expensive and highly experienced operator is needed to get reliable results. The analytical information obtained describes the situation in the sampling place during sampling period. When average levels for defined period are to be obtained, larger amount of samples are to be taken and analysed. Moreover, there is the risk of passing by of the short-time emission events. The passive samplers of SPMD type offer integrative response for the whole sampling period (which is usually from days to months). They are relatively cheap and quite simple to operate. They can be deployed in very remote areas because they don't need electricity. The mechanism of the pollutant uptake by SPMDs mimics the bioconcentration process observed at living organisms, therefore they sample only bioavailable fractions. The weakest point in the SPMD application is the quantitative evaluation. In this study we tried to evaluate the uptake mechanism of polycyclic aromatic hydrocarbons from the air in order to precise the quantitation of the results. Acknowledgement: This work was supported by the grant No. 205/01/0836 by the Grant Agency of the Czech Republic.

Oral: Friday/17:40

Pharmaceuticals in the Austrian environment – Analytical results

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11.567 pharmaceutical products are approved on the Austrian market in 2002. These products contain some 1.800 active ingredients in order to cure illnesses, diseases, pathological ailments, to ease pain, to prevent or to recognise. According to these positive purposes possible environmental hazards have been neglected for a long time. After application pharmaceuticals are excreted by urine and faeces in form of metabolites, conjugates or as unmodified species and therefore access the aquatic environment through municipal sewage and waste water. If these substances are not degraded entirely during waste water treatment processes an impact on the aquatic system cannot be excluded. Selected substances (lipid regulators, analgesics, antiepileptics, antibiotics and iodinated x-ray anticontrast media) were analysed in influents and effluents of Austrian Sewage Treatment Plants (STP) in 1999 and in the rivers Danube and Schwechat in 2001. Analyses were carried out by means of LC-MS/MS. One outcome of that study was that some compounds were reduced between influent and effluent (e.g. Caffeine, 99%), others could not be eliminated (e.g. Carbamazepine) and hence might be of environmental interest. In the Austrian stretch of the river Danube Carbamazepine, Caffeine and Iopromide were detected in all samples (n=10). A first risk assessment for these substances in the river Danube did not result in an acute risk to aquatic organisms.

Oral: Friday/18:00

Sonochemistry of carbohydrates: New improved eco-friendly acetalization of monosaccharides under hydrodynamic or acoustic cavitation

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Consistent with Green Chemistry requirements, natural sugar represent renewable source of basic or fine chemicals. Most of the time, these compounds are used in organic solvents where they are insoluble, under harsh experimental conditions. Ultrasound assisted transformations are improved in terms of reaction rates and yields and even in their chemo-, regio- and stereoselectivities. Recent efforts were brought to extraction and/or depolymerization of polysaccharides either in heterogeneous or homogeneous media, leading in particular to a potent anti-HIV derivative. Other synthetic sugar based compounds proved to exhibit interesting biological activities, such as new water soluble C-meso-glycosylated metalloporphyrins. Thus, acetalization is a frequent preliminary transformation in multistep syntheses from mono- or disaccharides, requiring a simple, mild protocol with high yields. However, the heterogeneity of the initial medium, in most cases, contributes to making the usual reactions slow. We turned our attention towards the synthesis of diisopropylidene and dicyclohexylidene acetals of glucose and mannose assisted by Ultra-Turrax (24 rpm) or 30 kHz horn. Although these two activations has been studied in homogeneous reactions, only few papers were dedicated to heterogeneous ones, especially in sugar chemistry. Ultra-Turrax assisted acetalization is the best method leading notably to 2,3:5,6-di-O-cyclohexylidene- α -D-mannofuranose in only 6 minutes instead of 60 minutes in a cleaning bath or 16 hours with shaking.

Oral: Saturday/8:00

New TiO₂-SiO₂ SBA mesoporous solids: characterization and application to the catalytic selective epoxidation of alkenes

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Selective epoxidation of alkenes by tert-butylhydroperoxide (TBHP) on solid catalysts containing titania is a non pollutant reaction after which the produced tert-butyl alcohol can be easily recycled to TBHP. Catalysts constituted of anatase TiO₂ deposited in the internal pores (diameter 40 to 70 Å) of mesoporous SBA silica were prepared under gas phase conditions with TiCl₄ as titanium source. Conditions of the deposition: composition and flow rate of the TiCl₄-N₂ gaseous stream, temperature of the deposition (200 to 400°C) and grafting time (0.5 to 32 h) determine the amount of TiO₂ deposited and its dispersion. These catalysts were characterized by chemical analysis, porosimetry by N₂ adsorption, X-rays diffraction, XPS, IR and UV-Vis spectrometries. Yield for the epoxidation of natural products (limonene, alpha-pinene) and cyclooctene reach 100% within 3 hours with 100% selectivity. Moreover we did not observe any leaching of titanium species after several cycles of reaction. Cyclohexene epoxidation was shown to be selective and allows to consider this alkene as a possible starting material for green production of adipic acid.

Oral: Saturday/8:20

Abatement of polyphenols in industrial waste-water: identification of new demethylating enzymes and their potential use in synthetic chemistry

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Phenolic compounds are widespread pollutants either as primary constituents of the agrochemical industry wastewater (olive oil, sugar, others) or as species naturally occurring in soil from lignin degradation. We have used a combined technology (anaerobic-aerobic biological degradation) for the digestion of organic compounds present in olive-mill water. We have shown that polyphenols, and methylated phenols are recalcitrant to such treatment. We have, thus, investigated the ability of bacteria that are able to metabolise phenol to adapt to grow on methoxy-substituted phenolic compounds and shown that this requires the expression of an O-demethylating enzyme. Such enzymes are able not only to demethylate polyphenols but, in combination with reduced cobalamin, as methyl transfer agent, they can be used for transferring the methyl group to other substrates. This ability has been used for the synthesis of methylated organic substrates using natural methylated phenols as methyl source.

Oral: Saturday/8:40

Green Fenton chemistry for removal of toxic organics from process wastewater

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Wastewater contaminated by unwanted organic compounds produced as by-products from dyestuffs syntheses poses a major problem in disposal as they are often too toxic for normal sewage treatment. Currently, many companies are using waste disposal companies to transport this toxic waste to landfill. However, this is a far from satisfactory solution as landfill costs are set to rise dramatically and secondary pollution is caused by transportation of the waste. The ideal situation would be where the by-product is eliminated entirely but this is often impossible due to processing parameters. The next best scenario is to treat the waste stream in situ and render it innocuous before it is sent downstream for normal disposal. Recently we have been investigating a novel process for the in-line purification of water polluted with organic compounds. This new system, which we call the Advanced Fenton Process, utilises the catalytic application of iron metal in conjunction with hydrogen peroxide to produce a high flux of hydroxyl radicals which are capable of destroying even the most recalcitrant of organics found in wastewater. This talk will concentrate on the degradation of phenol using the AFP and recent results, which have identified the numerous intermediates in the degradation.

Oral: Saturday/9:00

Removal of organophosphorus pesticides from water by electrogenerated Fenton's reagent

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Organophosphorus (OP) insecticides have become one of the most widely used groups of pest control chemicals. The toxicity induced by OP compounds results in rapid twitching of voluntary muscles and finally paralysis. The wide use of organophosphorus pesticides has created several problems, including the pollution of environment by pesticide manufacturers. Considerable effort has gone into assessing the risks of various OP insecticides. Unfortunately, people are often exposed to different OP insecticides in different dosages at different or overlapping times. In the goal to clean up wastewater containing organic toxic matter, many techniques are used. Among these, Advanced Oxidation Process (AOPs) have been successfully applied in degrading the organic compounds present in polluted water. In AOP, hydroxyl radicals (HO^\bullet) which are generated in solution, oxidize organic pollutants into their mineralization. The Electro-Fenton process is one of AOPs. In this process hydroxyl radicals (HO^\bullet) are generated through electrochemically assisted Fenton reaction. In this work we show the efficiency of the Electro-Fenton process to degrade three organophosphorus insecticides: malathion, parathion and tetraethyl pyrophosphate. The degradation kinetics and the COD removal have been investigated.

Oral: Saturday/9:20

Ozone wastewater treatment enhancement with ultrasound

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Organic matter treatment is becoming problematic due to the complex chemical structure of xenobiotic compounds. Classical techniques are not sufficiently efficient and new engineering is required. Methods based on the generation of very reactive species like hydroxyl radicals which conduct to fast and non-selective oxidation of the organic matter, become attractive. Ozonation, ultraviolet irradiation, ultrasonics, Fenton oxidation, etc are the most useful Advanced Oxidation Technologies. Despite some primary results which confirm the enhancement of degradation efficiency, ozone combination with ultrasound has received little attention. Our work try to understand the interactions between ozone dissolution and ultrasonic effects in order to optimize the method. Results show an increase of oxidative species due to the dissolved ozone decomposition under ultrasound. The process was found dependant of ultrasonic frequency and power. If an equilibrium is reach between dissolved and gaseous ozone, hydrogen peroxide formation which characterize radical activity does not seem to be regulated. This combined technique exhibits high efficiency towards refractory organic compounds degradation. Hydrophobic fluorinated compounds which are resistant to the other methods are degraded by this way. Acknowledgement: This work is supported by Programme AVENIR Région Rhône-Alpes and Blanchon Syntilor company.

Oral: Saturday/9:40

Application of high rate ballasted flocculation technology for storm flow treatment

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Water Companies are being challenged to eliminate all discharges of untreated wastewater caused by combined sewer overflows. Wet weather inflow and infiltration, combined with urban development and deteriorating infrastructures, have overloaded collection systems, severely straining downstream wastewater treatment plants which leads to overflow events with little or no treatment. Significant risks to receiving water quality, public health and aquatic life can occur due to these wet weather events. An innovative treatment technology to address wet weather events is the ballasted flocculation process. The principal benefits of a ballasted flocculation treatment system for wet weather flows include vastly reduced space requirements, rapid start-up and response times, relative insensitivity to fluctuations in raw water quality, and removal rates greater than conventional systems. The OTVB pilot study protocols consisted of a number of phases, with a minimum of two storm events each week. The various types of operating regime included the investigation of buffered and unbuffered (direct) storm flushes, the trials of various coagulants and polymer. With high levels of solids removal in a compact footprint, the Actiflo process provides a cost competitive alternative to the conventional design brief of two hours storage for treating storm flows.

Oral: Saturday/10:20

Innovative methods for treatment of hazardous waste

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The present trend in industrial operations is to minimize or eliminate the waste volumes generated from these activities for both cost efficiency and environmental compliance reasons. Several innovative low-cost technologies have been recently developed that address these issues in waste minimization. These technologies include non-aqueous precision cleaning techniques for removing micro-contamination. A precision disassembly system employing advanced microabrasive technology to recover precious metals and remove hazardous materials from complex small parts. A simple optimized decontamination system for surface-contaminated metals with a precision sampling technique to measure the effectiveness of the decontamination process. A universal low temperature oxidative method that effectively removes mercury contamination from a wide variety of waste materials. And a new thermal treatment process for recycling of mercury-containing fluorescent lamps. Details of these processes and their advantages and limitations will be described, and results from specific applications will be discussed. Direct comparison with current commercial treatment processes for comparable applications shows the overall unit costs (capital, administrative, operating, and waste disposal costs) for most of the present methods to be at least 30 to 50% lower, while meeting or exceeding emission standards.

Oral: Saturday/10:40

Catalytic decomposition of perfluorocompounds (PFCs)

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Reduction of global warming gases released into the atmosphere is becoming an essential task in semiconductor industry. We have developed a PFC decomposition system that utilizes a highly active and stable catalyst. The catalyst requires only water and air as reactants. CF₄, CHF₃, C₂F₆, C₃F₈, C₄F₈, C₅F₈, C₄F₆, NF₃, SF₆ are decomposed by more than 99%. Such gases as CO, NH₃ and CH₂F₂ can also be abated efficiently. Our catalyst forms only CO₂ and HF as decomposition products of carbon-based PFCs, and HF is effectively removed by water within the system. In addition to the above features, our catalyst retains high performance under high concentration of PFC as demonstrated by a continuous run for about 4000 hours. This allows treatment of exhaust PFC from etchers using energy-saving N₂ purge systems resulting in high concentration PFC. We present here some of the fundamental data obtained in the laboratory and the actual data taken by a FT-IR analysis method during the treatment of semiconductor etcher effluent gas with our commercialized catalytic decomposition system.

Oral: Saturday/11:00

Biodegradation of chemicals in soil at presence of natural adsorbents

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One of the reasons of low effectiveness of soil bioremediation is high toxicity of the chemicals to microorganisms and plants. The objective of our research is to extend application of soil bioremediation through introduction of natural adsorbents reducing the biotoxicity of the chemicals. The experiments were carried out with various soils, chemicals and several adsorbents in laboratory and out door conditions. It was demonstrated that adsorbents decrease chemical concentrations in soil solution and so create favorable conditions for growth of degrading microorganisms. Meantime, the chemicals mostly remain available for microbial transformation due to reversible adsorption. Some chemicals (chloroanilines, phenols) are totally degraded by specific microorganisms. The others (2,4,6-trinitrotoluene and polychlorinated biphenyls) are transformed to products, which are strongly bound to soil matrix. In addition, the influence of some adsorbents on soil properties and fertilities were also studied. It was indicated that some adsorbents decrease soil bulk density and water evaporation and simultaneously increase water holding capacity, soil porosity, aeration. Therefore the introduction of some adsorbents does not influence negatively on soil properties, while high doses of other adsorbents could substantially decrease soil fertility. Thus, the adsorbent applications should be careful with due the regard of their influence on soil properties.

Oral: Saturday/11:20

Zinc aluminogallate spinel catalysts for NO reduction by hydrocarbon under oxygen- rich conditions

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Zinc aluminogallate fine powders with a single phase of spinel were synthesized by a co-precipitation method from a mixed solution of nitrate salts in the presence of aqueous ammonium carbonate. This powder was tested as a catalyst for NO reduction in the presence of water vapor and sulfur oxides for very long service periods. High durability was observed for the reduction of NO by C₂H₄, maintaining a high stability for over 100 h. The catalytic activity of spinel powder increased with an increase in ZnO loading up to 30-mol% and then decreased after that. It was evidenced that activity and selectivity of the investigated materials could be qualitatively correlated with the part of the strong acid centres measured by TPD of NH₃. The catalytic properties of zinc aluminogallate spinel make them an advanced material suitable for NO_x elimination from the exhaust of diesel engines.

Oral: Saturday/11:40

The fate of six polycyclic musk compounds and one metabolite thereof in a representative Swiss waste water treatment plant

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Sewage sludge contains nearly all important compounds originating from the antroposphere and can therefore be considered as a mirror of our society. This property is used in the SEA project (observation of the metabolism of the anthroposphere) that aims to monitor the emissions from the anthroposphere and the release to the environment by observing the flux in sewage sludge. Polycyclic musks, which are used as fragrances in detergents, softeners and cosmetic products are presently studied. Monitoring of these compounds requires known transfer coefficients from waste water to sewage sludge. These coefficients were established for six polycyclic musk compounds (Galaxolide, Tonalide, Celestolide, Phantolide, Traseolide and Cashmeran) in a Swiss waste water treatment plant by analysing different water and sludge samples. Calaxolidone, a metabolite of Galaxolide, was analysed in order to monitor possible degradation. The results of the analysis of 21 water samples showed that polycyclic musk concentrations decrease by about 75% during the waste water treatment process, whereas the metabolite's concentration remains stable. No correlation between the concentrations of the different compounds in waste water could be established, indicating that dissimilar mixtures of polycyclic musks are used. Results from the sludge analysis will be presented and discussed at the conference.

Oral: Saturday/12:00

Ozone deposition over maize and wheat-straw in nighttime and daytime conditions from eddy correlation measurements

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Tropospheric ozone (O₃) has deleterious effects on vegetation affecting plant stomatal functioning and photosynthesis. Understanding the mechanisms of ozone deposition to vegetated surfaces is therefore of primary importance. One key question is to distinguish stomatal from non-stomatal pathways. In this sense, an experiment was carried out from late June to mid-October 2002 in an agricultural area near Paris, France, where among other measurements, O₃ fluxes were measured, by eddy-covariance, simultaneously over a maize crop and a wheat-straw field. On both surfaces, nighttime ozone deposition velocity (Vd) is correlated with the friction velocity u* however the ratio Vd / u* is strongly dependent on the relative humidity RH. A simple parameterization of nighttime Vd as a function of u* and RH has been established for each site. This parameterization has in turn been used to estimate the "non-stomatal" component of the daytime deposition velocity in order to compare it with the measurements of Vd. Preliminary results suggest that daytime ozone deposition over the wheat-straw remains essentially controlled by u* and RH, whilst stomatal control dominates ozone deposition over the maize crop. Results will be presented following a more detailed analysis, aimed at quantifying precisely the stomatal and non-stomatal components of daytime deposition velocity.

Poster: AtCh-1

Assessing air quality in urban areas using a GIS

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Air quality degradation results from a wide variety of human activities, either past or ongoing. Monitoring and assessing the air quality should be considered for two reasons. Most of the polluted sites are closed to urban communities, and sometimes they are even completely surrounded by highly populated areas. Populations and environmental groups put pressure on public authorities and they ask for air quality improvement. Atmospheric inventories are an essential tool in the management of local air quality. They allow to examine the geographical distribution of pollutants across a region and to assess the relative significance of different sources of air pollution. The paper will present firstly the problematic of environmental management in urban areas and the application of GIS (Geographical Information System) as a tool for data collection and analysis. The overall goal of this study is to develop an integrated monitoring system, a supporting spatial data set for evaluating the air quality in urban areas. Specific objectives of this study included: determining the values of pollutant concentration in air, categorizing parcels as to their vulnerability and establishing measures for air quality improvement based on the above analyses. The results of this study will be used to demonstrate the utility of such an analysis tool in implementing a monitoring program for air quality in urban areas.

Poster: AtCh-2

Chromato mass spectrometer for research of substances polluting the atmosphere

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Now it is established, that the basic sources of the atmosphere pollution except transport are Industrial Companies. An ecological status of Baku and other industrial cities of Europe isn't consolatory. Concentration of NO_x, CO₂ and C₅H₄O₂ exceed maximum concentration limit in 10-15 times. The registration of these substances polluting an atmosphere on the level of maximum concentration limit in sight of the big quantity of preventing substances is difficult. On this methods of the analysis of these substances should possess with the high sensitivity, specificity both self-descriptiveness and identify the wide scale of substances at the level concentration of 10⁻⁵ – 10⁻⁷ %, and sometimes lower. The most sensitive method to the listed characteristics is the Chromato Mass-spectrometer one with its high resolution, high sensitivity and reproducibility of the results. As a Mass – spectrometer we had used the Time of Flight principle of division of ions in axial-symmetric electrical field, a corner of turn of ions in which makes 254°. Due to good dividing properties of the gas-liquid Chromotograf the problem of imposing of the mass - spectra of complex components is solved. An opportunity of such symbiosis is, that on separate components accounting sensitivity reaches 10⁻¹⁰ – 10⁻¹¹ %.

Poster: AtCh-3

Tropospheric oxydation of benzen with the radical hydroxyl: The rate constant [297-383]

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The rate constant K1 of the reaction of hydroxylradical with benzen has been mesured by the dicharge flow technic with detection of OH by resonance fluorescence and photon counting. The mesurements are performed between 297-383K temperatures in the fall of pressure rang of heliumbetween 0.5-10 Torr. The parameters K0 and Koo of the true formalism are derived.

Poster: AtCh-4

Automobile emissions measured at its source in a road tunnel near Paris

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We are studying the physico-chemical evolution of urban air pollution. Field campaigns on various issues are performed continuously and new laboratory experiments are currently developed in our laboratory. I will present results obtained during a recent field campaign: The physico-chemistry of the particulate French automotive emissions have been studied in real circulation conditions in a road tunnel (under La Défense, A14). Pollutants from such a site are not photochemically processed and thus represent the original emission at its source. Furthermore, the wide distribution of car types encountered in real circulation conditions assures representativity of the (French) car park. In France, the proportion of Diesel engines is bigger than in other industrialised countries. After sampling, the concentration of 16 PAHs and their Gas/Particle partitioning was determined by GC-MS analysis. Particulate concentration of some elements were determined using X-Ray fluorescence methods. Temperature, relative humidity, wind speed as well as CO and NO_x levels were also monitored. The results show clearly that volatile PAHs exhibit a bimodal size distribution. In contrast, less volatile PAHs, like benz(α)pyrene or benzofluoranthene, are found only on fine particles. These and other results will be discussed and compared to similar campaigns in other countries.

Poster: AtCh-5

Determination of enantiomeric monoterpenes in terrestrial plant emission and in the atmosphere using b-cyclodextrin capillary chromatography coupled with thermal desorption and mass spectrometry

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For the first time, enrichment on solid sorbents followed by thermal desorption has been used for the determination of the enantiomeric signature of monoterpenes in the gaseous emission of terrestrial plants. A b-cyclodextrin capillary column has been used for the separation of critical pairs. The temperature program and column loading were optimized for making the accurate quantification of individual enantiomers possible by mass spectrometry. The resolution achieved was sufficient for separating enantiomeric monoterpenes from other biogenic and anthropogenic VOCs present in air and vegetation emission samples. The method has been applied to the determination of the enantiomeric ratios (ERs) of monoterpenes in the gaseous emissions of some evergreen plants and in the open atmosphere.

Poster: AtCh-6

Application of $\delta^{18}\text{O}$ water analysis on the study of hydrological renewal in an Alpine Lake (Lago della Serrai, Trentino, Italy)

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The alpine Lake of Serrai (S = 0.44 km², V = 3 million m³, z_{max} = 17 m), located in a table-land at 1000 m asl and with a tourist relevance, has been recently involved in some massive events of eutrophication and consequently largely investigated. $\delta^{18}\text{O}$ water measurements were used to study the hydrological renewal of the lake and the possible vertical water movements during thermal stratification. Both the lake on two water columns at the points of maximal depth and the main tributary waters (surface and underground ones), have been checked for some years. The $\delta^{18}\text{O}$ parameter appeared useful for our aim, not being significantly influenced by the biotic activity of the lake. Conservative trends along the years of the isotopic values have been ascertained. Interesting considerations on the summer renewal of the hypolimnion during the summer resulted. These waters do not seem to be influenced by exchange with epilimnetic waters, but renewed by tributary waters, probably by the underground ones.

Poster: Stls-1

Stable isotope geochemistry of Pleistocene travertines from Budakalász (near Budapest, Hungary)

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The principal goal of this work is to carry out a detailed C and O stable isotope study on the Budakalász travertine. Minissale (2002) suggests that travertines may preserve a valuable record of paleofluid composition and paleoprecipitation. Therefore, the fossil offspring deposits have a great significance in paleohydrological and paleoclimatological point of view. The original C isotope ratio could be calculated from the CO₂ isotope ratio of the travertines using the equation suggested by Panichi and Tongiorgi (1975) on the basis of Italian thermal springs and associated travertines (Minissale, 2002): $\delta^{13}\text{C}(\text{CO}_2) = 1.2\delta^{13}\text{C}(\text{trav}) - 10.5$. The two facies types of travertine can be distinguished on the basis of data from the isotope study. According to the classification system of Pentecost (1995), the travertine can be thermogene or meteogene. In the Budakalász travertine the $\delta^{13}\text{C}$ values are between those of thermogene and meteogene types. The thermogene travertine, showing massive texture and with low organic material content, deposited from high-temperature thermal springs. The meteogene travertine is soft which formed low-temperature springs and is characterized by high organic material content. Selected travertines were analysed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ using Finnigan 250 Delta-S mass-spectrometer at University of Florence.

Poster: Stls-2

Origin and atmospheric flux of Upper Carboniferous and Lower Permian methane in Poland: isotopic approach

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Methane is an important greenhouse gas. Recent studies indicate that coal mining, natural gas ventilation and gas transmission losses are one of the greatest causes of a total annual global flux from all sources. The main objectives of the present study are to compare stable carbon isotope composition of methane from Lower Permian gas fields and Upper Carboniferous coalbed methane from Polish basins with the atmospheric methane, evaluate the quantity of methane flux in specific areas and assess the importance of various controlling natural (geological, as faults and outcrops) and human activity (coal mining, ventilation, production, transportation and distribution) factors that influence the flux. Stable carbon isotope composition of methane from the Upper Carboniferous coalbed gases and Permian natural gases in Poland are highly variable and change from -79.9 to -24.6‰ and from -34.6 to -23.4‰, respectively. Isotopic studies reveal the presence of two genetic types of Carboniferous coalbed methane: thermogenic and microbial, and only thermogenic type of Permian methane, generated at least during two separate phases. Stable carbon isotope composition of atmospheric methane sometimes allows flux sources to be distinguished. The research was partly financed by State Committee of Scientific Research (Grant No. 9 T12B 026 19).

Poster: StIs-3

¹⁴C-age of urban grasses as an indicator of fossil fuel CO₂ pollution

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Measuring the amount of fossil fuel carbon stored in the vegetation by CO₂ photosynthesis is crucial to understanding the mechanisms ruling climate changes. In this respect, highly polluted areas such as major towns represent "natural" laboratories because fossil fuel CO₂ (¹⁴C-free) is isotopically distinct from mean atmospheric CO₂ (¹⁴C-labeled). A ¹⁴C study of urban grasses shows that plants store up to 13% of fossil fuel carbon, and that fossil fuel CO₂ pollution is unexpectedly highly stratified. ¹⁴C composition of urban grasses is thus a novel parameter to assess the impact of fossil fuel derived CO₂.

Poster: StIs-4

Natural ^{15}N abundance in two Nitrogen saturated forest ecosystems at Solling, Germany

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This research deals with a comparative study of two different N-saturated forests such as beech and spruce forests at the same location of Solling, Germany. The present results show that ^{15}N natural occurrence in the rainfall (both above and below canopy) at the site of Solling is similar ($^{15}\text{N} = -15\text{‰}$ to $+19\text{‰}$) to other sites of the world (such as NITREX sites, USA etc). Furthermore, ^{15}N values in the soil water ranged from $-4.32 (+2.09)$ to $+5\text{‰} (+1.47)$, which also corresponds to the NITREX sites and other sites of Europe and USA. In the both forests, ^{15}N enrichment of both $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ showed a decreasing trend of their values from bulk precipitation to upper soil layer, but increasing again in the deeper soil layer. The mineral soils at the both sites showed characteristic low (negative) ^{15}N values in the organic layers, increasing strongly in the mineral soil to positive ^{15}N values.

Poster: St/S-5

Stable and radioactive isotopic approach of natural sparkling water sources

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Considering the necessity of knowledge pathways by which natural sparkling water moves from its origin over and through the ground to streams and also the possible interaction between its pathway and other water sources in the area, an extensive isotopic monitoring of Borsec hydrologic catchment has been done. The entire monitoring activity has been started two years ago, with the entire cycle - sampling, preparing and analyzing for Deuterium, Tritium and Oxygen-18. In order to define an adequate discussion basis, all the values have been considered in correlation to a geographical informational system -a spatial database for Borsec area. In a such way, iso-concentration curves have been plotted on a hydrologic map for above-mentioned area. For every sampling point, shown on the map, the temporal dependence of concentration values has been associated separately for Deuterium, Oxygen-18 and Tritium. Based on the built mapped isotopic database, consideration about the water sources separation and time residence of water in the ground has been made, in a visual special application.

Poster: St/Is-6

Activated sludge exopolymers separation and identification using size exclusion chromatography and infrared micro- spectroscopy

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Extracellular polymeric substances (EPS) were extracted from activated sludge from wastewater treatment plant by resin exchange method and analyzed. The separation and identification of EPS were carried out using size exclusion chromatography in connection with Fourier Transform Infrared Micro Spectroscopy (μ FT-IR). Chromatogram of extracted EPS exhibited seven peaks of different molecular weights from 670 to 45 kDa, with majority of macromolecules within 67 – 200 kDa range. Moreover, all the polysaccharides had very small sizes < 1 kDa and were less represented than proteins. Strong association of polysaccharide and protein was observed. Infrared results revealed the presence of several types of polysaccharide, proteins, organic acid and salt organic acid. Protein differed mainly in the length of their alkyl chains up to 12 CH₂ and in ratio of ester/acidic functionalities

Poster: CoOM-1

Diffusion limited sorption by microporous hydrous ferric oxide: A matter of pore sizes

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Hydrous ferric oxide plays a significant role in the sorption of organic and inorganic contaminants in soils, aquifers and aquatic environments. The mineral forms so-called microporous aggregates: to reach the surface sites, the sorbates must diffuse through pores of nanometer (and subnanometer) size. Diffusion controls the sorption kinetics. Analysis of the pore size distribution of hydrous ferric oxide aggregates shows continuous, probably fractal distribution, whereby the intermediate range of pores (order of magnitude 2 to 6 nm) represents a major portion of the total porosity. These pores are large enough to allow free motion of ions but small enough that the surface electrostatic forces exert an influence on the whole pore volume. We have developed a model specific for this range of pores. It combines surface complexation and intraparticle diffusion. The model determines ion concentrations in the pores by imposing the condition of electric neutrality on the pore wall/ pore space system and by relating the concentrations in the pore solution and bulk solution by a Boltzmann factor. On the basis of experimental data we will discuss validity of the novel diffusion model.

Poster: CoOM-2

Release and transport of colloids from the unsaturated zone under natural conditions: a lysimeter study

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Release and redistribution of organic colloids is controlled by the flow regime. Colloidal phase components play an important role in transport of strongly sorbing solutes. Organic colloids like humic substances, viruses, bacteria, fungi, etc., may act as possible sorbents for hydrophobic contaminants and thereby increase their mobility in natural porous media. It is therefore mandatory to study the release, transport and immobilisation of soil-borne colloids in order to assess the risk for colloid deep seepage and groundwater pollution. The natural soil hydrological regime shows strong temporal variations, ranging from fast downward flow events to stagnation or even reversal of flow direction, according to the amount and distribution of precipitation and evapotranspiration. To study the mobilisation and transport of DOM in soils in response to the climatic conditions, we installed 10 natural gradient lysimeters. Colloid release behaviour was monitored event triggered for two years. Results show increased export rates immediately after dry periods. At the same time, the EC is lowered, and the turbidity of the seepage water increases. Dispersion of the flocculated colloidal DOM, micro-erosion, and rate-limited release of DOM are important processes which control the fate of organic colloids in soils under natural flow conditions.

Poster: CoOM-3

Molecular dynamic study of the order-disorder transition in schizophyllan

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Schizophyllan is a natural beta-(1,3) glucan polymer with branched beta-(1,6) residues, which is of environmental, medical and industrial interest. This polysaccharide forms a triple helix in aqueous solution, with the branched lateral residues directed towards the outside. It has been shown experimentally that schizophyllan undergoes a highly cooperative order-disorder transition around 7 degrees C in water. Although it is known that the transition involves the lateral glucose residues and tightly-associated water molecules, its detailed mechanism is yet unknown. Four molecular dynamics simulations of a schizophyllan fragment at two temperatures and with two different boundary conditions have been performed in order to investigate the mechanism of this order-disorder transition.

Poster: CoOM-4

On-site measurement of colloid size distribution in surface water by using single particle counter: a new tool for aggregation kinetic studies

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The unstable nature of the natural colloids and the difficulties to keep samples unchanged between the sampling site and the laboratory call for measurements of colloid characteristics on-site. The use of a single particle counter system (SPC) enable the rapid determination of colloid size distribution and number concentration in various surface waters, with the possibility to perform on-site measurements. The number concentration measurable without any pre-treatment ranges between 10^4 to $8 \cdot 10^8$ ml⁻¹, distributed into 19 size classes between 50 and 2000 nm. This covers most of the concentrations encountered in natural waters. Batch experiments on salinity effects have been performed on samples from the Vistula (Poland), a river contaminated by salty mining drainage waters. Elapsed time between sampling and measurement ranged from 1 to 2 hours. NaCl addition (35 mM) in samples having low ionic strength (1.6mM NaCl-equivalent) induces a marked aggregation of colloids, whereas such addition to downstream waters containing 9 mM NaCl-equivalent induces a very minor change only. This shows that aggregation already occurred in the river as a result of the change in the ionic strength due to the mine water discharge, and any addition of salt has only a small effect on the aggregation.

Poster: CoOM-5

Quality of humic acids extracted from artificial composts. FT-IR and ¹³C-RMN study

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This study is aimed at characterizing humic acid-like of composts prepared from domestic organic wastes (HADu), sawdust (HASc), used coffee (HACf) and farmyard manure (HAFm). An integrated approach using elemental analysis, UV-Vis and Transform infrared, fluorescence and liquid state ¹³C NMR was applied to characterize these substances. Elemental analysis and E4/E6 ratio give values close to those characterizing young humic matter. Nitrogen content was very related to that of the initial waste being high for HADu and HACf and low for HASc and HAFm. FT-IR and ¹³C NMR spectra showed that HADu and, at less extent, HACf were more aliphatic and dominated by N-containing groups while HASc HASc and HAFm were characterized by high substituted aromatic groups and lignin's structures. Fluorescence spectroscopy was not able to detect differences between the studied humic acids. However, the presence of high amino groups content, low degree of aromatic polycondensation and simpler structural components were common characteristics of all the HA. In conclusion, this study gives evidence for the great influence of the composition of the parent material on the chemical and functional composition of HA obtained by composting process. Environmental and agricultural effects of composts should be viewed in this context.

Poster: CoOM-6

Fulvic acid models generated by computer – comparison to experimental elementary analysis and mass distribution

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Humic substances represent one of the major natural organic matter fractions in freshwaters. They are expected to control the possible interactions among the different types of organic and inorganic aquatic colloids. To understand the role of humic substances in microscopic processes such as complexation, adsorption, and coagulation, structural models must be developed at the atomic level. In addition, as no unique and universal structure exists to our knowledge, series of humic structures must be generated by using judicious physico-chemical and mathematical rules. To generate statistical series of structures, a program called FULVITOR is used. To build a structure the program is used to connect fragments which are randomly selected in a fragment database with various chemical groups. Results of Suwannee River fulvic acid analyses are used to define a specific fragment database. The comparison of elementary analysis and mass distribution obtained from these series of structures and the experimental results is discussed

Poster: CoOM-7

Abundance and chemical features of organic matter in particle size fractions of a forest soil

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Soil organic matter (SOM) plays a major role in carbon and nitrogen cycle. Three kinetic pools are usually distinguished in SOM, the most stable exhibiting residence times up to millenia. Physical protection by minerals is often considered as responsible for this stability. However soil constituents like black carbon exhibit a high intrinsic resistance to biodegradation. To examine the features and relative importance of these two stabilization pathways, detailed information is required on SOM composition in different particle size fractions. Three particle size fractions (sand, silt and clay) were separated from a forest soil. Each fraction was submitted to lipid extraction, fulvic and humic acid removal and acid hydrolyses including HF/HCl. The remaining insoluble residue, i.e. the non-hydrolysable refractory organic matter (ROM) was submitted to chemothermal oxidation to isolate the black carbon. Lipids were analysed by GC/MS and ROM by spectroscopic methods. Lipids are relatively more abundant in the clay fraction whereas ROM and black carbon mainly occur in the silt one. Comparison between the three fractions points to strong similarities in composition between the silt and clay fractions although a relative decrease in carbohydrate content and an increase in aliphaticity is noted from the silt to the clay.

Poster: CoOM-8

The role of fulvic acids on colloidal aggregation

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In recent years, considerable progress has been made in understanding the mechanisms of polymer-induced colloidal aggregation, largely as a result of experimental studies with model systems. In this study we have systematically examined the coagulation kinetics of hematite induced by increasing salt (KCl) concentrations in presence and absence of fulvic acids (FA). KCl concentrations between 10 and 250 mM were studied for a colloid concentration of 10 mg.L^{-1} and a FA concentration of 5 mg.L^{-1} . In presence of FA stability curves determined as a function of ionic strength, were displaced towards more stable systems. pH also played an important role as systems were much more stable under alkaline pH conditions. Photon correlation spectroscopy (PCS) was employed to follow the evolution of aggregate size. The structure of the aggregates formed were determined using static light scattering (SLS) and transmission electron microscopy (TEM) and quantified via their fractal dimensions.

Poster: CoOM-9

Modeling organic-colloid transport and organic-colloid assisted transport in soil

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Colloidal organic matter (COM) has been shown to strongly affect contaminant fate in porous media. Research has mainly focused on processes leading to mobility enhancement of pollutants. Carrier facilitated mobility of contaminants applies only to such environmental conditions where the COM have to be considered a non-reactive mobile-phase constituent, i.e., neither sorption nor partitioning of COM to the immobile solid phase occurs. This is specifically the case for porous media which is either in sorptive equilibrium with COM or has unfavorable conditions for COM sorption. The presence of COM may also lead to reduced contaminant mobility due to immobilization of COM and thus of the COM-associated contaminants. The scope of the present paper is to elucidate the effects of mobile organic colloids on the flow and transport of solutes and on other porous media parameters. This knowledge is of prime importance for an accurate prediction of contaminant fate and for the interpretation of laboratory and field scale breakthrough data. We will employ experimental data and numerical case studies based on simulation scenarios in order to analyze the competing processes, to discuss their properties and to derive conditions favourable for enhanced or reduced mobility of contaminants in the presence of COM.

Poster: CoOM-10

Soil ecotoxicity testing with the collembola *Folsomia candida*: early detection of effects through biomarkers

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The effect of xenobiotics on soil invertebrates needs to be assessed as they play an important ecological and functional role in the soil. However, the evaluation of sublethal effects usually implies test designs of several weeks. The aim of this study was to investigate the effects of the pesticide dinoseb on life cycle parameters and biomarker responses of the springtail *Folsomia candida* (Collembola) in order to establish a relationship between short term (biomarkers) and long term effects (reproduction). Juveniles were exposed to artificial soil contaminated with dinoseb. At different time intervals, mortality, reproduction, length, lipid and protein content, weight, and Hsp70 induction were determined. After 6 days of exposure, the biomarker levels were increased in the exposed organisms compared to the control. This stimulation seems to indicate that collembola exposed to dinoseb adopt a strategy consisting in stimulating their growth in order to reach sexual maturity more rapidly. Temporal analysis showed that after 21 days most biomarkers decreased. In the case of dinoseb, the selected biomarkers do not allow to detect an effect at a lower concentration than the classic endpoint reproduction, but the observed stimulation can be a pertinent early effect indicator.

Poster: Ecot-1

Re-evaluation of the potential risk of systemic insecticide to non-targeted insect species

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Systemic insecticides were launched from the middle of 1990's. Because they were considered only as soil and seed treatment, they were not subjected to the full evaluation procedures, especially concerning the possible effects on pollinators such as honeybees. In the case of imidacloprid and fipronil, bees appeared as very sensitive to low dose of the toxics during their foraging activity. Sub-lethal effects on feeding occur in the range of a few µg/kg from a contaminated source. Studies related to the sub-chronic toxicity also reported that imidacloprid induces about 50% mortality after a 8 day exposure period at 0,1 µg/kg. Besides, new analytical developments shown that nectars and pollens are contaminated with such low levels of imidacloprid, especially in the cases of sunflowers and corn. Here, the averaged values are 3 and 3.5 µg/kg in pollens of sunflower and corn, respectively. More or less severe clinical signs were also observed in the case of fipronil with a contamination of the feeding source at a few µg/kg. The risk was then re-evaluated with a PNEC/NEC ratio in the range of 1 to 10. Such value reports on a probable situation of hazard for bees foraging in field conditions applying in the cases of sunflowers and corn crops.

Poster: Ecot-2

Trichloroacetic acid behaviour in forest and agricultural soils

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Trichloroacetic acid (TCA: CCl₃COOH) is a phytotoxic chemical detected in all environmental compartments. As well as direct atmospheric deposition of TCA to soil, it may also be produced and degraded within the soil. The behaviour of TCA in soils is poorly characterised yet the soil is believed to be the key to understanding TCA cycling in the environment. Uncertainty is due, in part, to the absence of a direct whole-soil analytical method specific to TCA. Using a decarboxylation to chloroform method on soil spiked with TCA we have demonstrated complete mass balance but that only ~20% of TCA is recovered by aqueous extraction. Field surveys at Scottish upland forest and moorland and lowland agricultural soils show that TCA concentrations decrease with soil depth, the highest concentrations (400 ng g⁻¹ fwt) occurring in litter layers under Sitka spruce forest. Using lysimeters we have measured environmental input and output fluxes of TCA to soil and investigated the recovery of artificially added TCA. Less than 30 % of added TCA is detected in drainage from forest and agricultural soils compared with ~100% in undosed control lysimeters. Soil TCA concentrations remain unchanged during the experiment, indicating that soil TCA.

Poster: Ecot-3

Increasing validity and reliability of bioassays by newly developed automatised high-throughput test systems

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Nowadays, single species bioassays like bacterial and algal growth inhibition assays and genotoxicity assays can be performed automatically using liquid handling stations and robotics. These innovative technical methods allow the on-line documentation and control of incubation parameters like temperature and light intensity. Furthermore, large numbers of toxicants can be characterised simultaneously with high-throughput microplate test systems. Reliability and reproducibility of bioassays can be proved routinely in these test systems by testing reference toxicants in each test performed. Additionally, far more treatments and more parallels can be tested. The benefits of these measures are demonstrated at the Aachen University of Technology by experiments with a high-throughput algal growth inhibition assay. Comparative studies on toxicity of chemicals are carried out with erlenmeyer flask assays. Statistical evaluation shows, that the results are nearly identical. On the other hand, the strong dependency of the EC-values on the toxicological endpoint used for evaluation shows, that there is a strong need for harmonisation. Reliability and repeatability of test results can be easily assessed by routinely testing K₂Cr₂O₇ or other toxicants in parallel. It is proposed to include confidence limits for EC-values of reference toxicants as validity criteria for individual tests into the standards

Poster: Ecot-4

The effects of endocrine disruptors to expressed cDNA profiles in *Oryzias latipes* using real time RT-PCR

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The purpose of this study is to compare and classify the level of four different gene expressions, i.e. beta-actin, estrogen receptor, cytochrome P450 aromatase and p53, using real time RT-PCR base on the Taqman probe method. The genes for the estrogen receptor, cytochrome P450 aromatase and p53 were selected to detect estrogenic potential, cytotoxicity and carcinogenicity, respectively, in addition to the use of beta-actin as a positive control. Through the quantification by real time RT-PCR, it was found that three genes mentioned above expressed differentially dependent upon the exposure time (1, 2, 4, 10 days) and concentrations of the endocrine disruptors, beta-estradiol, and nonylphenol. The estrogen receptor was expressed highly after exposure to both of the chemicals separately, indicating that nonylphenol has a serious impact on the Medaka's endocrine system. However, the p53 gene was expressed only when nonylphenol was added, according to the real time RT-PCR results. This seems to indicate that the effect of each EDC on the cDNA gene profile should be different, a type of a fingerprint. This work was supported by the National Research Laboratory (2001 NRL) program of Korea Institute of Science and Technology Evaluation and Planning (M10104000094-01J000004100). Authors are grateful for their support.

Poster: Ecot-5

Polybrominated diphenyl ether flame retardants in fish bile and livers from Swiss rivers

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Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants that are starting to receive a lot of attention due to their similarity in structures to PCB and reports of their wide spread and increasing concentrations in the environment. They are additive chemicals in a myriad of products such as textiles, polyurethane foams, circuit boards and plastics. They leach out over the lifetime of these products and enter the environment. The less brominated congeners such as the penta-BDE have been shown to disrupt endocrine and hepatic system functions as well as compromise neurodevelopment. Methods were developed for the determination of PBDEs in fish liver and bile. The liver was extracted by accelerated solvent extraction (ASE) and the bile by liquid-liquid extraction. The samples were analyzed on a Fisons 8060 GC coupled with a Fisons MD800 MSD in +EI mode using a 30 m DB-5 column. Recoveries for BDE-28, 37, 47, 66, 99, 100, 153, 154 and 183 in the bile ranged from 81-109%. Detection limits in the bile (0.5 g) ranged from 400 pg/g to 3.3 ng/g and for 1 g of liver 200 pg/g to 1.6 ng/g. The results are presented for fish collected in four Swiss rivers.

Poster: Ecot-6

Post registration monitoring as a tool to investigate effects of pesticides on vertebrate wildlife in England and Wales

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A system of post registration monitoring for pesticide poisoning incidents has been operating in England and Wales for over 30 years. The scheme relies on suspected incidents being reported and investigates poisoning of terrestrial vertebrate wildlife and companion animals as well as beneficial insects such as honeybees. One of the purposes of the scheme is enforcement of correct pesticide use and many incidents arise from careless or deliberate pesticide misuse. Another purpose is to provide real information on pesticide poisoning. This can be used to refine the risk assessment process or to modify the conditions of use of a pesticide although there are some limitations to the information produced by the scheme. Over time the types of pesticides involved in incidents has changed and anticoagulant rodenticides have become an increasingly important cause of pesticide incidents. Advances in methodology have been made leading to an improved capability to detect exposure to these compounds. Recent developments have been made which enable the scheme to investigate some current concerns regarding potential effects of pesticides on honeybees.

Poster: Ecot-7

Production of metal-binding peptides by phytoplankton in metal contaminated estuarine waters

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Metal-binding peptides such as phytochelatins and glutathione are produced by a number of organisms, including marine phytoplankton, for various cellular functions such as metal detoxification and regulation of metal concentrations inside cells. These peptides can bind heavy metals through coordination with the SH groups in their structures. The Fal Estuary is one of the most metal contaminated areas in the United Kingdom, as a result of inputs of heavy metals from acid mine run-off. Water samples were collected at low tide during Spring/Autumn 2002 for analyses of metal-binding peptides. Phytochelatin and glutathione were determined in all samples in the particulate phase. These compounds were observed throughout the Fal Estuary except in the Mawe site. The highest phytochelatin concentrations (179 pM) were found in the Restronguet Creek, which is fed by the Carnon River, the principal source of metals for the Fal system. These results are comparable with literature values for contaminated waters. Trace metals and chlorophyll a determinations in the samples will allow better interpretation of the data. Our future work will involve fieldwork and laboratory studies focusing on phytochelatin production by resistant algae species present in the system.

Poster: Ecot-8

Cd bioaccumulation by the freshwater alga, *Chlamydomonas reinhardtii*

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Short-term uptake of cadmium by *Chlamydomonas reinhardtii* was studied as a function of Cd speciation in a well defined, aqueous medium. Uptake fluxes were examined for free cadmium concentrations ranging from 10^{-10} M to 5×10^{-4} M in the presence of ligands forming both labile and inert hydrophilic complexes (NTA: $\log K=11.0$, IDA: $\log K=7.0$, citrate: $\log K=5.4$). A first order biological internalization, as predicted by FIAM (Free Ion Activity Model), was observed for the entire range of Cd concentrations studied. Nonetheless, under some circumstances, some ligand effects were observed for experiments in which $[Cd^{2+}]$ was maintained constant while both the total Cd and ligand concentrations were increased. Accumulation of $NaH^{14}CO_3$ and ^{14}C -sorbitol were examined in parallel to the bioaccumulation results in order to explain ligand effects. Cd adsorption to the cell wall was also examined (10^{-10} - 10^{-2} M $[Cd^{2+}]$). In this case, no saturation of the cell surface was observed, even for the highest concentrations examined suggesting that a large number of co-ordination sites were present. In such a case, single site models such as the Langmuir adsorption isotherm are not useful for predicting Cd binding to the cell wall. The biological transfer of metal across the cell membrane are discussed with respect to the chemistry of the complexes in solution.

Poster: Ecot-9

Phytochelatin induction in the freshwater alga *Scenedesmus vacuolatus* depending on cadmium speciation

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Phytochelatin (PCs) are intracellular metal-binding polypeptides, produced by algae when they are exposed to high metal concentrations, in order to reduce the cytotoxic metal and avoid non-specific binding with biomolecules. Algae are observed to grow optimally depending on species and ranges of exposures to free metal ion concentrations. This study aims at investigating how metal speciation interacts with phytochelatin content under various degrees of cadmium stress. For this purpose, phytochelatin inductions are studied in the green microalga *Scenedesmus vacuolatus* exposed to a range of free cadmium concentrations ($pCd^{2+}=13.05$ to 7.06). At these exposures, the growth rate of the algae is reduced to 50% of the maximum and the algal cellular thiol pool changes. Indeed, the total glutathione concentration and the PC2-PC4 content are observed to increase in the algae with increasing Cd exposure. Phytochelatin production is observed to start at pCd^{2+} 9.51, PC2 being the most dominant species (13.4 amol/cell) whereas at pCd^{2+} 7.06, the induction of PCs raises considerably and PC3 becomes the most important species (387 amol/cell). These observations suggest that phytochelatin are not sufficient to detoxify completely the intracellular metal. Further studies in cadmium bioaccumulation will show us if Cd is exceeding the phytochelatin concentrations.

Poster: Ecot-10

Trace-elements speciation in agricultural soil and microscopical analysis of plant tissues. Interdisciplinary study of trace-elements distribution and their uptake by flax plants

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Flax seeds are used in animal food because of their high content in Omega 3. A number of trace-elements (TEs) - essential as micronutrients, however toxic at supraoptimal concentrations - can accumulate in the plants at quantities incompatible with their introduction in food chain. In order to control this risk and evaluate the uptake of TEs, it is necessary to assess the contents of various species of TEs in the soil and in the plants (total content and contents of each organ). We were mainly interested in evaluating the presence of Cu, Ni, Pb and Zn in soils on which flax plants were grown. Two situations have been compared: the first (Normandy) corresponds to fields into which some sludge of water-treatment were brought in agronomic doses and the second (Paris Region) corresponds to plots of land irrigated by waste water over a long period which led to an accumulation of TEs. We are currently performing TEs extractions from soils and plants using different methods: data of sequential and total extractions (assisted by microwaves) will be presented. The content, localization of TEs in flax plants as well as their possible effects on the tissue organization will be presented.

Poster: Ecot-11

Enantioselective respiration rate and uptake of aminoacid by microorganisms in Zn contaminated soil

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There is general consensus that microbiological activity may hold potential as an early indicator of stress in soil quality. Among analytical approaches, results on the respiratory response of soil microbial biomass of unpolluted and polluted soils added with free aminoacids suggest that microorganisms might selectively discriminate the use of amino-stereoisomers. In this work we investigated the enantioselective uptake of glutamic acid (L, D, and racemate L+D) by soil micro-organisms in a Zn polluted soil. L/D respiration ratio did not change significantly in polluted and unpolluted soil within 6 hours of incubation. By contrast, the uptake of the D chemical form within 6 hours occurred only in polluted soil whether it was given pure or as racemate chemical forms. As a consequence L/D uptake ratio clearly distinguished polluted soil from the unpolluted one, establishing the basis for its use as a microbiological index to evaluate the disturbance or compromise of biological status of soil.

Poster: Ecot-12

An artificial neural network for the characterization of plants health status using chlorophyll fluorescence measurements

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The need for fast methods for plant health status survey and plant classification is today an urgent request. The analysis of the OJIP Chlorophyll a fluorescence rise by the JIP-Test has shown to be a valuable tool in plant vitality monitoring. Moreover, it has been found that the fluorescence kinetics hides a built-in barcode that can be used to classify the characteristics of the measured samples. We have used an artificial neural network (Kohonen's Self Organising Map SOM) to classify fluorescence curves measured with a portable fluorometer from twelve well-selected and physiologically characterized breeding lines of Barley (*Hordeum vulgare* L). These lines were split into 3 categories by their capability to resist drought stress. A SOM was generated using the measured Chlorophyll fluorescence curves, and the neurons of the map show well-defined patterns or groups reflecting barley varieties and drought stress resistance categories. Further improvements in the performance of the presented classification routine are subject of investigation as well as for the SOM algorithm and for experimental data gathering and handling. JIP-Test analysis combined with Self-Organizing Maps obtained from the Chlorophyll fluorescence kinetics measured from over many years selected Barley varieties will be presented.

Poster: Ecot-13

Chloroacetic acids in environmental processes

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Chloroacetic acids (CAA), especially trichloroacetic acid (TCA), have been considered to be solely of anthropogenic origin (formed in the atmosphere by photooxidation of C2-chlorocarbons) and as such - pollutants of herbicidal properties - to be one of the stress factors affecting conifers. Our studies on the effects of TCA on Norway spruce/soil system - using radio-indicator methods - have elucidated the fate of TCA to some degree. Recently, there has been another source of CAA (or TCA, resp.) identified: soil in which humic and other organic substances may be degraded by microbial processes to CAA and chloroform. This finding changes the situation in the research of the role of CAA in the environment considerably. If CAA are continuously produced and delivered from the soil to the roots, trees are exposed to CAA stress from biogenic sources. On the other hand, CAA are biodegraded by enzymes of bacterial or plant origin in the soil thus participating in the degradation of humic substances and their precursors. We intended therefore to widen the view from fate studies of TCA in Norway spruce to degradation and formation of CAA in soil. For this purpose ¹⁴C and ³⁶Cl labeled compounds were prepared and used.

Poster: Ecot-14

Bacterial life strategies in a pristine and oligotrophic river

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The different life strategies of heterotrophic planktonic and attached bacteria and major bacterial groups had been investigated in the Tagliamento River (Italy). Abundance and biomass production of planktonic and of substrate-attached bacteria were inversely correlated, with low abundance but high production for attached cells and vice versa for bacterioplankton. In oligotrophic surface waters, low temperatures and low total organic carbon and soluble reactive phosphorous (SRP) concentrations limit microbial activity. In samples collected, eubacteria dominated the water column (~70%) and substrate-attached communities (~90%). Eubacteria were dominantly comprised of alpha-and beta-Proteobacteria and Cytophaga-Flavobacteria, with highest abundance of alpha-Proteobacteria. The majority of attached bacteria formed microcolonies in the oxygenated hyporheic zone. Atomic force microscopy (AFM) with bacteria kept in buffered aqueous phase demonstrate that single coccoid-shaped cells form aggregates or colonies in association with organic and inorganic particles, microscopic algae, and organic polymeric material. Likely, attached cells develop exopolymeric structures to colonize the surface of the carbonaceous substrate. We could not detect any formation of bacterial biofilms. Due to minimal differences in community structure among bacterial samples, we propose that in competition for scarce resources, cells explore the environment for nutrients, and therefore live either planktonic or attached as microcolonies.

Poster: Ecot-15

The influence of additives on the ecotoxicological characteristics of environmentally acceptable lubricants

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The collaborative research centre SFB 442 aims at developing environmentally acceptable lubricants. Fluids are investigated as well as the ecotoxicologically relevant constituents, lubricant additives, which are usually added to base oils in order to enhance their technical performance. For optimizing lubricants, their environmental characteristics have to be considered as well as the technical properties of the fluid during usage. Biological tests are necessary when environmental characteristics are examined, because they provide information on combinatory effects of different constituents. A test battery consisting of several biological tests is used for the investigation of single additives (e.g. tributylphosphate). Difficulties in assessing the ecotoxicological potential of lubricants arise due to the lack of information on relevant constituents of the water extract used in the tests. As a result, both positive and negative environmental effects of lubricant additives are detected. The stability of base oils increases by using certain additives and, therefore, the degradability maintains, but base oils with additives prove to be more problematic with respect to the environment. The results of the bioassays for single additives provide transferable data for the design of lubricants optimized with respect to environmental and technical characteristics.

Poster: Ecot-16

Impact of nonylphenol on soil fungi

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Nonylphenol is an endocrine-disrupting chemical widely distributed in sewage sludges as a mixture of isomers. The impact of nonylphenol on soil microorganisms, following sludge spreading on agricultural soils, is poorly known. Amounts of the chemical have been determined in the soil solution following soil spreading with sludges from two origins. Then, we present our laboratory experiments intended to assess the effects of nonylphenol on soil fungi, when exposed to the same range of pollutant concentration. In that purpose, we followed several biomarkers including fungal biomass, spore germination, morphological alterations, and enzymatic induction.

Poster: Ecot-17

A fast routine for monitoring plant health status

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There exist very complex mechanisms at different levels of molecular organization by which plants interact with their environment. We have studied the response of barley (*Hordeum vulgare* L.) and lentil (*Lens culinaris*) plants to different actinic light adaptation periods using OJIP Chlorophyll a Fluorescence measurements. The plants were exposed to 1s light pulses (600 Wm^{-2}) every min with actinic light (18 Wm^{-2}) between the light pulses. This light regime repeated 5 times. The fluorescence produced during the light pulses was recorded with a portable fluorometer. The fluorescence data have been used to study different energy fluxes such as light absorption and electron transfers in leaves. We have investigated the photosynthetic behaviour of the plants during the fast fluorescence rise (OJIP). The collected fluorescence data have been interpreted by using mathematical expressions in terms of biochemical and biophysical meaning which define the physiological state of the plant. On the basis of the observed fluorescence responses a screening procedure for monitoring the health of barley and lentil plant has been developed. Several JIP-Test parameters show differences in barley varieties and lentil varieties as well, for example the Relative Variable Fluorescence and the Maximum Yield of Primary Photochemistry after dark and light adaptation.

Poster: Ecot-18

Elemental sulfur, an important acute but transient toxicant in sediments

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The involvement of elemental sulfur in the acute toxicity of contaminated sediments has recently received increased attention. Dilution of elemental sulfur dissolved in organic solvent solutions and mixing of (anoxic) sediments containing elemental sulfur in water produces a toxic form of sulfur as tested using a bacterial luminescence test and lethality tests with crustacea, amphipods, and fish larvae with a flow-through exposure test. To provide more informations on the environmental relevance of these observations, studies were conducted to examine the forms of sulfur in sediments, to follow its transformation and the related toxicity. Octameric elemental sulfur was identified by means of GC-MS analysis in anoxic surface sediments from Sweden, and additionally quantified in sediments from Germany and in a reference material from New York and New Jersey (USA). The transformation into precipitated octameric sulfur was identified and quantified in operationally defined fractions of the German sample and the reference material. Results of the related toxicity test will be presented.

Poster: Ecot-19

Ecotoxicological potential of DDT and its metabolites

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Sediment samples from rivers and lakes of Berlin/Germany were analyzed by GC/MS/Screening target and non-target screening analysis from 1993-1999. DDT and its metabolites DDD, DDE, DDMS, DDMU and DDCN were the most abundant compounds of the class of chlorinated pesticides in the sediments in a wide range of samples. This fact and the lack of information of the ecotoxicology of the most DDT metabolites was the reason for subsequent ecotoxicological analysis. The acute toxicity of selected DDT metabolites (o,p'-DDT as reference, p,p'-DDMS, p,p'-DDMU, p,p'-DDCN and DDA) was determined by the permanent cell line RTG-2 from the gonads of the rainbow trout (*Oncorhynchus mykiss*) and the estrogenic potential was analyzed by the Dot-Blot/R-Nase-Protection-Assay. The results indicate a high cytotoxic potential of the most tested substances in comparison to the reference o,p'-DDT. The estrogenic potential determined has the order o,p'-DDT > p,p'-DDMS > p,p'-DDMU >= p,p'-DDCN. DDA had an antiestrogenic effect. The investigations showed, that risk assessment of environmental samples based on chemical analyzes of a few priority compounds defined in national and international lists and measure programs is not to be able to estimate the real toxic potential of single compounds or mixes of substances (combinatory effects). The development of bioassay directed fractionation and the application of grades assessment policies seems to be an effective strategy to solve this problem.

Poster: Ecot-20

Self-Organizing Map (SOM) for monitoring the evolution of *Rhizobium* nodulation status in *Vigna unguiculata*

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Chlorophyll a fluorescence is a useful and non-invasive tool to screen for the effects on many biotic and abiotic parameters of photosynthesis in plants. The polyphasic OJIP Chl a fluorescence rise emitted by leaves after excitation with red light was measured with a portable fluorometer. The collected data were analysed using the JIP-test which provides biophysical parameters indicating Photosystem II properties. Seeds of *Vigna unguiculata* were sterilized before germination. Seedlings were planted in Magenta jars (used for hydroponic cultures) filled with a nitrate-deficient solution (B&D solution). The roots of some of the plants were inoculated with *Rhizobium* sp. strain NGR234 (109 bacteria/200 µl) four days after germination. The other plants were grown on various concentrations of KNO₃ (0, 0.5, 1, 5, 10 and 20 mM). The plants were followed for 5 weeks. During this time fluorescence measurements were done every week on the first and second mature leaves. We have used an Artificial Neural Network (Kohonen's Self-Organizing Map or SOM) to analyse the raw fluorescence data. The generated map shows very well defined zones creating a gradient from low to high nitrate concentrations. The data of the *Rhizobium* inoculated plants are moving in the fluorescence SOM map, with increasing age to zones of the data reached with a higher nitrate concentration, according to the expected nitrogen supply pattern. This permits us to establish a method for screening the evolution of nodulation as well as nitrogen deficiency in vivo on the level of the leaves.

Poster: Ecot-21

Interactive toxicity of metal ions and arsenate species on *Vibrio fischeri*. A statistical approach

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Dramatic expansion of industrial and urban areas in recent decades has caused increasing concern on environmental safety. As a consequence, it is necessary to provide information concerning the actual impact of isolated chemicals or complex mixtures of contaminants, especially on aquatic ecosystems. This also raises the question of change in toxicity of a given chemical due to variations in the physical properties of water and the interactions with other metals or chemical species, which may be present at variable concentrations. Therefore, our experiments were focused on the study of interactive toxicity between 1) metal in binary mixtures and 2) arsenate chemical species. Toxicity was evaluated using the Microtox® bioassay based on change in light emission by the *Vibrio fischeri* luminescent marine bacteria. A statistical approach founded on testing the null hypothesis of additive toxicity was applied in order to evaluate metal ions and arsenate species interactions. It is remarkable that Cu, with a high degree of toxicity, interacted antagonistically with Pb and Co, whereas an additive effect was found for Cu-Zn and Zn-Pb mixtures. Finally, antagonism was described for mono and dihydrogen species interactions at pH 6-7.

Poster: Ecot-22

Assessment of the toxicity of triasulfuron and its photochemical degradation products, towards four different aquatic organisms

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Photodegradation is one of the main pathways in abiotic transformation of pesticide. Although this phenomena contributes to the elimination of pesticides in natural waters, the products formed (photoproducts) can be more toxic towards aquatic organisms than parent compounds. In this study, we have assessed the toxicity of triasulfuron, a sulfonyleurea pesticide used for the weed control in cereal crops, as well as photoproducts formed during photochemical degradation of triasulfuron under simulated solar irradiation. Several acute tests of toxicity have been achieved using species representative of the different trophic levels: algal tests (*Chlorella vulgaris* and *Selenastrum capricornutum*), duckweed test (*Lemna minor*), Lumistox (*Vibrio fischeri*) and test with *Daphnia magna*. Results indicate that the tested vegetal organisms are less sensitive to the photoproducts than to triasulfuron. On the contrary, *Daphnia magna* and *Vibrio fischeri* are not sensitive to triasulfuron but the photoproducts are more toxic. For these two species, a chronic effect can not be ruled out. Triasulfuron and its degradation products represent a real threat for aquatic ecosystem, not only because of their acute toxicity towards vegetals but also indirectly because algae and duckweed represent the base of trophic levels.

Poster: Ecot-23

Bystander exposure to pesticide spray drift: developing a risk assessment model

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Concerns have been raised in the United Kingdom, including articles published in the press, about the exposure of the population to pesticides which have been sprayed onto fields close to their dwellings or footpaths. One estimate indicated that there are 250,000 people whose gardens adjoin the sprayed land, and so potentially exposed to pesticides in spray drift. Further concerns have been expressed regarding whether the effects they see are just “socially unacceptable”, or present a potential health hazard. The Application Hazards Unit at CSL have recently generated potential bystander exposure data using modified in-house field methods to measure spray drift and bystander exposure. These studies were done with a tracer solution sprayed onto a mature cereal crop, using both conventional (flat fan) and low-drift (air induction) hydraulic spray nozzles. Static collection media were used to determine both the horizontal and vertical drift profiles, which were compared to deposition on two bystanders, wearing absorbent coveralls, positioned at set distances from the crop edge. Generating such data will provide a better understanding of the relationship between ground deposited spray drift and airborne spray drift. Furthermore the relative collection of airborne spray drift by 2mm diameter air lines and human subjects can be investigated.

Poster: HRAs-1

Evaluation of laboratory data for spray drift in a field environment

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Unsprayed buffer zones (UBZ) are used to protect aquatic organisms from exposure to pesticides as a result of spray drift. For arable crops this has traditionally meant 6m of unsprayed field adjacent to the watercourse. Recently introduced schemes such as LERAP in the United Kingdom, and similar schemes within the EU such as the Netherlands have allowed certain UBZs to be reduced to 1m if used with appropriate application equipment with reduced drift potential. This has led to greater use of low drift technology such as AI nozzles. Much of the work to determine drift reducing potential has been done with single nozzle outputs in wind tunnels. Field studies have recently been done in the United Kingdom with short crop (<15cm) and mature cereal crop (75cm) to evaluate the use of such laboratory data under field conditions. The field studies were done with a range of wind speeds. Initial indications are that the ground deposited drift from applications to mature crops is less than that predicted by wind tunnel studies and field studies with short crops. However, with mature cereal crops, initial indications are that there did not appear to be the reduction drift deposition as indicated with the laboratory data from wind tunnel studies.

Poster: HRAs-2

The consideration of environmental chemistry of toxic compounds in Health Risk Assessments (HRA)

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Contaminated Site Management must be based on Detailed Health Risk Assessments (HRA) to identify the most probable high value for site recycling. In this case acceptable toxic risks for future site users must be ensured. Only Site specific Rehabilitation Threshold Levels (RTL), defined by an HRA can give the guaranty for acceptable health risks and minimum contamination costs. The HRA based on different future site use scenarios can ensure the economically best adapted site development & rehabilitation strategy" to build an optimal surplus on property development. A Contaminated Site Management HRA must include mapping of contamination exceeding Health Risk and Rehabilitation Threshold Levels in areas of different future site remediation scenarios. This approach allows the best choice concerning the future site use strategy and the best balance between rehabilitation costs and property revalorization. If Health Risks are not acceptable, consequently, decontamination threshold levels are calculated for all pollutants and specific site use scenarios. The aim is to protect human beings from unacceptable risks. The RTL are calculated in the same way than risk quantification to obtain carcinogenic and non-carcinogenic risk values below the acceptable limits, as a maximal carcinogenic risk of $ICR < 10^{-5}$ and a non-carcinogenic risk of $RI < 1$.

Poster: HRAs-3

Toxic metabolites from explosives & chemical warfare agents on polluted military and armament sites and their consideration for Health Risk Assessments

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Lots of specific pollutants as explosives, propellants or chemical warfare agents could be present on military and armament sites. An Health Risk Assessment (HRA) must identify the real risks based on these initial pollutants and their breakdown products. The main problem is, that these breakdown products are not well known or simply not investigated. In this case very severe Health Risks may be strongly underestimated and site clean up can be proceeded in a wrong way. As for example the presence of TNT (2,4,6-trinitrotoluene) contaminations needs to verify pollution by metabolites such as nitro phenols, nitro cresols, amino toluenes, amino nitro toluenes, etc., and eventually former intermediary production compounds, as mono- and dinitro toluenes which have to be investigated. In case of contaminations by chemical warfare agents as S-Yperite (Sulfur Mustard), Lewisites, Clark 1 & 2, Adamsite etc., lots of breakdown products and eventually intermediary production compounds have to be considered in an Health Risk Assessment. Only if a complete knowledge about all toxic metabolites exist, future on-site Health Risks can be quantified and site specific Rehabilitation Threshold Levels (RTL) could be defined by an HRA to ensure Acceptable Health Risks and minimum decontamination costs.

Poster: HRAs-4

Detection of HAP by TRLIF

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In this work, we shall present the results we obtained on the detection of Poly-Aromatic Hydrocarbons molecules HAP by using Time Resolved Laser Induced Fluorescence TRLIF. Three molecules: chrysen, fluoranthen and pyren were studied. Thanks to the sensitivity of the technique and using spectral and temporal information, detection limits as low as 4. 10⁻¹⁰M were obtained for chrysen. We also showed, by using a microlaser, that it was possible to use this technique for the detection of HAP in environmental conditions.

Poster: OPan-1

The analysis of dioxins and related POPs using GC-High Resolution MS with the AutoSpec-Ultima NT

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'Dioxins' refers to a group of chemical compounds that share certain similar chemical structures and biological characteristics. Several hundred of these toxic compounds exist and are members of three closely related families: the chlorinated dibenzo-p-dioxins (CDDs), chlorinated dibenzofurans (CDFs) and certain polychlorinated biphenyls (PCBs). The detection of dioxins is a particularly demanding analysis due to the low level of regulatory exposure limits and the variety of complex sample matrices encountered. Analyses are most often accomplished using Gas Chromatography (GC) coupled to high resolution magnetic sector GC-MS instruments, which provide the necessary high sensitivity, selectivity and wide dynamic range to address this application. The AutoSpec-Ultima NT is the market-leading GC-high resolution MS instrument. A variety of other Persistent Organic Pollutants (POPs) provide the same analytical challenges and must be analysed in a similar fashion to dioxins and furans. The most important of these are Polychlorinated Biphenyls (PCBs) and Polybrominated Diphenylethers (PBDEs). Analytical and regulatory considerations will be discussed and example data shown.

Poster: OPan-2

Determination of alkylphenol endocrine disrupters in wastewater and the efficiency of their biological removal in four major Geneva sewage plants

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Four major Geneva wastewater plants were selected to test the efficiency of the biological removal of long chain alkylphenols and related alkylpolyphenoxyethoxylates. Three plants use a classical biotechnology. The fourth plant uses a modern biological process. A new analytical method, suitable for this study, of determination of isomeric 4-nonylphenols and 4-tert-octylphenol in wastewater using GC-MS has been developed. This procedure has been applied to the determination of the free alkylphenols as well as to 4-alkylphenol polyethoxylates and their various hydrosoluble metabolites after their cleavage with hydroiodic acid. The final degradation products in the environment of 4-alkylphenol polyethoxylates and their metabolites are the long chain free 4-alkylphenols, which are responsible of endocrine disruption in various animal species. The precision of the method and its accuracy are satisfactory with recovery rates above 74%. The relative standard deviation is lower than 6 % and the detection limits are below 22 ng/l for all analyzed compounds. Our results show that depending on the wastewater plant, the biological treatment is able to eliminate from 65 % to 92% of these endocrine disrupting alkylphenols, the average total concentration of alkylphenols at the effluent being about 4 µg/l.

Poster: OPan-3

Analysis of pesticides and metabolites at the ng/l level in surface water and groundwater using liquid chromatography tandem mass spectrometry

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A new method using liquid chromatography tandem mass spectrometry detection with electrospray ionization is presented. It allows the determination of relevant pesticides belonging to different classes (phenylureas, triazines, and acetanilides) and some metabolites in environmental waters at the 1 to 50 ng/l levels. Sample enrichment is performed in a one step solid phase extraction procedure using OASIS as sorbent material. Excellent and reproducible (low RSD) recoveries (higher 58 %) are obtained for all analytes. For most of the substances, linearity ranges from 0 to 4000 ng/l and detection limits vary between 0.1 and 50 ng/l. To improve the analysis of pesticides in the electrospray negative ionization mode, different post-column neutralization solutions were tested. Better results were obtained using a 1mM solution of Tris (2-amino-2-hydroxymethylpropanediol) at a flow rate of 50 µl/l. The influence of environmental matrix components, resulting in ion suppression, affecting sensitivity and quantification, was evaluated. It is shown that the use of internal standards is a safe means of producing reliable results for quantification purposes when it comes to liquid chromatography mass spectrometry detection. The method is being applied to the analysis of surface water and ground water samples for studies of pesticide fate and transport.

Poster: OPan-4

Capillary electrokinetic separation of polycyclic aromatic hydrocarbons using cetylpyridinium bromide

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11 polycyclic aromatic hydrocarbons including isomeric pairs were separated in capillary electrokinetic chromatography using a cationic surfactant, cetylpyridinium bromide (CPBr), as additive. Changes of electroosmotic and electrophoretic mobilities with increasing CPBr concentration were investigated. Under optimum separation conditions, running electrolyte contains 50% acetonitrile, 20 mM acetate, and 40 mM CPBr at pH=4.0. With the addition of 2 mM CPBr into the running electrolyte, dynamically coating is occurred in the capillary and electroosmotic flow is reversed. Significant retentions indicate solvophobic, n and p electron interactions between CPBr and PAHs without micelle formation.

Poster: OPan-5

Qualitative analysis of polymeric flocculants in sewage sludge by on-line-pyrolysis-GC-MS

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Flocculants are commonly used in sewage treatment plants for precipitating heavy metals and other contaminants in sewage water. Thus flocculants are abundant components in sewage sludges. Primarily investigation revealed ecotoxicological effects of these compounds in soils. As there are no analytical methods for detecting flocculants in environmental samples published so far, monitoring the pathways in the environment or accurate correlation with toxic effects cannot be made. This investigation presents first results on detecting polymeric additives in environmental samples. Two common flocculants, both based on polyacrylamides, were investigated by on-line-pyrolysis-GC. Pyrolysis of these substances revealed a characteristic elution pattern of only a few compounds eluting within narrow ranges. The molecular structures of three significant pyrolysis products were identified by on-line-pyrolysis-GC-MS. Characteristic ion-traces of these analytes were also detected in soil samples which were spiked with the two flocculants before analysing, as well as in a sewage sludge sample. The accordance of specific analytical data of the flocculants with those of the spiked soil samples and the sewage sludge sample allows the verification of the flocculants in the investigated samples.

Poster: OPan-6

In vitro immunosuppressive activity of the two main tautomers of an environmental contaminant the 4,5-ketol derivative of benzo(a)pyrene and some of its metabolites

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The two main tautomers of an environmental contaminant, the 4,5-ketol derivative of benzo(a)pyrene (BaP) were separated by HPLC, identified by NMR spectroscopy and by electrospray mass spectrometry. The in vitro immunosuppressive activity of the two tautomeric forms 4,5-H-4-hydroxy-5-oxo benzo(a)pyrene and 4-5-H-5-hydroxy-4-oxo benzo(a)pyrene were found less immunosuppressive than the mixture of the two tautomeric forms retaining a more lipophilic character most probably due to the existence of stacked configurations linked by hydrogen bonds. A metabolite was identified as the 7,8-dihydrodiol of the 4,5-ketol derivative of benzo(a)pyrene by electrospray mass spectrometry.

Poster: OPan-7

Development of a method for the analysis of glycol ethers and acetates in water samples using solid phase micro-extraction coupled to GC/MS

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Glycol ethers are a group of chemicals widely used as solvents in paints, cleaners and inks. They have received some media attention and are included on some government lists of hazardous substances because some of them were proved to cause adverse male and female reproductive effects and birth defects in rodent studies. These particular compounds are no longer employed, but there is a risk of environmental pollution by industrial release. To assess the impact of glycol ethers on aquatic environment, it is necessary to develop an efficient analytical method for these highly polar compounds, which are hardly extract from water. The aim of this study was to optimize and evaluate the performance of a method involving solid phase micro-extraction (SPME) coupled to GC/MS. The target compounds were 14 glycol ethers and 5 glycol ether acetates. The main parameters governing SPME, e.g. extraction mode, fiber coatings, temperature, ionic strength, extraction time, were optimized. For the developed method, the linearity and the detection limits were evaluated, as well as the repeatability. The proposed method consists in performing direct extraction with a polydimethylsiloxane/carboxen fiber at 70°C during 60 minutes. It allows the quantification of glycol ethers and their acetates at the ppb level.

Poster: OPan-8

Chemiluminescent determination of carbaryl by FIA based on cerium(IV) oxidation sensitized by rhodamine 6G

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The large amounts of carbamate pesticides used requires extensive monitoring in all types of environmental samples (their toxicity is by virtue of their ability to act as potent cholinesterase inhibitors). The aim of this work was to develop a simple and rapid method for the determination of carbaryl, not requiring sophisticated instruments but giving results comparable with those obtained by existing methods. The method described is based on chemiluminescence-emitting reaction between carbaryl and Ce(IV) in acidic medium in the presence of rhodamine 6G as sensitizer. The cerium(IV) concentration and the nature and concentration of the acid present in the reaction solution have a marked influence on the detector response and were investigated in order to obtain the maximum emission intensity. The results showed that the optimum reagent concentrations were: 25 mM Ce(IV) and 4 M HNO₃. Various fluorescent reagents were employed as sensitizers and the results indicated that rhodamine 6G is the best sensitizer in the present system. Other parameters were studied in order to establish optimum conditions for the measurement. A concentration of carbaryl versus chemiluminescence intensity calibration graph was obtained and the proposed method was applied to the analysis of carbaryl in soil and water samples.

Poster: OPan-9

Field-based Supercritical Fluid Extraction for organic compounds monitoring at industrially contaminated sites

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Rapid, cost effective field based methods of extraction and analysis are required to determine the concentrations involved in sites contamination by organic pollutants so that a risk assessment can be made. Supercritical Fluid Extraction is a method that utilises the solubilization power and the rapid mass transfer characteristics of non-toxic supercritical fluids (SF). It requires far less time to achieve extraction and uses only very small volumes of organic solvent. The aim of the present work is to develop a field-based SFE system for the recovery of organic contaminants (BTEX, PAHs) from soils and link this to commercially available immunoassay test kits. A simple, compact and robust SFE system has been constructed and was found to offer the same extraction efficiency as a well-established laboratory SFE system. Extractions on dry and wet real world samples gave similar recoveries to Soxhlet extractions with recoveries efficiency >60%. After optimisation of the immunoassay test kit, extracts from real samples were analysed in 10% MeOH. Immunoassay analysis show a linear response when plotted against GC-MS response, giving a good representation of samples contamination. The compact SFE device will be taken on a contaminated site for extraction and analysis of soil. SFE extraction recoveries will be compared to soxhlet extraction and all extracts analysed by GC-MS for validation of the immunoassay analysis.

Poster: OPan-10

Comparison of the analysis of 16 PAHs in water by HPLC using LLE and SPE as sample pre-treatment

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Determination of polynuclear aromatic hydrocarbons is very important in many laboratories of water quality control, due to their potential carcinogenicity and widespread occurrence in the environment. The Council Directive 98/78/EC states that water intended for human consumption shall be monitored on these parameters and meet the parametric values set out in Annex I (less than 0,10 mg/L for the sum of the concentrations of 4 PAHs and less than 0,010 mg/L for benzo[a]pyrene). The usual methodology of such analysis is based on liquid-liquid extraction, followed by evaporation/concentration and clean-up steps, and finally chromatographic analysis by HPLC with fluorescence and DAD detection. Solid Phase extraction (SPE) is an alternative sample preparation method for these compounds, in order to reduce solvent usage and to simplify the procedure. This technique has been applied to the analysis of 16 PAHs: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene in aqueous solutions. In this study we describe the validation of SPE-HPLC in the analysis of these compounds: linearity, precision, quantification limits and recovery studies. The results obtained suggest that this method can be an alternative to other sample preparation methods (LLE) already used in this field.

Poster: OPan-11

Strategy for the identification of unknown persistent bioaccumulating toxicants (PBT)

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PBT are defined as "Organic substances that are persistent, bioaccumulating and possess toxic characteristics likely to cause adverse human health or environmental effects". Procedures to identify unknown PBT in the natural and technical environment are highly required. Therefore a first sample pretreatment procedure was developed for this purpose. A simple pretreatment of lipophilic extracts with acidified silica can serve as a first easily performed attempt to identify unknown PBT. The procedure employed for the identification of unknown PBT resulted –besides the information about dioxin like toxicity- in some library matches which are depicted for an environmental sample (soil) and samples of technical origin (flue-gas, fly ash). Further toxicological investigations of the pure compounds found and characterized will identify those as PBT.

Poster: OPan-12

Detection of phenol, salicylate and BTEX by whole-cell biosensors

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Whole-cell biosensors were developed to detect environmentally toxic aromatic compounds such as phenol, salicylate, and BTEX (benzene, toluene, ethylbenzene, and xylene) compounds. Regulatory protein (NahR, CapR and XylR) encoding genes and their operating promoters were cloned by PCR from *Pseudomonas putida*. Firefly luciferase (*luc*), β -galactosidase (*lacZ*) and green fluorescence protein (*gfp*) as reporter genes were used to construct plasmids in which they are under the control of the regulatory protein genes and the promoters. To test their usefulness, pure chemicals as well as polluted sewages were assessed and the results were compared with chemical and GC analysis. The whole-cell biosensors, even without any pretreatment of samples, were shown to be able to quantify accurately with minimum detection limits of 0.5 μ M, indicating that these could be utilized in monitoring environmental pollutants.

Poster: OPan-13

Identification of compounds in the unresolved complex mixture (UCM) of hydrocarbons in biodegraded crude oil

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Colloquially known as 'humps', unresolved complex mixtures (UCMs) of hydrocarbons present in crude oils (obvious features of gas chromatograms of biodegraded oils) are probably amongst the most complex mixtures on Earth. Specifically, the monoaromatic UCM appears to be of particular environmental relevance because it has been demonstrated to impair the feeding rate of mussels (*Mytilus edulis*). Knowledge of UCM composition would therefore be crucial to an improved understanding of the environmental fate and toxicity of oil components. We have used preparative open column chromatography, high performance liquid chromatography, and capillary gas chromatography (2 stationary phases) and obtained fractions from a UCM of hydrocarbons in which up to 50% of the compounds were resolved. Resulting fractions and monoaromatic analogues synthesised in our laboratory were studied by GC-MS, GC-MS-MS, GCxGC and GC-ToF-MS. In addition to this characterisation, we have estimated that the UCM comprises some 250,000 hydrocarbons.

Poster: OPan-14

Biosensor for hips analysis

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Biosensor is a powerful technique for the ecological control, in particular for the measurements of common pollutants. Potentiometric biosensor on the base of immobilized in gelatin rat liver monoamine oxidase (MAO) and gas-gap electrode for monoamine and drug determinations have been designed in our previous papers. In the present research this MAO biosensor was used for the analysis of the hips (Rosa cinnamomea). The samples were from different growing zones - nearby or far from motor road. Gas-gap sensor on the base of glass disc pH-metric electrode was used as the analytical detector in the construction of biosensor. Ammonia, releasing during desamination of MAO substrates (serotonine, tyramine, benzylamine), changes detector potential. This change became lower in the hips presence. The size of this change depends on the quality of testing samples, that is on the hips pollutants. It was shown, that sample hips act as the reversible MAO inhibitors, the inhibitor effect of the more ecologically clean hips was two times less than that of the hips from the motor road. The calibration curves $E=f(-\lg[I])$, i.e. potential dependence of biosensor against the inhibitor (hips) concentration, at the certain substrate concentration were plotted.

Poster: OPan-15

Structural impact of organic material on the sorption of organic pollutants as revealed by solid state ^{13}C NMR spectroscopy

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The sorption behavior of hydrophobic organic compounds (HOC) strongly depends on elemental composition and structure of soil organic matter. To minimize negative effects on the environment detailed information about composition, structure and sorption parameter of organic sorbents is required. In this study equilibrium sorption isotherms were measured using different HOC for peat, natural and combusted coals and various top soils. The sorption data were analyzed by the solubility modified Freundlich sorption isotherm, resulting in an increasing sorption capacity from the natural to the thermally altered coals. High distribution coefficients were measured for soils, which have been under the influence of coal industry. The distribution coefficients were normalized to the organic carbon content (KOC*-values) and indicated differences in the composition of the organic material (OM). The structure of the OM was characterized by ^{13}C solid state NMR spectroscopy. The VACP/MAS technique enabled a clear differentiation between uninfluenced and contaminated soils by polarity and fraction of aromatic carbon. A positive correlation between KOC*-values and the sample's aromaticity was determined for the coals (including the Histosols), but was not conserved for the contaminated soils, due to the mixing behavior of different OM in terms of sorption capacity.

Poster: OPbp-1

Retention of three pesticides by a lignocellulosic substrate. Influence of metallic cations

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Pesticides, which are usually the result of chemical syntheses, are used to fight effectively against noxious organisms. However, many studies have shown that the contamination of surface waters is a consequence of their intensive use. The aquatic environment is directly threatened by these toxic substances. Moreover, groundwaters are also likely to be contaminated by the migration of the pesticides, which represents a risk for the resources of drinking water. The different processes that allow the transport of pesticides towards surface or ground waters are complex. The composition of soils, which contain minerals, organic matter, and metallic cations, plays an important role. In order to understand these processes, we have studied the retention of three pesticides (isoproturon, dimetomorph, and amitrole) widely used in the Champagne-Ardenne region. We first studied the sorption of these chemical compounds on a lignocellulosic substrate, as lignin is one of the principal components of the soil organic matter. Then, we carried out solution complexation studies between pesticides and metallic cations, such as Fe(III), Cu(II), Mn(II), and Cr(III), which are naturally present in soils or industrial waste. The main goal of this work was to study the ternary system composed of pesticide, organic matter, and metallic cation, in order to assess the influence of the metal on the retention process of pesticides

Poster: OPbp-2

Photochemistry of some sulfonylurea herbicides

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The photochemical behaviour of triasulfuron, 1-[2-(chloroethoxy)-phenylsulfonyl]-3-(4-methoxy-6-methyl-1,3,5-triazin-2yl) urea and Thifensulfuron-methyl 3-[3-(4-methoxy-6-methyl-1,3,5-triazin-2yl)ureidosulphonyl] thiophene-2-carboxylate, in acetonitrile anhydrous was studied. Photochemical reactions were carried out by using a high-pressure mercury arc and a solar simulator. Kinetic parameters and quantum yields were determined. The photolysis process in the organic solvent occurred with a first order kinetic reaction. The identification of photoproducts was performed by mass spectrometry. The photochemical reactions were also carried out in the presence of either a singlet or a triplet quencher. Substances used as inhibitors of the excited levels T1 and S1 showed that photodegradation of both herbicides begins from a triplet state T1. Mechanism of degradation was proposed. The main metabolites identified in acetonitrile were 2-chloroethoxybenzene for the Triasulfuron and a monosubstituted urea common for the Triasulfuron and for the Tifensulfuron-methyl.

Poster: OPbp-3

Photodegradation of pyrene in solution

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The effect of solvent on the rate and the mechanism of photolysis of pyrene was investigated. Solutions of pyrene were irradiated using a high pressure mercury lamp (254 nm, Pél = 15 W) and a simulated solar irradiation using a xenon lamp (SUNTEST CPS+ apparatus, 290-800 nm, P = 765 W m⁻²). Solutions were prepared in water, methanol, acetonitrile and cyclohexane at 5 10⁻⁷ mol l⁻¹ and 2.5 10⁻⁴ mol l⁻¹. Kinetic study shows that the photolysis rate of pyrene is dependent on the polarity of the solvent and on the concentration of oxygen. Quantum yields of photodegradation of pyrene (calculated in polychromatic light) increases with the increase of the polarity of the solvent indicating that the mechanism involved in the photochemical reaction, is mainly ionic. Moreover, oxygen was found to be an inhibitor of the photodegradation of pyrene. This mechanism was confirmed by flash photolysis experiments which show that radical cation (Py^{o+}) is preferentially formed in polar solvent (methanol, acetonitrile) whereas triplet state (3Py) is the main excited state observed in cyclohexane. On the other hand, both intermediates (Py^{o+} and 3Py) are formed in the polar solvent when oxygen is removed. According to these results, a mechanism of photodegradation involving Py^{o+} via its excited state and oxygen is proposed in solution.

Poster: OPbp-4

Photodegradation of pyrene sorbed on mineral supports and sediments

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The study describes the photodegradation of pyrene sorbed on different mineral supports and on sediments of Aiguebelette Lake (France). SiO₂, CaCO₃, Montmorillonite, were chosen as model supports because they are representative of the main constituents of soils and sediments. Pyrene is a Polycyclic Aromatic Hydrocarbons (PAH) which is very persistent in the environment due to its resistance to biological degradation. The PAH was either mixed mechanically with the support, or, introduced by the intermediate of a solution prepared in cyclohexane, at variable weight ratio (2 to 10 000 ppm). A thin layer of mineral supports and sediments were irradiated by simulated solar irradiation, using a xenon lamp in the SUNTEST CPS+ apparatus, with a 765 W/m² incident irradiance between 290 and 800 nm. The kinetic of pyrene degradation show that the half-lives of the pollutant depend on the nature of the support, and on the presence of water. The rates of pyrene photodegradation appear to be correlated to the direct light reflectance (L.R) of the supports, a higher degradation is observed with SiO₂ ($k = 10.4 \cdot 10^{-8} \text{ mol.L}^{-1} \cdot \text{s}^{-1}$, L.R = 636) and CaCO₃ than with Montmorillonite ($k = 5.1 \cdot 10^{-8} \text{ mol.L}^{-1} \cdot \text{s}^{-1}$, L.R = 186) and sediments

Poster: OPbp-5

Comparison of PAHs contamination of pastures located by various industrial and vehicular emissions sources

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To assess and compare pastures PAHs contamination, grass and soil were sampled in June along a distance of 500m from different sources: a highway, a thermal power station, a compost station and a petrochemical plant. Grass and soil have also been sampled at a control site in a rural area away from any identified contaminating sources. Total PAHs concentrations in grass range from 43 to 177 ng/g DW. The highest concentrations are detected near the compost station (177 ng/g DW) and the highway (100 ng/g DW) while at the control site, total PAHs concentration is 25 ng/g DW. Total PAHs concentrations in soil range from 1975 to 25430 ng/g DW. The highest values are detected in soil from the petrochemical plant (9090 ng/g DW) and the highway (25430 ng/g DW). These concentrations are respectively 43 times and 118 times higher than the concentrations detected in soil from the control site. Although the PAHs concentration levels in soils are different according to the sites, PAHs profiles in this matrix are similar. In grass, no compounds with more than four cycles are detected at the control site while five and six cycles compounds are detected in all the other studied sites.

Poster: OPbp-6

Geochronology of organic pollutants in riparian wetlands of the Lippe river (Germany)

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Persistent lipophilic organic pollutants such as PAC's, PCB's and organochlorines tend to be adsorbed to aquatic suspended matter and to be accumulated in sediments. Therefore aquatic particulate matter is an important sink for many classes of anthropogenic contaminants. Furthermore sediments act as "mind of the river" reflecting the historical development of the riverine contamination. During flood events particulate matter is deposited on floodplains and riparian wetlands. Thus these areas can act as ecological archives in case of undisturbed and periodical sedimentation. The aim of our study was an extensive and detailed geochemical analysis of organic pollutants in a dated core of a selected riparian wetland. Using this approach the temporal development of anthropogenic emission into the river ecosystem and its catchment area can be traced by organic pollutants (e.g. hexachlorobenzene, bis(chloropropyl)ethers, tributyl tin). This includes monitoring of increase, limitation or termination of emission and correlation with periods of industrial production or domestic usage of organic pollutants as well as prohibition of discharge or application. Our results allowed an detailed insight into the history of anthropogenic pollution for the Lippe river system for the period since 1940 with a deviation of approx. 3 years.

Poster: OPbp-7

Binding interactions of herbicide metabolites in an aqueous system containing DOM and clay minerals

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A small-scale dialysis device was used to investigate binding interactions of two triazine herbicide metabolites in aqueous systems containing dissolved organic matter (DOM) and a three-layer clay mineral. In a first variant, aqueous solutions of desethyl terbuthylazine (DT) and hydroxydesethyl terbuthylazine (HDT) were dialysed against an aqueous solution of peat humic acids (HA). Moderate binding interactions, as expressed by normalised complexation coefficients $K(\text{DOC})$ were observed for both compounds at neutral pH. Strongly increased $K(\text{DOC})$ values at pH 3 for HDT were attributed to additional electrostatic interactions between DOM and the protonated triazine compound. In a second variant, the DOM solution was replaced by an aqueous suspension of montmorillonite. Adsorption to the clay mineral increased with decreasing pH for both compounds. When HA was added to the montmorillonite suspension, no significant changes were observed for binding coefficients of DT. However, for HDT at pH 3.6, interactions with the combined montmorillonite/HA system were stronger than for each sorbent alone. To investigate potential competitive effects, dialysis experiments were carried out in a system of DOM solution versus montmorillonite suspension. Neither for DT nor for HDT, the presence of HA had a diminishing effect on adsorption of the compounds to montmorillonite.

Poster: OPbp-8

Biodegradation and bypass flow of deicing chemicals in calcareous gravel soils

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The maintenance of airports and air traffic during the cold season requires the application of deicing chemicals. These fluids consist mainly of glycols, formate or acetate. They contain various additives like the toxic and persistent benzotriazole, a corrosion inhibitor, at concentrations of several percent. A single airport may use some thousand tons of deicing chemicals per season, a considerable amount of which is emitted to the environment. The fate of these chemicals in soils and their possible release to the groundwater is of concern at many airports worldwide. We studied the input, transport and degradation of the primary components of deicing chemicals at a major European airport built on Pleistocene calcareous gravels. Soil column studies demonstrated a high potential for biodegradation in the topsoil material, confirming results from incubation experiments. Limited or no degradation, though, nor sorption were observed in soil materials from deeper layers. Field monitoring with lysimeters revealed transport into greater depths especially during periods of intensive deicing activity. Subsequent displacement or degradation depend on the water balance as controlled by precipitation and evaporation. Groundwater wells showed acetate, a possible degradation product, following a winter with an extremely high application rate of deicing chemicals.

Poster: OPbp-9

Identification and verification of new Tonalide transformation products in environmental samples

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As a new tool for environmental assessments, a combination of synthetic chemical and trace-analytical methods has been applied in order to investigate the presence of potential transformation products of Tonalide® a major synthetic musk compound (AHTN: 1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)-ethanone) used as artificial fragrance in various commercial perfume and hygienic products on the European market. Technical Tonalide® was used as parent compound for various transformation reactions under controlled laboratory conditions. These chemical reactions delivered crystalline products which were used for subsequent qualitative analyses in environmental samples. All laboratory experiments were performed in methanol under atmospheric conditions. Two main transformation products (5,6,7,8-tetrahydro-3-acetyl-5,5,7,8,8-pentamethyl-2-naphthalenyl-carbaldehyde and (5,6,7,8-tetrahydro-3-ethyl-5,5,7,8,8-pentamethyl-2-naphthalenyl)-methanol) as well as 3 minor oxidation products (5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)-methanol, 5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl-carbaldehyde and 5,6,7,8-tetrahydro-methyl-3,5,5,6,8,8-hexamethyl-2-naphthalenyl-carboxylate) were synthesised, isolated and identified in three human breast milk samples with 7-24 pg/g wet weight as well as in marine fish fillets: one saithe, one Thornback ray filet and two Haddock filet samples in concentrations between 8 and 18 pg/g wet weight).

Poster: OPbp-10

Degradation of monolinuron in water: comparison of oxidative and photolytic processes

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The massive and prolonged use of pesticides in agriculture may cause their frequent occurrence in natural water. Phenylureas are commonly applied for weed control, acting as herbicides through inhibition of the photosynthesis. They may damage non-target aquatic primary producers such as phytoplankton, periphyton and macrophytes and thus alter the ecosystem equilibrium. In general, the consequences of a contamination are dependant of the communities sensitivity and of the potential eco-toxicity and bioavailability of chemicals, considering both the initial compound and the by-products issuing from transformations. In aquatic ecosystem, the compounds may be degraded by biotic or abiotic processes. Some of the phenylurea by-products are known to present a phytotoxicity equivalent or even superior to the initial pesticide one [1]. The present study is focused on the degradation of monolinuron by the main abiotic processes, i.e. oxidation and photolysis. The similarities in degradation pathways will be underlined, comparing reactions performed under photosensibilised and oxidative conditions. The involvement of radicalar mechanism will be evaluated through the presence of initiators or scavengers. The probability of such reactions in the environment will be discussed. [1] Tixier C., Bogaerts P., Sancelme M., Bonnefoy F., Twagilimana L., Cuer A., Bohatier J., Veschambre H., Pest. Manag. Sci. 56 (2000) 455-462.

Poster: OPbp-11

Assesment of the occurrence of glyphosate and AMPA in Austrian rivers and groundwaters

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The herbicide Glyphosate is the world biggest selling and fastest growing agrochemical by far. Glyphosate is used as an agriculture herbicide and in non-agricultural areas, such as in home and garden, industrial, railroad and rights of way situations. In 2001/2002 37 river monitoring sites and 161 monitoring sites in groundwaters within the Austrain Water Quality Monitoring Network were monitored. The water samples were transported in PP-bottles within 24 hours after sampling in a cooling box to the laboratory where the samples were analysed based on the DIN 38407-22 method. In two rivers Glyphosate concentration permanent exceeds the 0,1 µg/l level. and in further 10 rivers Glyphosate was found in concentrations higher than 0,02 µg/l. AMPA was found in 26 rivers >0,02 µg/l and in 12 Rivers the AMPA concentration was permanent higher than 0,1 µg/l with a maximum of 3,39 µg/l. The Glyphosate findings do not correlate with the corresponding AMPA values. The AMPA concentration were found to be 5 to 27 times higher. The high AMPA concentrations correlates with waste water treatment effluent which may contain AMPA as a metabolite of aminopolyphosphonates. In the analysed groundwater samples from 161 sites only at two sites AMPA was determined permanent higher than 0,1µg/l. Glyphosate never exceed 0,1 µg/l. In a laboratory experiment we investigated the degradation of Aminopolyphosphonates as a source of AMPA and Glyphosate in surface waters.

Poster: OPbp-12

Persistent organic pollutants (POPs) in sediments of reservoir lakes in the Ruhr Valley

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The Ruhr Valley, NW-Germany, is one of the biggest industrialised areas in Europe. For centuries it has been famous for coal mining, metal processing industry and the corresponding environmental pollution. However, during the last decades emissions have been decreasing. Sediments act as sinks for hydrophobic organic contaminants and can be seen as archives of historic pollution. Dated sediments from 2 reservoir lakes along the Ruhr River have been analysed. Persistent organic pollutants (POPs) belonging to various compound classes, including PCBs and PAHs, have been detected. Historical trends of PCB loading show higher levels between 1950 and 1990 with a maximum around 1970. PCB congener analysis reveals that penta- and hexachlorinated biphenyls are present throughout the cores. Sediments accumulated around peak concentrations are dominated by the tri- and tetrachlorinated biphenyls, which are main constituents of hydraulic fluids often used in coal mining. PAHs in the reservoir sediments originate from combustion sources as well as uncombusted fossil fuels. The maximum of PAH contamination dates back to 1955. After 1960 concentrations decrease rapidly. PAH source apportionment by alkyl homologue distributions reveals a domination of alkylated PAHs over parent compounds from the mid 50s to the mid 80s suggesting predominantly fossil fuel input.

Poster: OPbp-13

Development of a hyphenated technique suitable for the monitoring of trace level VOCs in hyperbaric diving environments

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Divers working on the sea bottom in the North Sea (100 m) work under a high pressure (10 bar) and live for 3 – 4 weeks in pressure chambers - hyperbaric chambers - between working shifts. It is therefore necessary, to minimise exposure burdens, to ensure that the atmosphere is very clean, which calls for contaminant monitoring. The problems are (i) the compounds which may be detected will not be known in advance, (ii) the concentrations are expected to be very low, and (iii) the samples must be taken by unqualified personnel and transported ashore. Details will be presented of the solid adsorbent preconcentration approach, using Tenax TA, coupled to thermal desorption GC-MS for analysis. Generation of standard atmospheres for calibration and comparison against a CRM have enabled the method to be validated. Sources of error associated with storage in sample cylinders have been investigated, suggesting that only electropolished stainless cylinders are suitable.

Poster: OPbp-14

Transformation and binding of TNT in soil

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TNT is one of priority soil pollutants in many developed countries. The objectives of this study was to elucidate mechanisms of TNT transformation in soil during soil self decontamination or bioremediation. The experiments were carried out with ¹⁴C-TNT introduced to different soils from USA and Russia. Some soil samples were amended with charcoal and planted with corn, what sharply accelerated soil decontamination. The phyto- and microbial toxicity of the amended soils was reduced tremendously. It was indicated that different intermediate oxidation and reduction ¹⁴C-products were accumulated, and their accumulation was accelerated in the charcoal amended soils. Formation of -NO=N- and -CH=N- bonds in soil has been previously demonstrated through NMR spectroscopy in experiments with [¹⁵N₃] TNT. The suggested mechanism of TNT transformation and binding in soil includes simultaneous formation of hydroxylamino and amino-derivatives as well as alcohol, aldehyd-derivatives and probably benzyl-radicals. These intermediates interact with each other and with the active groups of soil humic acids or with oxidation groups on the surface of charcoal micropores. It results in formation of stable polymerized and bound products of TNT in soil which are not toxic to soil biota and plants. Thus, the potential use of charcoal for soil bioremediation has been demonstrated.

Poster: OPbp-15

Aqueous phototransformation of two carbamate pesticides: ethiofencarb and oxamyl

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Carbamate pesticides are widely used for the crop protection. In the past, the utilisation of carbamate compounds was favoured over the prohibited organochlorine pesticides because they offer the advantage of being easily degraded in the environment. However, it's well recognised nowadays that the degradation products may be more toxic and more stable than the parent compound. Furthermore the new European drinking water directive 98/33/CEE fixes the limit concentration at 0,1 µg/L for the metabolites. It is therefore necessary to elucidate the mechanism of the transformation processes such as the photodegradation in order to assess the level of contamination of the water. The aim of our study is to determine the kinetics of phototransformation of two currently used carbamates (ethiofencarb and oxamyl) and to identify the main by-products. The experiments were carried out in purified water and in natural river water from Martinique (a French West Indies Island). The irradiation has been performed either with monochromatic lamp (254 nm) or polychromatic lamp starting at > 280 nm. Analyses by GC/MS and LC/MS allow the attribution of structure for different degradation products. The kinetics and degradation pathways will be presented during the conference.

Poster: OPbp-16

Determination of Cr, Cu and Ni in potable, surface and groundwaters using simultaneous multielement Electrothermal Atomic Absorption Spectrometry

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The European Directive 98/83/EC states that water laboratories should monitor several metals in potable waters. Analysis of metals are usually done, in our laboratory, by Single Element Electrothermal Atomic Absorption. A Multi Element method can improve the speed of the analysis, reducing costs. This method was developed for Cr, Cu and Ni in potable, surface and groundwaters. Samples and standards were acidified to 0.5% in nitric acid and two chemical modifiers were used (Palladium nitrate 1000 ppm in citric acid 2% and magnesium nitrate 1000 ppm). A Perkin Elmer SIMAA 6000 Spectrometer, equipped with transversely heated graphite atomizer, was used for measurements. The working ranges established were 2 to 10 mg/L for each metal. The detection limits obtained (0.5, 0.3 and 0.4 mg/L for Cr, Cu and Ni) were lower than those required by European Directive 98/83/CE (5.0, 200 and 2.0 mg/L for Cr, Cu and Ni). The results of the recovery tests were in the 89-110 % interval. Certified reference materials gave results in good agreement with the recommended values. The performances of both methods are statistically equivalent. Therefore, Multielement analysis also provides accurate and precise results for these type of samples.

Poster: TEam-1

A remote access water sampler for lakes

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It is desirable to collect water samples in lakes at short time intervals (roughly daily) when investigating certain processes, for example, particle settling, wind-generated resuspension of sediment, the effect of high river discharge, release of chemicals from sediment and the growth and collapse of a phytoplankton population. A remote access water sampler (RAS), developed by McLane Research Laboratories for use in the ocean, has been modified for lakes. The main modification was a reduction in weight from 120 to 55 kg in air. The equipment was deployed on four occasions to take daily samples for between 8 and 14 days. Daily grab samples were also collected and the concentration of total phosphorus, Zn, Cd, Cu, Pb, suspended solids and chlorophyll a determined in all samples. A comparison of the concentration in the RAS with that in the grab samples allowed the faithfulness of the RAS to be assessed. There was no difference between the concentration in the RAS and in the grab samples. Only on one occasion was the chlorophyll a and suspended solids concentration lower in the RAS. These results support use of the RAS for studies of the behaviour of solids and chemicals in lakes.

Poster: TEam-2

Intercomparison of methods used to study the chemical speciation of heavy metals in natural waters

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It is now widely accepted that the free metal ion is the fraction of trace metals that cause the most important biological effects. Consequently, speciation studies are generally used to estimate their toxicity. Most of the techniques used are based on measurements after equilibrium has been reached between an added ligand or adsorption site with the natural complexing ligands and metal ions in the sample. Other techniques determine the respective labile metal fraction relying on the kinetic stability of the non-labile fraction. The speciation of Cu^{2+} and Pb^{2+} in a sample of water from the "Ria de Aveiro" (Portugal), has been determined with techniques of both categories using the following 5 analytical methods: 1) Anodic Stripping Voltametry (ASV) with hanging mercury drop electrode and with mercury film electrode; 2) Cathodic Stripping Voltametry using oxine as competitive ligand; 3) Solid Phase Extraction (SPE) using a chelating resin (Chelex 100) and a cation-exchange resin (Amberlite CG-50). The results obtained for the 5 methods have been compared. The respective labile metal fractions are different for each methods except for ASV with mercury film electrode and the resin Amberlite CG-50 which led to similar results.

Poster: TEam-3

Small continuous monitoring network for nitrate determination in groundwater

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The objective of this study was to estimate the temporal variability of nitrate in groundwater within a small hydrological catchment contaminated during the last decades by intensive agricultural practises. Three different sites were selected to conduct the experiment, providing simultaneous measurements of nitrate concentration in groundwater. For that purpose, multiparameter probes designed by the BRGM for unattended, long-term, continuous in-situ monitoring of freshwater were used. The probes can measure simultaneously a full range of parameters including temperature, conductivity, dissolved oxygen, pH and up to two chemical species (ion selective electrode). Some previous studies showed that temperature, as well as ionic strength and chemical species such as bicarbonate, natural organic matter and suspended matter can severely interfere on the determination of the nitrate content in surface and groundwater using an ion selective electrode. Thus, the nitrate ISE was calibrated using the known amount added method first in the laboratory at various temperatures and second every 3-4 weeks in the field. Moreover water samples were frequently collected for analysis in the laboratory, by means of Ion Chromatography, in order to evaluate the degree of accuracy and the quality of the data measured by the probes.

Poster: TEam-4

Commercial silicone plates for organotins passive sampling in sea water

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Since 1940s, mono and dialkyl tins are used as polymer stabilisers as for example in PVC. Also since the late 1950s trialkyl organotins (tributyltin (TBT) and triphenyltin (TPT)) have been used as biocides in applications such as antifouling paints or pesticides. Even if TBT-based antifouling paints have been banned for boats less than 25 m length by the European Union in 1989, they still occur in the aquatic environment. Due to their persistence and toxicity these compounds and their metabolites are of major concern and are included in the EU priority contaminants and the EPA candidate contaminant list. Passive sampling present several advantages in front of traditional sampling methods. This technique permits time integration, improvement of the detection limits and finally the estimation of the bioavailability of the studied contaminants. In this work, an inexpensive passive sampler based on commercial silicone plates was studied in order to check its suitability for environmental monitoring. The behaviour of TBT, TPT and their metabolites (DBT, MBT, DPT and MPT) was observed controlling parameters as contaminant concentration, silicone plate size, water temperature and exposition time. Distribution coefficients were calculated as a first step for field in situ measurement.

Poster: TEam-5

Development of a colorimetric method for arsenate determination, application to arsenite oxidation by different common reagents

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Based on arsenate and phosphate similar properties, a colorimetric method using the formation of an arsenomolybdate complex was developed. The influence of complex formation time, daylight, temperature and competitive anions (silicate and sulphate) upon complex formation was determined. Optimal complex formation was reached in 1 hour at 20°C and was slightly favoured when developed at daylight. The formation rate decreased with decreasing reaction temperature and no influence of any of the competitive anions tested (at the given concentrations) was pointed out. The detection limit of this method was 20 µg As(V)/L. Through arsenate determination, this colorimetric method allowed to compare arsenite oxidation efficiency of five oxidants commonly used. H₂O₂ and MnO₂(s) were not considered as effective oxidants as a high excess was necessary to ensure As(III) oxidation. NaOCl and KMnO₄ were promising oxidants as they allowed complete arsenite oxidation with a small excess for NaOCl or less than the stoichiometric rate in the case of KMnO₄. FeCl₃ was the most effective oxidant among the reagents tested here. This simple, fast and sensitive arsenic determination method is suitable for field analysis, specially for waters containing low levels of phosphate and organic matter

Poster: TEam-6

A new method of simulating nitrate transport in diffuse pollution

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Non-point source pollution is in focus in many countries today to fight increasing eutrophication problems. Nitrate transport is a crucial part in the whole process of nitrate fate. Previous methods for simulating the nitrate transport process usually involved solving the complex advection-dispersion equations. A new alternative method, nitrograph method, is introduced in this paper. Different from the previous methods, the nitrograph method utilises the distribution of nitrate concentration with cumulative drainage to achieve the aim of simulating nitrate concentration at the output point. A nitrograph is defined as the distribution of nitrate concentration with cumulative drainage at the output point, which also can be considered to be the probability density function of the amount of drainage required by nitrate in the transport process from input point to output point. A gamma function with two parameters is adopted to simulate this distribution. Compared with previous methods, this method is simpler and needs less parameters. Experiments of monitoring nitrate leaching process have been undertaken at laboratory column scale and large pilot scale to validate this method. Examples of application of the methods at those scales, and their scale up to river catchments are given. Results are presented for the White Cart catchment in Glasgow, United Kingdom. The adaptability of the method to scale-up and the sensitivity of parameters to scale are critically discussed.

Poster: TEam-7

Metals distribution obtained by gel probes through the sediment/water interface in a Mediterranean Lagoon

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Thau lagoon (France) is characterized by intensive shellfish farming causing elevated sedimentation of particulate organic carbon and subsequent intensive biodegradation. In order to depict biogeochemical processes involving trace metals on a millimeter scale, samples were collected with dialysers and gel probes at the sediment-water interface. We prevent spatial heterogeneity problems using a DET/DGT combination adapted from Davison's DET device. We assume that if we put DET and DGT back to back on the same device in the sediment, the two front membranes will be in contact with the same environment. In order to check on calculated concentrations for metal elements with DGT's method, we analyse Fe and Mn on both gel supports. DET results show that, within the ten top centimeters of sediment, Sr, Ca, Mg and Na concentrations reach sea water values. This leads to infer that DET data are robust and show that these species are conservative in this zone. Fe and Mn results exhibit profiles with similar pattern on both faces but with different concentrations values. Our work shows that DGT method can be efficiently calibrated with back to back DET data.

Poster: TEam-8

Complexing gel integrated microelectrode arrays for direct detection of free metal ion concentrations in natural waters

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Measurements of relevant fractions of trace metals in natural waters are essential to improve our understanding of their behavior and long-term impact. Free metal ions is of particular interest since these species are related to biological uptake. There is however actually no analytical technique which allows their direct detection in complex media. Therefore a novel Complexing Gel Integrated Microelectrode (CGIME) for specific monitoring of free metal ions in natural waters has been developed. It is based on the Gel Integrated Microelectrode (GIME) and the Diffusion Gradients in Thin-films (DGT) principles. The surface of an Ir-based microelectrode array is covered with a 4 mm thin Microchelex chelating resin which in turn is covered with a 300 mm thick agarose gel. The Hg layers are electrochemically deposited and reoxidized through both layers. During equilibration with the test water, metals accumulate on the Microchelex resin in proportion to the free metal ion concentrations. After equilibration, the sample solution is replaced by an acidified electrolyte solution. The metals accumulated are released by the acid, and immediately measured by the voltammetric microsensor. Laboratory optimization of the key analytical conditions and on-field applications in sea water will be shown.

Poster: TEam-9

Speciation of copper and zinc in natural river water: comparison between diffusive gradients in thin films (DGT) and voltammetric measurements

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The results showed strong linear positive correlation between DGT and ICP-MS measurements (total dissolved) regardless the concentrations of organic complexing ligand (NTA) for both metals. Regardless the concentration of NTA and total Cu, the DGT measured around 30 % of total dissolved Cu. The concentrations of free Cu ions measured by CLE/CSV were around 10-8-10-7 % of total metal concentration for the solutions with no added NTA, and around 10-4 % for the aqueous solutions with spiked NTA at somewhat lower pH. DGT measured around 10 % of total Zn concentration, regardless the concentration of organic ligand (NTA). The free Zn ions measured by CLE/ASV were around 2 % of total metal concentration measured by ICP-MS and the ratio was decreasing with increasing Zn concentration. The results clearly show that iminodiacetic acid as a functional group (part of an ion-exchange resin Chelex-100, used as a binding agent in DGT) competes effectively with NTA ligand for metal (Cu and Zn) ions.

Poster: TEam-10

Heavy metal analysis in soil at contaminated sites

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The establishment of soil quality standard represent a target for which scientist and authorities should aim. In the characterisation of soil quality at contaminated sites, Italian legislation specify the limits for heavy metals, according to the final destination of the site after remediation (residential or industrial). These soils which have been drastically disturbed, often filled with alien materials, have developed peculiar characteristics which are recognised as being different from agricultural or natural soils. Heavy metal analysis on the only soil fraction less than 2mm, which is generally used for the analysis of agricultural soil can be in most cases misleading. The proposed method consider that heavy metals sorb to clay, silt, and organic particles. Most of these particles tend to adhere to the larger sand and gravel which often represent more than 50% of a soil at contaminated site. The procedure consist of sieving soil in three fractions (F1>2cm, F2>2mm, F3<2mm) to separate the small particles from the larger by breaking adhesive bonds. Determine the relative percent weight (A1, A2, A3) of the three fractions, and analyse the subdivided material separately to obtain a thorough understanding of soil contamination by the final concentration expressed as $C = (CF1.A1) + (CF2.A2) + (CF3.A3)$

Poster: TEam-11

Experimental study of uranium transport at the marine sediment water interface

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Even if extensive lab and fieldwork has been done to determine geo- or biogeochemical reactions that precipitate uranium ore, dominant pathways of uranium accumulation in anoxic marine sediments remain to be demonstrated. In this work, we utilize bioreactors to validate possible mechanisms and extract kinetic information that applies to in situ conditions. The bioreactors experiments are run in N₂ Flushed gloves box. Coastal seawater spiked with uranium (4 times the natural background) is injected through the reactor during 24 hours. We injected a second solution after the first 24 hours, when steady state is reached. This second solution is spiked with bromides associated with a microbial inhibitor. Bromide is used as a tracer of dispersion (D). The presence of chemical gradients within the reactor implies the utilization of a numerical 1-D model [AQUAQIM 2.0 : Reichert, 1998] to separate transport from reaction effects and finally, calculate a dispersion coefficient (D) and extract kinetic parameters. We observe that uranium is trapped in anoxic marine sediments (cores from Bay of Biscay) during our bioreactor experiment, because concentration of uranium decreases drastically from the injection concentration level to almost zero in a few hours.

Poster: TEam-12

Multi Physical-Chemical Profiler for real-time continuous in situ monitoring of specific fractions of trace metals and master variables

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Novel analytical tools allowing real-time monitoring as well as detailed temporal and spatial evolution of the distribution of specific metal species and master variables is of prime interest to better understand the role and the fate of trace metals in coastal aquatic ecosystem. State of the art in the development of a Multi Physical-Chemical Profiler (MPCP) will be presented. It has been developed to allow simultaneous in situ, autonomous monitoring of three specific fractions of Cu(II), Pb(II), Cd(II) and Zn(II): i) free metal ions concentrations which is known to be related to biological uptake, ii) the dynamic Me species which are potentially available for organisms, iii) the particulate and colloidal species (total extractable Me concentration minus dynamic fractions) which play important role in transport properties and residence time, as well as master variables (pressure, temperature, pH, oxygen, conductivity, salinity, redox E and chlorophyll a). It is based on unique gel integrated voltammetric microsensors, a submersible probe with three independent measuring channels, a submersible flow-injection system, integrated conventional physical/chemical sensors. The characteristics of the microsensors and main components of the probe will be summarized. Its environmental utility will be illustrated with examples of laboratory characterization and preliminary in situ application.

Poster: TEam-13

Capabilities of PLM devices for speciation and detection of trace metals in waters

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In natural aquatic systems, trace metals are distributed in various chemical forms playing specific environmental roles. However, many trace analysis methods have no inherent speciation capabilities whereas the assessment of health hazards, toxicity and bioavailability is based on levels of specific chemical forms rather than on total concentration levels. The emerging Permeation Liquid Membrane (PLM) technique based on liquid-liquid extraction seems to be promising for speciation studies and offers the following advantages: i) the analyte detection is separated from the sample matrix; ii) the metal species is enriched providing the ratio between strip and source volumes is smaller than unity; iii) under appropriate conditions, PLM can concentrate selectively the different metal fractions. The versatility of the technique allows to implement different types of supported liquid membranes in particular flat sheet and hollow-fibre supports. Both these types of device have demonstrated the ability to preconcentrate selectively and efficiently Cu and Pb ions owing to the selective metal carrier didecyl-1,10-diazacrown6 and lauric acid dissolved in the organic solvent constituting the liquid membrane. The speciation capabilities of such devices will be shown by studying the metal flux variations *versus* concentration ratio $[M]/[L]$ where L is a metal ligand such as sulfosalicylic acid and M such as Cu(II). Application of in-situ preconcentration for free metal ion determination in natural water will be also presented.

Poster: TEam-14

Characterization of the labile complexes measured with DGT by means of numerical modelling

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The Diffusion Gradient in Thin films technique (DGT) recently emerged as a convenient way of in situ exploring the speciation of trace metals. The device is composed of a layer of hydrogel backed by a binding-layer (Chelex 100). Once deployed, the device sequesters metal ions on the binding resin, creating a diffusion gradient between the bulk solution and the inside. This gradient induces a constant diffusion flux, which characteristics are directly related to the physics of the gel and the concentration of labile metal in the solution. The formal modeling of the fate of the metal species within a DGT during an experimental deployment is presented. It allows to clarify the relations between the flux of metal accumulated on the resin and both its speciation in the bulk solution and its physico-chemical characteristics. Several simulations are compared with experimental data obtained with inorganic and organic copper-complexes. The model is able to predict that the thicker the gel, the more labile the complex appears, and that the slower the diffusion of the metal-ligand complex in the gel, the less labile it appears, although spending a longer time within the diffusion gel. Those predictions are experimentally validated

Poster: TEam-15

FTIR characterization and monitoring of the organic part of mercury polluted soil

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FTIR spectrometry is used to investigate environment-linked problems and pollution diagnostic. Metals complexation by humic acid, a significant compounds of the organic part of soil, leads to observable structural changes on the infrared spectra. These biopolymers might be utilized as indirect pollution indicators. Humic acid is a macromolecule consisting of several aromatic rings containing carboxylic and phenolic functional groups, capable of interaction with heavy metals, such as cadmium and mercury. In addition to FTIR spectroscopy, we have confirmed the humic acid-heavy metal interaction through acidity titration and by flame atomic absorption spectroscopy (FAAS). The spectra show that the typical band of the COOH function at 1715 cm⁻¹ decreases with the increase in mercury concentration. The peak is only a weak shoulder for a mercury concentration of 4 g/l we could follow easily the COOH band intensity decrease. This shows the carboxylic sites occupation as and when the mercury concentration increases until the entire band disappearing. This indicates an important humic acid sites occupation by mercuric ions. The band of the resulting salt is noticeable at $\nu(\text{COO}^-)_{\text{asym}} = 1595 \text{ cm}^{-1}$. These results are corroborated by flame atomic absorption spectrometry.

Poster: TEbp-1

Study of contamination of groundwater in the Mostaganem city plateau (West Algeria)

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Aiming at determining the groundwaters contamination in the Mostaganem city plateau (West Algeria), we have analyzed 90 water points through the whole area. The results found show a chemical degradation of the waters quality, particularly in the South and the Southwest of the plateau. The nitrates content in the ground water is relatively high, beyond the allowable limit of 100 mg.L⁻¹. The results show that 69% of the analyzed water points present a nitrate concentration higher than 50 mg/L of which 15.5% have a concentration higher than 100 mg/L. On the other hand, the nitrite concentration is higher than 0.1 mg.L⁻¹ in only 6% of the investigated sites. 8.3% of the points have a phosphate concentration higher than 0.5 mg.L⁻¹ but only 1.2% of these have an ammonium concentration higher 0.5 mg.L⁻¹. The Water contamination by metallic elements is more worrying, especially near Hassi Mameche and Ain Tedles cities, as the analysis results show a simultaneous presence of cadmium, copper, iron, manganese, and lead with concentrations than the allowable limits fixed by WHO. The use of cards of the Mostaganem plateau area as compared with pollution cards established by Geographical Information System has clearly shown the fragility and vulnerability of this area water table.

Poster: TEbp-2

pH dependence of copper adsorption in vineyard soils of Geneva canton

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Vineyard soils are enriched with copper as a result of long-term phytosanitary treatments. The role of pH in copper retention in seven vineyard soils of Geneva having HNO₃ (2M) extractable Cu concentrations ranging from 58 to 489 mg/kg, was investigated by batch equilibration adsorption curves for pH values from 4 to 6. The adsorption curves fit to Freundlich adsorption model: $q = K_f C^n$ where q: Cu adsorbed (mg/kg), K_f: Freundlich constant, C: Cu in solution at equilibrium (mg/L), n: power coefficient <1. For each soil the logarithms of K_f and n are linearly correlated to pH. For all the soils together, regionally useful approximate linear relations for K_f and n were obtained

Poster: TEbp-3

Heavy metal contamination in soils and waters around the Dongil Au-Ag mine area in Korea

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In order to assess the level of heavy metal contamination and their behavior in the soil-water system of the abandoned mine area, tailings, soil and water samples were collected from the Dongil Au-Ag mine area in Korea. Tailings and soil samples were decomposed by an aqua-regia and then all samples including water samples were analyzed for As, Cd, Cu, Pb and Zn by ICP-AES. Mean concentrations of As and other heavy metals in tailings were 8,970 As mg/kg, 7.0 Cd mg/kg, 7,806 Cu mg/kg, 5,070 Pb mg/kg and 1,130 Zn mg/kg. The levels of heavy metal contamination in soils are higher than those in world average soil. Especially, As (37 mg/kg) and Cu (130 mg/kg) are elevated in agricultural soils. Concentrations of As and SO₄ in mine water was 0.52 mg/L and 114 mg/L, respectively. In groundwater, these elements were detected up to 0.024 mg/L and 253 mg/L, respectively. This groundwater is used by drinking water around the Dongil mine area and the level of SO₄ is higher than permissible concentration for drinking water in Korea. Therefore, the mine tailings including the sulfide gangue minerals such as arsenopyrite can be the main pollution sources of heavy metals in soil-water system in this area.

Poster: TEbp-4

Cadmium sorption by free and immobilised bacterial cells. Comparison between linear and nonlinear models

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The study of the adsorption of cadmium by free bacterial cells (*Bacillus*), and immobilised bacterial cells in alginate beads is realised in ultrapure water. The immobilisation in alginate beads permits the survival of the micro-organisms in non ideal conditions. The aim of these experiments is to determine the maximum uptake of the biosorbents (*Bacillus* alone, alginate beads alone and immobilised cells). The adsorption parameters are determined with linear (Freundlich and Langmuir) and nonlinear models obtained with EasyPlot software. EasyPlot software has a least square fitting routines for fitting nonlinear models. We found similar maximum uptake, whatever the model used. The appropriateness between the two types of models permit us to conclude that cadmium adsorption can be considered as a monolayer phenomenon. The following affinity can be proposed for the cadmium adsorption: Alginate beads alone < immobilised cells < free cells, obtained with the b Langmuir parameter and confirmed by the K Freundlich parameter. On the contrary, the maximum uptake gives the following series: free cells < immobilised cells < alginate beads. The three biosorbents are interesting biosorbents to check cadmium pollution. The use of these biosorbents can be interesting in water medium and in soil polluted.

Poster: TEbp-5

Probing ions - gel interactions through diffusion and partitioning of solutes: Enlightening the behavior of the agarose gel

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Among the versatility of their applications, agarose gels are used as anti-fouling layer, deposited on electrochemical sensors working in environmental aquatic media, to allow quasi-free diffusion of small molecules, while preventing the incoming of colloids and larger aggregates. To prevent misinterpretation of quantitative measurements of trace compounds with analytical techniques using gels, we have investigated solute - gel interactions, focusing on agarose hydrogels. The nature and the density of charged sites in agarose gels have been studied. To investigate the solute-gel interactions resulting from charge effects and specific binding, diffusion and partition coefficients of various ions have been measured as a function of ionic strength and pH. The large majority of gel's binding sites are pyruvate groups. The Donnan potential and the charge density of the gel have been evaluated. The partition coefficients of ionic solutes vary with the ionic strength, because of the screening of the gel's anionic sites as predicted by Boltzmann and Poisson-Boltzmann equations. As expected from the Manning's theory, the diffusion coefficient of cationic species is reduced at low content of salt. In addition to electrostatic effects, specific interactions have been detected between metal ions and the gel.

Poster: TEbp-6

DOOM-MB, a database on organic matter – metal binding data

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It is well established that natural organic matter (NOM) is a significant complexant and buffer for metal ions in natural water systems. The key parameters that quantify and facilitate prediction of metal-NOM interactions are the affinity constant and the binding capacity. We have undertaken an extensive critical analysis and interpretation of all such data published for complexation of trace metals by NOM in natural waters. This study is based on the compilation of data published over the last 35 years and on the reinterpretation of these data in terms of the binding heterogeneity of NOM. A spin-off from this project is the construction of a web-based database, DOOM-MB (Database On Organic Matter – Metal Binding) that will soon be freely available. The database will contain affinity constant and binding capacity data for different types of NOM: whole waters (so called "LIL2" ligands), isolated humic substances and non-degraded biota-derived material (bacteria, phytoplankton, and their exudates). Data are stocked in a database server Oracle 8i (8.1.7) (hosts SUN SPARC with UNIX SOLARIS 2.6). The application (written in PL/SQL) is stocked in the database and served for the web by an Oracle Application Server v4.0.

Poster: TEbp-7

Sb(III) oxidation by H₂O₂ in aqueous solution

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Antimony is ubiquitously found in the environment as a result of natural processes and human activities. Although it is considered to be a pollutant of priority interest by USEPA and EU, it is one of the elements that have received the scantiest attention in environmental studies. Antimony is mainly found in two oxidation states (III and V) in environmental, biological and geological samples. Both oxidation states are characterized by different chemical behaviour, bioavailability, and toxicity. The presence of significant amounts of Sb(III) in oxic waters and of Sb(V) in anoxic ones has often been reported. This is in contradiction with thermodynamic predictions. Several processes may influence oxidation and reduction rates, including chemical and photochemical transformations and biological mediated reactions. At the present time, kinetic information for redox reactions of Sb in natural waters is limited and rate constants are generally unknown. Since H₂O₂ is a potential candidate for the chemical oxidation of Sb(III) in natural waters, in this study the oxidation of Sb(III) by H₂O₂ has been investigated in NaCl solutions over a wide range of pH, ionic strength and oxidant concentrations. The corresponding rate constants have been determined.

Poster: TEbp-8

Study of the solubility of antimony trioxide under natural seawater conditions

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Antimony production and use has steadily increased. More importantly, uses of antimony have changed over the years. Traditionally, antimony was used in lead-antimony alloys. Bulk secondary antimony can be recovered as antimonial lead, most of which is regenerated and then consumed by the battery industry. Nowadays, the main form of antimony used is as Sb₂O₃ which cannot be recycled. The major use of Sb₂O₃ is as a flame retardant synergist in plastics, paints, adhesives, sealants, rubber and textile back coatings. Sb₂O₃ is currently undergoing a Risk Assessment under the EU's Existing Substances Regulation (793/93/EEC). On the other hand, airborne supply to aquatic and terrestrial systems is important for the environmental fate of antimony and, although not much information is available on the species of antimony actually present in the atmosphere, antimony is mainly emitted as its oxides from smelting operations and combustion of coal and refuse incineration. Although the dissolution of Sb₂O₃ certainly plays a central role in antimony environmental fate and bioavailability, existing data are very sparse. In this study, the rate of dissolution of Sb₂O₃ has been investigated in NaCl solutions under natural seawater conditions. The effect of various parameters (temperature, pH, ionic strength) has been considered and the dissolution mechanism discussed.

Poster: TEbp-9

Release of nitrogen from resuspended sediments: a Thames Estuary study

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The bioavailabilities of adsorbed nitrogen species in estuarine sediments are typically determined through single-volume extraction of filtered sediment with an ion exchange solution, such as 2M KCl, at a solution to solid ratio of 10-20. This may underestimate the potential release of nitrogen during sediment resuspension, where the solution to solid ratio can increase by at least two orders of magnitude. Thus, knowledge of how sedimentary nitrogen behaves under such hydrodynamic conditions is necessary if the environmental impact of sediment displacement operations, such as dredging, is to be understood. In this study, the release of ammonium and the methylamines was measured in simulated resuspension experiments using sediment from the Thames Estuary, United Kingdom. Surface sediment was resuspended in filtered overlying water (1g L^{-1}) at a concentration representative of the SPM concentrations measured in the estuary, and sampled over 48 hours. Dissolved concentrations of the analytes increased rapidly, with equilibrium occurring after 2 hours. Desorption typically accounted for >99.9% of the final analyte concentrations. Single-volume extraction of sediment consistently underestimated concentrations of adsorbed analytes (typically 40-50%), when compared with the results of simulated resuspension. Thus, it appears that conventional adsorption measurements may not realistically reflect sediment nitrogen fluxes to the water column.

Poster: TEbp-10

Metal pollution in the waters of the Guadalquivir estuary after the Aznacollar spill (South-Western of Spain)

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The Aznacollar accident is the worst disaster related to acute pollution happened in Spain (1998). The toxic spill of the pyrite mine released 4 million cubic meters of acidic water and 2 million cubic meters of toxic mud containing high amounts of heavy metals into the Agrio River and then passed into the Guadiamar River, where the authorities tried to stop them. Nevertheless, 4 Hm³ of the polluted water were conducted through a channel towards Brazo de la Torre tributary and directly discharged into the Guadalquivir River, near Doñana Park, the major marsh protected area in Europe. So, we study the distribution of four heavy metals (Cd, Pb, Cu and Zn) in the waters of the Brazo de la Torre tributary and the Guadalquivir estuary during two years after the disaster (2000-2001) and after the Spanish authorities reduced the potential impact of the mud with cleaning and remedial activities. The speciation analysis was carried out classifying metals in several fractions: particulate, ionic forms, labile forms and strongly forms, associated with organic or inorganic matter. The results can allow assessing the differential behaviour of each metal and illustrating the potential value of the spill-induced pollution in the area.

Poster: TEbp-11

Environmental quality of riverine and aquatic sediments from the Gulf of Cádiz, Spain

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Due to mining of sulfide deposits and to intense industrial activity, the Southwestern coast of the Iberian Peninsula encompasses one of the most polluted estuarine systems in Western Europe. In the present work, the total concentration, distribution and the possible geoaccumulation of organic matter and key heavy metals (As, Cr, Cu, Hg, Ni, Pb & Zn) in sediments from three main locations in western Cádiz Gulf (southwest Spain) was studied. An extensive sampling campaign along the Guadiana river, Guadiana and Huelva (Tinto and Odiel rivers) estuaries and in offshore associated sediments, was conducted during 1998. Heavy metals, total organic carbon and sulphur were analysed in the fine sand fraction (< 0.2 mm) of 105 sediment samples. In addition, as background for analysis, two borehole samples were taken in the Guadiana and Huelva estuaries. Chemical numerical and a weight-of-evidence complementary approaches were used to contribute in assessing the quality of riverine and coastal environment of the area under study. Principal Component multivariate analysis was performed on the data to group areas with a similar degree of contamination

Poster: TEbp-12

Interaction of a lignocellulosic substrate with chromium(III)

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A number of components of natural organic matter, especially lignins, are able to sorb organic pollutants or to complex metallic cations. Lignins, that present a great content of potentially metal-complexing functional groups, find an application in water purification systems. The complexation process affects the transport in soils, water and sediments of the metals and organic pollutants. Reactions between transition metals and lignins can occur in aqueous phase or at solid-solution interface. In solution, the soluble lignin fraction leads to complexation reactions with metallic cations by interaction between these cations and small soluble lignin molecules. At solid-solution interface, sorption reactions occurred, leading to surface complexes. In order to complete previous works about Fe(III), Cu(II), and Mn(II) which are very abundant in soils, we present here a study of the interaction between a lignocellulosic substrate extracted from wheat straw and the toxic cation Cr(III) which is found in industrial waste. The main factors (pH, kinetic, concentration) governing the sorption properties of lignin and some quantitative sorption results are presented throughout batch experiments. The geometry and the structure of the surface complexes with chromium are studied by electron paramagnetic resonance (EPR) and X-ray absorption (EXAFS and XANES) spectroscopies.

Poster: TEbp-13

Trace metals in different soil types of Estonia

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Regular measurements of environmental pollutants are usually carried out within national monitoring programmes. Information on soil attributes that influence environmental processes is often missing. Environmental characteristics such as soil texture, pH, organic matter (OM) content, red ox potential, etc. and soil matrix can modify the bounding of pollutants to the solid phases, their speciation under physico-chemical interactions or biological transformations. The aim of this paper is to present field-scale data on selected heavy metals (Cu, Pb, Cr, Zn and Cd) in different soil types of Estonia. The soil samples were taken from humus horizon and pH values, surface area and distribution of pore volumes, content of OM, and bulk chemical composition was characterized. Element and soil specific features of trace elements were evaluated based on field data and laboratory experiments (spiked samples). Regression analysis was performed using OM and Ca²⁺ data as the soil characteristics and trace metal concentrations. The mobility and bioavailability of heavy metals was found highly site-specific. The role of system properties in speciation of pollutants was discussed

Poster: TEbp-14

Sporadic heavy metal contamination of the Nant d'Avril, a small river close to Geneva, Switzerland

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The assessment of the water quality of rivers having a portion of their watershed industrialised or urbanised highly depends on the sampling strategy. Sampling based on regular frequency, or integrated water samples may not record acute contaminations which last few hours or less. Therefore a specific sampling strategy has to be implemented, based on a continuous monitoring of water parameters that can be used as indicators of potential contamination. The Nant d'Avril is a stream which drains a small part of the Canton of Geneva, but includes a industrialised area, the CERN, agriculture lands and vineyards. Continuous monitoring of conductivity and pH of the river water permits to trigger water sampling during discrete contamination events. During these events, contents of some heavy metals, especially Pb, Zn and Cu, are many fold higher than during normal periods. The timeframe of the events clearly denotes the anthropogenic origin of these inputs.

Poster: TEbp-15

Heavy metals (Pb, Cu, Cd) monitorization in the city of Lisbon using the white poplar (*Populus*) as bioindicator

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This work presents a monitorization of heavy metals (Pb, Cu, Cd) concentration in urban areas as a result of traffic emissions, using as bioindicator a common species available in the whole city of Lisbon. The chosen bioindicator were white poplar (*Populus*) a deciduous species which guaranties new leaves each year. White poplar leave samples were gathered in eight areas ranging from high to low traffic intensity, high to low density of population and open to closed topology using standardised gathering methods. For the digestions of the leaves classical humid and dry digestion methods were initially used. These procedures are time and reagent consuming so a microwave digestion method was optimised to deal with this type of sample. The latter method, once optimised showed to be fast, clean and efficient. The analytical methods used for the heavy metals determination were atomic absorption spectrometry with graphite chamber and anodic stripping voltammetry. The contends in heavy metals determined in eight areas of Lisbon city are according with the traffic intensity, in areas of intense traffic were obtained the higher values of heavy metals. The results obtained by the two methods agree within the experimental error.

Poster: TEbp-16

Evaluation of lead concentration over Tehran metropolitan

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Considering the traffics volume in Tehran, the lead measurement in city's atmosphere is of prime important. For the first time in Iran a procedure was adopted for organic lead determination in air by the department of air pollution in Research Institute of petroleum Industry (RIPI). The determination of lead in air were carried out in five locations for the period of nine months. The results indicated that concentration of inorganic and organic lead ranged respectively from 0.24 to 3.4 microgram per cubic meter and Trace amount to 15.15 microgram per cubic meter as Pb. Concentrations were generally highest in densely traffic areas, intermediate in commercial areas, and lowest in residential areas. The effect of inversion phenomena and metrological parameters were the main reasons for increasing of average lead concentrations in autumn and winter.

Poster: TEbp-17

The role of coarse colloids as a carrier phase for trace metals in riverine ecosystems

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Colloids are defined as particles having at least one dimension between 1nm and 1 μ m (IUPAC) and which are small enough not to be subject to gravitational forces (i.e. they do not sediment in water) but large enough to form an interface onto which environmental contaminants can adsorb. However, fractionation of bulk water samples into a particulate and a total dissolved (i.e. colloid + truly dissolved) phases is often accomplished by filtration at 0.45 or 0.22 μ m. Although partly justified by historical and practical reasons, the use of such operational procedures results in the inclusion of coarse colloids (between 0.45 and 1 μ m) into the particulate fraction. Using cascade filtration, we quantified the fraction of trace elements associated with coarse colloids in a number of rivers having widely different geochemical characteristics and subject to various degrees of anthropogenic impacts. We show that for Al, Ti, and Pb, the proper evaluation of the coarse colloidal fraction affects the values of particle/total dissolved (Kd) and colloid/truly dissolved (Kc) partition coefficients by a factor of 2. Furthermore, association with coarse colloids may have important implications for the assessment of transport, loading and potential bioavailability of metals in rivers.

Poster: TEbp-18

Enzymatic production of non ionic biodegradable surfactants: sugar esters

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The large number of studies to take advantage of enzymes in efficient, cost effective and environmentally friendly industrial processes, is well known. Lipases are heavily exploited not only for their natural hydrolytic activity but also for the possibility to perform esterification in anhydrous controlled reaction environment. A new group of non ionic, biodegradable and mild surfactants was synthesized via esterification of fatty acids with sugars. Actually, by controlling the chemical weight of the surfactant hydrophobic chain (fatty acid length chain) out of the hydrophilic part (sugar), it is possible to cover all the range of surfactants properties (emulsifying, solubilizing, detergent, wetting agents). Glucosilmyristate production was chosen as lab scale reaction model. Several factors affect the kinetic of reaction such as the water activity in organic solvents, the complex phase system formed during reaction and the kind of immobilized lipase. The obtained reaction rate was 16 g glucosilmyristate h⁻¹ g⁻¹ lipase at the temperature of 60 °C despite the strong solubility difference of reagents (glucose and myristic acid in organic solvents suitable for a clean process). From the information achieved at lab scale, a semibatch environmentally-friendly process is being developed. Sugar water was the final waste and the removal of water occurs inside a dehydrating module out of the reaction system, not via gaseous phase.

Poster: PrGr-1

Sonochemical decomposition of substituted anisole

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Sonochemical treatment is a process technology that holds promise for safely and economically destruction of organic compounds in aqueous media. In this work, we focus attention on decomposition of anisole and substituted anisole (-OH, -CH₃) that mimic structural elements found in industrial and natural water. Experimental results indicate that reaction rates are associated to the driving frequency and increase with ultrasonic power applied. Analyse of the by products point out that depending of the hydrophobic character of the target molecules, the destruction can follow different ways: -thermal destruction in gas phase, -thermal destruction in super critical conditions, -radical reaction with hydroxyl radical. These results are consistent with the mechanism of the sonochemical action which is focused around the behaviour of the ultrasonic bubble of cavitation that works as a microreactor. Compounds with high fugacity enter into the bubble and are thermally eliminated at high rate. Hydrophilic compounds react at lower rate with -OH radicals outside of the bubble.

Poster: PrGr-2

New amines for carbon dioxide separation from a gas mixture

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Carbon dioxide is the largest contributor to the greenhouse effect, being produced in the combustion of fossil fuels as oil, natural gas or coal. Several technologies have been developed for separating carbon dioxide: absorption by liquid amines or solid materials or membrane separation. In this paper we discuss the ability of diamines for the capture of carbon dioxide from gas mixtures. The kinetics of CO₂ uptake for four new amines is compared with that of absorption of CO₂ by MEA that is used in industrial applications. We show that the new amines have twice the capacity of MEA as CO₂ absorbent. This fact is of great interest, as increasing the amount of absorbed CO₂ per unit of absorbent is a key factor for reducing the separation costs. The mechanism of absorption will be discussed

Poster: PrGr-3

Comparison of lead and cadmium uptakes by three sulfur-containing ligands immobilized on silica gels. Adsorption isotherms and kinetics

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Thiol- and amino-functionalized silicas were usually employed for removing heavy metal ions from waste water, the thiolated adsorbent exhibited a higher complexation affinity for Hg^{2+} while other metal ions such as Cu^{2+} , Zn^{2+} , Cr^{3+} and Ni^{2+} showed exceptional binding ability with its aminated analogue. In this study mercaptopropyl functionalized silica, SiS, was compared with two aminoethanethiol modified silica gels, SiNS and SiNMeS, for their ability to remove Cd^{2+} and Pb^{2+} from aqueous solutions. Adsorption was performed using a batchwise process and the maximum adsorption capacities were obtained for lead and cadmium with all materials. A kinetic study showed the equilibration time was shorter for lead (less than 1h) than for cadmium (>3h). The adsorption isotherms obeyed the Langmuir model. The calculated parameters indicated a comparable removal capacity of SiNS and SiNMeS, slightly greater than SiS. This study underscores the different behaviour of the SiNS and SiNMeS compared to the SiS towards lead and cadmium uptake.

Poster: PrGr-4

Utilization of the electro dialysis technique to regenerate granular adsorbent bed saturated by sulfur

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The desulfurization of petroleum products is an important operation as the sulfur oxide gases evolved from the combustion of these products result in acid rains. Therefore, removal of sulfur is essential before the combustion of fossil fuels. Aimed at cutting down cost of desulfurization technique various techniques have been tested in the past decade. The main purpose of this work was to develop a novel treatment method to regenerate the SO_2 saturated column by utilization of three compartments electro dialysis equipped with exchange membrane ADP, CDS and bipolar membrane. Electro dialysis equipped with three compartments were utilised under various experimental parameters to determine the optimum conditions of the recovery of column particles saturated by SO_2 .

Poster: PrGr-5

Synthesis, characterization and metal uptake behaviour of mercaptoacetamide ligand immobilized on silica - Environmental application

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Chemically modified silicas have been drawing increased attention as sorbents for high-performance liquid chromatography and as supports in heterogeneous metal complex catalysis. Lately, they have found application in the extraction of metal ions from solutions. We are interested by environmental application for such supported molecular trap which allowed trace amount metal cation uptake. Thus, in order to investigate the effect of the solid support on the metal uptake capacity, we have synthesized and studied various N,S silica bound ligands. In the present work, we report on the properties of mercaptoacetamide ligand. Functionalised supported molecular trap was produced by reaction of protected-thiol mercaptoacetamide with 3-aminopropyl modified silica gel. The sorption and properties of the material towards heavy metal cations were investigated using batch method. In parallel, we have studied the coordinating properties of the ligand in synthesizing the related complexes, in homogeneous solutions, with the mercaptoacetamide bearing a silatrane function thus allowing free modelisation of the silica surface.

Poster: PrGr-6

Environmentally benign techniques (ultrasound and microwaves) for chemical transformations

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The application of ultrasound can accelerate chemical transformations and examples of it in organic fine synthesis are numerous, especially in reactions via free radicals. A very important new domain is the use of ultrasound for the destruction of organic material in industrial waste liquid. Toxic pollutants resisting to other treatments are destroyed by ultrasound. The application of microwave heating can accelerate chemical transformations in solution as well as in the solid state, lead to products in a short time with high purity and yields. The aim is to search for a specific microwave effect and to scale up the reactions. Moreover, it is not always necessary to work in presence of a solvent, and this aspect is of particular interest to industry and important for the environment. Taking advantage of the beneficial effects of these two techniques in green chemistry we have accomplished the preparation of few cation exchanged and pillared clays by ultrasound and microwave techniques. These catalysts have been characterized by X-ray diffraction, EDX-SEM and AAS techniques. These catalysts have been further used to accelerate some reactions like preparation of quinones, oxidation of polynuclear hydrocarbons and protection of alcohols as ethers to give products in higher yields, under milder conditions and in some cases even in the absence of organic solvents.

Poster: PrGr-7

Determination of optimum condition on synthesis of zeolite from coal fly ash using an experimental design

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The objective of this study was to define an optimum condition on fly ash synthesis, which would conciliate a high cation exchange capacity (CEC) of synthesized zeolite. To achieve this goal, the strategy relied on the use of experimental design methodology. The effects of five parameters including sieve size, activated temperature, NaOH concentration, reaction temperature, and reaction time were determined by using the two factorial design approach to specify the significant parameters on the formation of zeolite from fly ash. In the first step, the reaction temperature was found to be the most important parameter and two other significant parameters are activated temperature and reaction time. The second step of this studied, the three significant parameters were controlled at the various values and the cation exchange capacities (CEC) were determined for an optimum condition. Reaction temperature, activated temperature, and reaction time were in the range of 40 to 150 °C, 800 to 1100 °C and 12 to 96 hours, respectively. The results showed that the optimum condition, which exhibited the highest CEC (616 mmol/kg) of synthesized zeolite at reaction temperature of 110 °C, activated temperature of 800 °C, and reaction time of 96 hours.

Poster: PrGr-8

Extraction of phenol derivates by sulfuric acid salts of trioctylamine

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The extraction of pyrocatechol, m-cresol or 2-chlorophenol from an aqueous phase using sulfuric acid salts of trioctylamine (TOA salts) was carried out. The effects of the operating conditions and parameters, such as: initial concentration of solute, pH-value, organic solvents, concentration of TOA salts, volume ratio of organic phase to aqueous phase and temperature, on the extraction of solutes were investigated in detail. DIPE (diisopropyl ether) provides a high extraction capability of solute from organic phase. Among these three solutes, 2-chlorophenol is easily extracted by TOA salts. The reaction of solute with NaOH to form an organic-soluble phenoxide ion is used to explain the low extractability of solute at high pH-value. A simple mathematical model was derived to explain the results for the relation between the distribution coefficient and the initial concentration of solute in the aqueous phase. High volume ratio of organic phase to aqueous phase is recommended in order to obtain a high value of distribution coefficient.

Poster: PrGr-9

7 Gliding arc degradation of dyes (Orange II, Methylene Blue, Cristal Violet, Malachite Green and Methyl Red) in aqueous solutions

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Exposure of aqueous solutions of dyes to activated species of humid air non thermal plasma of gliding arc type leads to oxidative degradation of the solutes. The dyes selected for the study have different chemical structures, either azoic: Orange II, Methyl Red or heteropolyaromatic Methylene Blue or cationic :Cristal Violet, Malachite green. The UV-VIS spectra of the five dyes were recorded during treatment, which allowed to calculate kinetics constants. Chemical Oxygen Demand was measured, and confirmed the degradation of dyes. The selected dyes contain three different types of aromatic structures: azoic, heteropolyaromatic and triphenyl. The decolourisation of Orange II is obtained after 223 min of treatment, and 313 min for Methylene Blue. The decolourisation time of the Crystal Violet, Malachite Green and Methyl Red were 58 min, 35 min and 50 min respectively. The kinetics constants of tested dyes, namely, Orange II, Methylene Blue, Crystal Violet, Malachite green, Methyl Red are 0.0084, 0.005, 0.0326, 0.1006 and 0.2566 min⁻¹ respectively. The degradation of dyes follows an overall pseudo first-order kinetics, and the kinetics constants are linearly dependent on the current. The mineralization of dyes has been followed using a overall technique. The disappearance of the COD expresses the detoxification level of water.

Poster: DuWa-1

Caracterisation of soft drink wastewater and treatment

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The soft drink industry generates a significant volume of wastewater. Atypically soft drink facility will generate a waste of 1 to 2 Brix sugar, which translate a biochemical oxidation demand (BOD) of around 7g/l to 14 g/l. this varies depending on the product being produced and the way water is used in the plant. Typically waste of sugar water comes from the rinse of blending containers spillage in the canning or bottling production lines. During year of 2001-2002, we conducted campaigns of characterization of the rejections of a soft drink factory to evaluate the assessment of the liquid rejections, and to measure the various parameters of pollution, which constitutes the source data for designing of a wastewater treatment plant. Initially we were interested in the impact of each activity of the process on the effluent quality. We made follow-ups of the flows and flows of pollution on the level of each outlet. Then, we made several characterizations, which frame a great margin of variation of the parameters of pollution. We also carried out tests of physicochemical treatment on the wastewater. The results obtained showed, that the site rejects approximately 500 m³/d, these rejections are characterized by a great alkalinity and salinity.

Poster: DuWa-2

Critical level of hydrogen peroxide in decolorization of an azo dye by UV/H₂O₂ process in a continuous circulation reactor

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Combining UV radiation and H₂O₂ has been applied in Advanced Oxidation Processes to treat different industrial wastewater. The photochemical decolorization of Acid Blue74 was studied in an UV/H₂O₂ continuous circulation reactor with a 15 W low pressure mercury lamp. At regular time intervals samples were collected and analyzed by UV/VIS spectrophotometer to determine the decolorization rate. We have established a mathematical relation between the pseudo-first order rate constant and the relative concentration of H₂O₂ level in the reactor. The calculated values are in good agreement with the experimental data. The model can be useful in determining an optimum H₂O₂ dosage. The model parameters have been determined.

Poster: DuWa-3

V.O.C. co-treatment by adsorption and V-UV photolysis

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During the last decade, developments in the area of chemical water and air treatment have led to an improvement of organic pollutants oxidative techniques, in particular when using photochemical methods. They are generally referred to as Advanced Oxidation Processes (AOP). AOP are entirely based upon oxidative degradation reactions, in which organic radicals are generated through photolysis of the organic substrate or consecutively to a reaction with hydroxyl and/or oxygen radicals. In this study, the combination of adsorption with V-UV photolysis was investigated. V-UV photolysis is the vacuum ultra-violet irradiation of pollutants. This method is very efficient for water treatment since it leads to water molecules photolysis and therefore to an important hydroxyl radicals production. Until now, it was scarcely used for gaseous stream treatment, and never used for adsorbent regeneration. V-UV photolysis was used to regenerate commercial zeolite, useful here as a pollutant reservoir. Total degradation of pollutants, at relatively high concentrations, and complete and rapid regeneration of adsorbent was obtained, indicating a major influence of ozone.

Poster: DuWa-4

Heterogeneous catalytic wet air oxidation, a technology for removal of organic pollutants in water

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Wet air oxidation (WAO) is a technology of considerable practical relevance for the treatment of non-biodegradable pollutants, concentrated industrial effluents from chemical, pharmaceutical, textile/paper or food industries. Since wet oxidation is prohibitively expensive, catalytic WAO is carried out to reduce the severity of the operating conditions required. Metal ions could be dissolved in the reaction medium, but they have to be recovered in the treated water. Alternatively, heterogeneous catalysts which is easily recoverable can achieve the oxidation treatment in a continuous, one-step process. The catalysts should be active and resistant to leaching in acidic and oxidizing medium. Only noble metals supported on carbon, TiO₂ or ZrO₂ supports fulfil these requirements. Successful total oxidation of model compounds and of industrial effluents from paper pulp industry have been achieved in batch or in continuous reactors. Bioassays were found as a complement to chemical analyses for ensuring the toxicological impact on the ecosystem.

Poster: DuWa-5

Effect of silica additive on the thermal stability of vanadia-tungsta-titania catalysts in the SCR process

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Vanadia-titania mixed oxides are widely used in the industry for the selective catalytic reduction of NO_x by ammonia. On these catalytic systems, the anatase to rutile phase transformation is considered to represent the major factor of deactivation. The aim of the present investigation was to study the effect of SiO₂ addition on the thermal deactivation of V₂O₅/WO₃/TiO₂ catalysts. Commercial TiO₂/WO₃ (90/10w/w) and TiO₂/WO₃/SiO₂ (81/9/10w/w) powders were mixed with vanadium and extruded in the form of honeycomb monolith. In order to simulate long term operation, samples were calcined from 580°C to 750°C. The structural, morphological and chemical-physical changes caused by calcination were investigated by XRD, SEM, BET measurements, Raman spectroscopy and the catalytic activity was measured. This investigation confirmed that the degradation of the catalytic properties are strongly correlated to the structural ageing and that this behaviour is mainly related to: i) anatase to rutile phase transformation, ii) marked decrease of the catalyst surface area, iii) segregation of WO₃ phase, iv) segregation of SiO₂ phase. The temperature at which these phenomena occur, strongly depends on the addition of SiO₂. In fact, the addition of this oxide, stabilized the material increasing the temperature of the anatase to rutile transition and retarding the collapse of surface area.

Poster: DuWa-6

Bromate ion levels and futur minimizing treatment in three water treatment plants

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The occurrence of bromate in water is due to bromide oxidation during the ozonisation stage. It can also originate from the sodium hypochlorite solution added during the chlorination of water. It has been classified as a "supposed carcinogen compound for human" by the International Agency for the Research on Cancer (IARC) in 1990. The last European Directive 98/83/CE takes these by-products into account. Bromate ion exceeding 10 µg/L will be prohibited after the 25th December 2008. This parametric value is exceeded in summer in the three water treatment plants of SAGEP, company that produces drinking water for Paris (France). So the question is: what can we do to reduce bromate concentration in water. First, the best hypochlorite solutions are needed. Actually, bromate concentrations up to 857 mg/L have been found in the commercial hypochlorite solutions used in the SAGEP water treatment plants. Second, ozonisation have to be optimized by reducing the criteria Ct. Ct is the product of oxidant residual by the contact time.

Poster: DuWa-7

Iron-TAML® Activator of Hydrogen Peroxide for pollution treatment: Environmental application to Textiles dyes

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Several oxidation technologies demand the eradication of chlorine-based oxidants because they produce chlorinated byproducts, some of which are the most toxic compounds known. As an alternative to chlorine-based oxidants, hydrogen peroxide, yielding the green byproducts of water and oxygen, has made an appreciable contribution to a cleaner chemical industry. Unfortunately, a major problem with hydrogen peroxide is that it performs too slowly as an oxidant for some useful commercial and industrial processes. A new series of iron macrocyclic complexes Fe-TAML that activate H₂O₂ and perform selective green oxidation to destroy a persistent pollutant, was developed. The aim of the present study is to investigate the degradation of textile dyes by peroxide hydrogen catalysed by Fe-TAML complex, the examination of influence of some oxidation factors (Temperature, pH, catalyst dose) on the degradation rate of aqueous dye solutions as well as the analysis and identification of degradation products of dyestuff will be investigated.

Poster: DuWa-8

Degradation of EDTA during the wastewater treatment process

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EDTA is an extremely powerful chelating, it has the potential to affect the behavior of toxic heavy metals in the environment. The discharge of wastewater treatment plant (WWTP) is one of the main sources of EDTA in the aquatic environment. This lead us to investigate the effect of the wastewater treatment processes on EDTA degradation. The physico-chemical treatment affect neither EDTA concentration nor its speciation. During this step the photodegradation of Fe(III)EDTA is neglectible due to the high water turbidity, the adsorption of metallic complexes of EDTA (Me-EDTA) is not significant, the concentration of FeCl₃ added for phosphate precipitation is too low to influence EDTA speciation. During the biological treatment we detected degradation, reaching up to 44 % of total EDTA concentration, one third is due to photodegradation of Fe(III)EDTA and two thirds to biodegradation of other Me-EDTA. To our knowledge, this is the first measurement of EDTA biodegradation in a conventional WWTP. Degradation of EDTA was not observed during the night and the winter in the biological step.

Poster: DuWa-9

Removal of Cr(VI) from aqueous solution by redox and complexation reaction with a lignocellulosic substrate extracted from wheat bran

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Under the current trend of world-wide environmental regulations, industries must control waste water and hazardous wastes that they generate. There is a great local demand in the design of low cost waste management techniques to remove heavy metals present in nearly all industrial effluents. The use of common techniques like precipitation, solvent extraction, ion exchange resin etc. is rather limited due to their relatively high cost. Nowadays an effort has to be made towards finding inexpensive and efficient adsorbents which can be used in a complementary way to usual depollution techniques. To this objective we evaluate the potentiality of a lignocellulosic substrate extracted from wheat bran in the removal of Cr(VI) from aqueous solution. Previous studies have demonstrate the interesting properties retention of such substrate towards heavy metals ions like Cu(II), Pb(II), Ni(II), Cd(II), Zn(II). Sorption experiments of Cr(VI) has been monitored by the batch method. We study the kinetic of the adsorption and conversion reaction into Cr(III) as well as the influence of pH, and analytical concentration of Cr(VI). Analytical methods were developed to distinguish between total concentration (Cr(III) and Cr(VI)) in aqueous solution and those of Cr(VI). X-Ray Photoelectron Spectroscopy (XPS), IR, EPR, and SAX spectroscopies, analytical microscopy were used to determine the oxidation state of chromium sorbed onto lignocellulosic moieties and to study structural and functional modifications of the substrate induced by the conversion reaction.

Poster: DuWa-10

Control of denitrifying reactor by determination of nitrogen forms

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One innovative and emerging technology is biological denitrification for nitrate removal of waste water. Fluidised bed reactors offer superior performance compared to complete-mix and fixed-bed biofilm reactors because the biofilm is evenly distributed throughout the reactor, while the liquid regime of a fluidised bed offers all the advantages of a plug-flow reactor. Fluidised bed reactors however require greater recirculation of the effluents to achieve sufficient nitrate removal, thus they require more process control. Several research needs for the evaluation and optimisation of the performance of fluidised bed and reactor, and the determination of the kinds of natural and synthetic organic compounds that can be biotransformed. In the present investigation, nitrogen forms were measured for optimisation of the performance of denitrifying reactor. The concentrations of ammonia in the influent and effluent of reactor were analysed by spectrophotometric method. The use of high-performance liquid chromatography (HPLC) for the determination of nitrite and nitrate is potentially very attractive, as it is much more rapid, sensitive and selective than methods based on colorimetry. A method was developed for analyzing nitrite and nitrate anions using reversed-phase chromatography and indirect UV detection. The organic compounds were determined by high-performance liquid chromatography and gas chromatography.

Poster: DuWa-11

Photocatalytic degradation of Acid Blue 25 in aqueous solutions by UV-irradiated titania

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Waste waters generated by the textile industries, well implanted in Tunisia, are known to contain considerable amounts of non fixed dyes, such as Acid Blue 25 (AB 25), an anthraquinone dye. Among the various processes for treatment of these effluents, heterogeneous photocatalysis appears as a very efficient destructive method. In this work, the photocatalytic degradation of AB 25, was investigated in TiO₂/UV aqueous suspensions. The influence of parameters governing the kinetic such as mass of catalyst and photon flux was evaluated. The photodegradation rate was determined for each experiment and a pseudo first-order kinetic law was found. The photobleaching of the solution was observed by spectrophotometry from the characteristic absorption at $\lambda = 600$ nm. A comparison between the decrease of AB25 concentration, measured by HPLC-DAD, and the bleaching of the solution showed that some of the intermediate products formed were coloured. Some of them were identified using the HPLC-MS technique. The mineralisation of the molecule was followed using ionic chromatography and COT-meter measurements. The total degradation lead to formation of inorganic ions such as nitrate, ammonium, and sulfate ions. These results suggest that TiO₂/UV photocatalysis may be envisaged as a method for treatment of diluted wastewaters in textile industries.

Poster: DuWa-12

Industrial slag as new environmental material for agronomic application?

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Iron and steel plant induced a large amount of secondary products such as slag and ashes. Due to their high content of heavy metals (Zn, Pb, Cr,...) these materials represent an important environmental problem. They present some heterogeneous sizes and a high solubility in water (and therefore a potential remobilization of toxic elements) so their storage is an expensive solution. One of the new answers is first to stabilize these ashes on a long term basis, then to find a possible economical application. In our study, we propose a low cost environmental process which allows to trap the heavy metals in some insoluble phases (like calcium phosphate), to homogenize the size and finally resolve their storage. Moreover, prospected study has been achieved to follow the fertilizing potential. The results clearly show that slags can have a high added value material for agronomic application as fertilizer with delayed effect.

Poster: DuWa-13

Treatment of industrial wastewater of Mostaganem consisting of organic metallic compounds by gliding arc plasma in humid air

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Within the Mostaganem (West Algeria) city area dairy produce factories, sugar refineries and paper mills reject effluents consisting mainly of organo-metallic constituents. These wastes are drained, untreated to the Mediterranean Sea, or treated with expensive and sometimes inefficient chemical processes. The treatment of the waste with the gliding arc plasma in humid air as a function of exposure time shows a significant abatement in the chemical oxygen demand (COD), below the allowable limit for industrial effluents. An increased mineralization is observed in comparison with the untreated wastes. Some industrial plants within the Mostaganem city area are split up in units specialized in dairy produce of milk and derivatives (OROLAIT), paper industry (SONIC) and sugar refining (ENASUCRE). Their effluents are all drained into the Mediterranean sea of the Cheliff River. The effluents are analyzed as the factory drain flow according to AFNOR standards. The plasma treatment of these effluents results in the abatements of the COD and an almost entire mineralization. The results obtained show a significant decrease in the COD with an abatement rate of 92% for the OROLAIT industry, 89% for ENASUCRE plant effluent and 78% for SONIC industry. The degradation of the organic part of these effluents is accompanied with more mineralization.

Poster: DuWa-14

Removing of Cd²⁺ and Co²⁺ from water media, by strong interaction with a Ni-H catalyst surface

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Effluents from mineral processing and metal finishing industries contain small amounts of heavy metals (arsenic, mercury, cadmium, chromium, lead...) in the ionic form (M^{x+}). Heavy metals are very harmful (cancers, kidney disorders...) and they are bio-accumulative. According to the Surface Organo-Metallic Chemistry (SOMC) on metals concept, M^{x+} ions could be reduced by the hydrogen adsorbed on an active surface and deposited as "adatoms" on the "host" metallic surface. We will demonstrate in this communication that nickel catalyst can be successfully used to remove cadmium or cobalt ions from aqueous solutions. Cd²⁺ and Co²⁺ have been allowed to react with the surface of reduced nickel particles in water. Two hydronium ions are produced for each cadmium adsorbed showing the oxidation of the adsorbed hydrogen. The following mechanism is proposed : Cd²⁺ + 2Ni_s-H --> (Ni_s)₂Cd + 2H₃O⁺ Up to now, remaining Cd²⁺ or Co²⁺ concentration as low as 20 ppb can be achieved and lower concentrations may be expected. This process for water treatment differs from cementation since only hydronium ions are produced. Since nickel dissolves in acidic media, an accurate pH regulation at a neutral level is required.

Poster: DuWa-15

The photocatalytical removal of nitrogen oxides over the TiO₂ powder and sprayed coatings

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TiO₂ is one of the most important photocatalyst used for the removal of pollutants from water and air. Two crystalline forms are known for TiO₂: rutile and anatase structures. The anatase phase, by annealing at temperatures higher than 650K changes into the rutile form. Both phases are implied in the phenomenon of photocatalysis, but many results in the literature show that anatase is the most efficient. Our work focused on the diminution of nitrogen oxides (NO_x) by the photocatalysis process over titanium dioxide, an experimental set-up designed and realized in laboratory was used for the evaluation of the photocatalytic characteristics of the TiO₂ powder and thermal sprayed coatings. Different processes of thermal spraying were used to elaborate the TiO₂ photocatalytic coatings. A special attention was devoted to the effect of the purity, the anatase to rutile ratio, the coating thickness, the porosity rate and the specific surface area. Differences between the efficiencies of the TiO₂ powder and the sprayed coatings were obtained. We present a preliminary study to assess the main coating characteristics that have an effect on the photocatalytic properties of TiO₂ plasma sprayed coatings.

Poster: DuWa-16

Solar radiation and catalytic degradation of organic pollutants

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The people, with their own imprudent activity, making the environment on the border of the acceptable load and sustainable development. This reason brief the necessity to develop the procedures and processes for purification contaminated atmosphere, hydrosphere and soil. The purification takes care of the commercial and alternative methods, with little possibility to use the renewable energy sources. The paper has been considering one of the alternative methods. In spite of that, the degradation of the organic pollutants in the water environment to take care of the titanium dioxide, which is a catalyst, and sunlight which is a radiation source. The compounds which can meet in the environment (alcohols, ketones, phenols, amines, PCBs, pesticides,...) have been degrading in spite of that, and we get nontoxic forms: water, carbon dioxide and simple mineral acid. A reactor model using Langmuir-Hinshelwood form kinetics for performing reaction destruction organic compounds. The best results in this reaction achieves when the destruction has been performing with hydrogen peroxide. As catalyst we have been using novel anatase titanium dioxide powder namely HombikatUV100. The maximum photonic efficiency which could be attained with HombikatUV100 is about for times higher than of TiO₂-powder. The superior results HombikatUV100 give only sunlight which have wave length below 400nm. This wave length are prerequisite for the process. In this paper, I give technical-technological solution of pilot plant for purification effluents, which have been deriving from chemical industry.

Poster: DuWa-17

Comparison of the reactions of o-methoxybenzoic acid with various disinfecting agents in water

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The preparation of water for human consumption is a major industry. Addition of oxidants to water as part of water treatment operations can generate a variety of disinfection by-products with adverse health effect. Chlorine, sodium hypochlorite and ozone are widely used as disinfecting agents. In present study o-methoxybenzoic acid was selected as model organic compound to investigate its reactions with chlorine, sodium hypochlorite and ozone. Reactions of the acid with chlorine and sodium hypochlorite are quite straightforward. Substitution of two hydrogen atoms for chlorine takes place. Chlorodecarboxylation leads to the corresponding mono-, di- and tri-chloromethoxybenzenes. Comparison of the assortment and relative amounts of reaction products demonstrate lesser chlorination activity of hypochlorite than of chlorine. The degradation of methoxybenzoic acid during ozonation starts with hydroxyl radical attack and concurrent decarboxylation giving corresponding phenols followed by the cleavage of any bond of the benzene ring. Oxalic and glyoxalic acid are the only compounds detected at the highest ratios acid/ozone. The ozonation products are less toxic than the chlorination ones. Nevertheless formation of phenols at ozonation stage of water treatment could be a source of hazardous chlorophenols and haloforms during final chlorination.

Poster: DuWa-18

Recovery of zinc and lead from electric arc furnace dust by hydrometallurgical way

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The aim of this work is to study the feasibility of a new hydrometallurgical process for treating Electric Arc Furnace Dust. At first, a leaching is carried out with hydronitritotriacetate anion. The treatment of different EAFD samples allows the total leaching of ZnO and PbOHCl without solubilizing iron. Zinc and lead are recovered in the leachate by precipitation of metallic sulfides with Na₂S₄, which can be used in their own metallurgy as raw materials whereas the reagent is recycled in the process. Solid residue still contains an important amount of zinc under ZnFe₂O₄ form. The extraction of this element requires the destruction of the ferrite structure which is performed using FeCl₃.6H₂O and allowing the recovery of zinc as ZnCl₂ and iron as Fe₂O₃. Separation of both products is obtained by simple aqueous leaching. The whole zinc is extracted and ultimate solid residues, which are iron-rich, can be recycled in steel industry.

Poster: DuWa-19

Evolution of chemical, thermal and microbiological properties of lignocellulosic materials during composting

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The reliability of composting as a recycling strategy and use for soil remediation rely on the quality of the end products obtained. However, due to the nature of the decomposition processes and the high number of organic wastes available, no single parameter can give an exhaustive evaluation of compost stability. We studied the dynamics of transformation and the degree of stability in a composting process by integrating different approaches. Compost samples from cotton cardings and yard wastes with different ages were characterized for their chemical, thermal and microbiological properties. Humification parameters of the end products (0.2 and 81% for HI and DH, respectively) showed a greater degree of stability than usually found in well stabilized compost. Thermal analysis displayed an evolution of organic materials towards more stable fractions: thermostability index R1 increased from 0.41 to 0.77 during the first 60 days and correlated with both HI ($r = -0.94$ $P < 0.05$) and DH ($r = 0.97$ $P < 0.05$) humification parameters. Microbial biomass and BNIN/N ratio allowed for the evaluation of the degree of stabilization of the end product. The simultaneous monitoring of different parameters, reflecting distinct aspects of the composting process, could give a deeper and more complete description of the degree of stabilization and quality achieved by the organic substrates.

Poster: DuWa-20

Formation of NO_x precursors in relation to the air supply during waste combustion - Investigations by means of online High-Resolution FTIR-spectroscopy

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In an research program aiming for low NO_x combustion as an example of process optimisation, our investigation focuses on the simultaneous measurement of primarily released N-substances from the fuel bed. The devices used for routine observation of MSW incineration emission are designed to work well in clean gas conditions, under consideration of the few leftover matrix substances. Reactive substances are not measured routinely. When it comes to investigations on gases sampled right above the grate in the combustion chamber, however, high-sophisticated measuring techniques are essential. Thus, an online High Resolution FTIR-Spectroscopy method was applied. Various N-containing waste fractions were used for the thermal treatment in laboratory furnaces to learn about the accuracy of this method. The combustion gases were sampled by means of self-designed probes and FTIR gas cells. By tracing characteristic vibration bands of NO and its precursors, the distribution of reactive N-substances released in the gas phase were quantified. These data are strongly related to the process parameters used. High Resolution FTIR-Spectroscopy constitutes an efficient tool for investigations in complex combustion gases, allowing fast online screening for differences and changes in gas composition as a result of variations in process parameters.

Poster: DuWa-21

Use of sodium carboxylates for selective precipitation of metallic cations in industrial liquid wastes

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Each year in France, the detoxification of liquid wastes from surface- finishing industry generates about 200.000 tons of metallic hydroxide sludge. Since April 1998, the regulations levels concerning their storage in specialized landfill have become much stricter and a new regulation concerning the storage of ultimate wastes has to come into effect from July 2002. At present time, the management of these liquid wastes has to be turn towards beneficiation. Metals recycling need a selective recovery of each of them. From a technological and economic point of view, one of the best ways to investigate seems to be the selective precipitation of metallic cations using sodium carboxylates. The determination of metallic carboxylates solubilities allows the establishment of solubility diagrams which are used to predict the possibilities of selective recovery of metals in different mixtures. A laboratory-scale study has showed that the separation is effective in the case of binary or ternary mixtures like Fe/Zn, Ni/Zn or Fe/Cr/Ni.

Poster: DuWa-22

Washing of power station heat exchanger by recycling of wash-water

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An essential part of water resources are used in industrial processes for cooling or washing purposes. In both cases the used water gets back in the environment in a polluted state. The water-use reduction technologies are spreading mainly in waterless areas. In oil burning power stations the heat content of the hot flue gas is used for pre-heating of the air supply. As a result for this there is a substantial chromium- and vanadic compound deposition in the heat exchanger, and in addition the material of the heat exchanger is corroded as well, resulting an essential ferri-ferrous- and manganese compound content. The heat exchanger should be washed by alkali water to improve the heat transfer. The disaggregating material is called Ljungström mud and was a toxic waste. The task was to determine the technological parameters, the treatment and recycling possibilities of Ljungström mud and wash solution. In our investigation we were looking for a process needing minimal investment and minimal treating equipment in the power station, but completely conforming to the measures of legal force. The toxic metal ion removal of calcium hydrate precipitate form was chosen to keep the limiting values of the regulation for toxic metal ions.

Poster: DuWa-23

Efficiency of TiO₂ nanoparticles as photocatalysts

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Heterogeneous photocatalysis is a promising technique for the detoxification of water and air. This process consists of an illumination of semiconductors with energy greater than the band gap. There is ejection of an electron from the valence band to the conduction band, leaving behind positive holes. TiO₂ is actually the most employed photocatalyst. One of the major limitations in photocatalysis is the relatively low value of overall quantum efficiencies combined with the necessity of using near ultraviolet irradiation. Many successes in enhancing the photocatalytic activity are getting by preparation of TiO₂ nanoparticles. For TiO₂ synthesis, different methods of preparation were tested, such as Emulsifying-Gelation, sol-gel route under reflux and semibath-bath two stages mixed reaction. The obtained products were in all cases treated at 550°C (during 2hrs or 10hrs). The best result of photodegradation activity was obtained using TiO₂ prepared by mixing Ti(OC₃H₇)₄ with Methanol in Ethanol solutions. The water was added dropwise under reflux for 6h and heated for 10h at 550°C. XRD analysis showed existence of anatase and rutile with the ratio 23% by weight of rutile close to TiO₂ P25. The amount effect of Methanol, water, temperature and time of reflux were studied. The overall catalytic performance has been suggested to be dependent on quite numerous parameters including particles size, surface area, the ratio between the anatase and the rutile crystal phases and the nature of compound will be degraded.

Poster: DuWa-24

Biomass remediation: Hybrid calcium silicates prepared from rice hull ash

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Rice hull is an agricultural by-product, composed by organic materials (fibers, polysaccharides, etc) and an inorganic silica matrix, which accounts for approximately 20-30% of rice hull mass. This material is usually burned at the fields, generating suspended silica particles in the atmosphere). This is a very common practice in countries such as Brazil, China and India. There are many problems associated to this procedure (soil impoverishment, health and environmental damage). Considering the huge amounts of rice hull (around 12×10^6 ton/year, only in Brazil), there is a continuous search for the development of productive uses of rice hull. Commercial cements are mainly composed by two calcium silicates, namely, Ca_3SiO_5 and Ca_2SiO_4 and are produced at temperatures around 1500°C . The main objective of this project is the production of Ca_2SiO_4 and related materials from the rice hull ash. The present work shows a new, synthetic method to synthesize hybrid cements (calcium/titanium silicates). The method is based on the dissolution/precipitation behavior of this biogenic silica (tridymite) in the presence of calcium hydroxides and titanium oxide. It allows the introduction of titanium atoms into the silicate structure, in several proportions. The synthesis is completed at 800°C , rendering the new hybrid cements.

Poster: DuWa-25

Coupling solar and biological processes for the degradation of a dye biorecalcitrant pollutant

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Wastewater containing 5-amino-6-methyl-2-benzimidazolone (AMBI) used in the manufacture of dyes was characterised as bio-recalcitrant by means of different biodegradability tests. In order to enhance the biodegradability of this pollutant, photocatalytic degradation methods were explored. The systems $\text{light}/\text{TiO}_2/\text{O}_2$, $\text{light}/\text{TiO}_2/\text{H}_2\text{O}_2$, $\text{light}/\text{Fe}^{3+}/\text{O}_2$ and $\text{light}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ were compared. The iron photo-assisted systems exhibited the most interesting behaviour, from the kinetic and engineering points of view, especially if it is combined with a biological process. To compare the efficiency of these systems, several parameters were studied: a) dissolved organic carbon and initial compound concentration, b) the average oxidation state, c) the toxicity, d) the biodegradability of photo-treated solution. At lab scale using a solar lamp, the degradation rate of the system $\text{light}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ was the most efficient, but the $\text{light}/\text{Fe}^{3+}/\text{O}_2$ system does not need H_2O_2 addition and this improves the economical requirements of the system. Using scientific information gathered at lab scale, we carried out field experiments under direct sunlight. At field scale $\text{light}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ was five times more efficient than the $\text{light}/\text{Fe}^{3+}/\text{O}_2$ system. Nevertheless, from the economical view, more detailed research has to be led to get sure if, with solar energy, the addition of H_2O_2 can be avoided.

Poster: DuWa-26

Biodegradability and toxicity of tannery wastewater

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Wastewater from leather tanning industry can be polluted heavily containing inorganic and organic contaminants. The mineralisation of these organic contaminants is not always possible, but an enhancement of biodegradability of tannery wastewater is desired. Therefore degradation and advanced oxidation processes (AOP) applying UV, TiO₂/UV, O₃ and O₃/UV at different pH were performed to improve biodegradability of mechanically pretreated tannery wastewater while in parallel *Daphnia magna* toxicity (G_D) was monitored. Toxicity testing (G_D) and chemical analyses of sum parameters, e.g., total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD₅) were performed. In parallel substance specific gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/MS (LC/MS) and tandem mass spectrometry (MS/MS) were applied to monitor changes in the pollutant spectrum and to identify precursor pollutants and their degradation products. The treatment of tannery wastewater by O₃/UV at pH 11 resulted in a reduction of COD and BOD₅ while TOC was reduced marginally. In parallel *Daphnia magna* toxicity testing (G_D) proved a decrease in toxicity from 6 to 4. GC/MS, LC/MS and MS/MS analyses allowed the identification of phenolic compounds, benzothiazoles, aromatic hydrocarbons, nonylphenoethoxylates (NPEO) and polyethyleneglycols (PEG) in mechanically pretreated wastewater and in wastewaters after AOP.

Poster: DuWa-27

A comparative study of dye adsorption by granular activated carbon and water hyacinth powder

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The community own hand-made textile weaving industry produces only a small volume of colored wastewater. The conventional colored wastewater treatment technologies are too costly to bear and too complicated to handle. The possibility of using Water Hyacinth (WH) powder to decolorize wastewater containing Methylene Blue (MB) and Direct Blue 168 (DB) was studied. Its effectiveness was compared to an activated carbon (AC). The equilibrium of WH-MB and AC-MB adsorption are obtained after 2 hrs, while WH-DB and AC-DB takes longer than 10 and 21 hrs respectively. The pH range of 4.0 to 9.0 has only little affect on all adsorption systems but the WH-DB adsorption is greatly decreased at pH < 9.5. The adsorption of MB and DB on WH and AC are found to conform to the Langmuir and Freundlich Isotherms. The order of adsorption capacity are WH-MB > WH-DB > AC-DB. The WH-MB adsorption is an exothermic reaction while WH-DB and AC-DB are endothermic reaction. WH and AC required to treat a batch of wastewater (200 liters) containing 100 mg-DB/l to the concentration of 10 mg-DB/l is 0.8 and 2.4 kgs respectively. The treatment method is easy to handle and requires no special skills for a person to operate and to maintain. WH is readily available at low or no cost makes the regeneration not necessary and the spent WH could be burnt.

Poster: DuWa-28

Effect of Fe/As on arsenic removal by Fe(II)/O₂ process

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In this batch study arsenic synthetic wastewater were experimentally treated by Fe(II)/O₂ process at various contact times, iron and arsenic concentration in order to investigate arsenic removal efficiency. The finding show that this process effectively remove arsenic from the synthetic wastewater. The contact time has affected on arsenic removal efficiency. The more contact time, the more arsenic efficiency is. At initial iron concentration of 5.0 and 10.0 ppm, arsenic removal is effective. The Fe/As ratio has only affects on arsenic removal efficiency at initial iron concentration of 2.5 ppm. Although arsenic removal efficiency at initial iron concentration of 10.0 ppm is high, iron removal efficiency is about 55.7 %. Thus, it has to remove iron to meet standard (1.0 ppm).

Poster: DuWa-29

Characterization of oil shale ash by BET analysis and solid-state NMR spectra

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Massive quantities of ash are produced worldwide when fossil fuels (mainly coals) are combusted for electricity generation. The characteristics of ash particles are of importance in view of their potential applications. In the present study, ten different ash samples obtained from various stages of oil shale combustion in a thermal power plant (Eesti EJ, Narva, Estonia) were characterized by particles morphology using two methods: NMR and BET analysis. ²⁷Al and ²⁹Si MAS-NMR spectra of the samples were recorded and analyzed. In the majority of samples the aluminum was in tetrahedral coordination state, whereas its octahedral coordination was found only in few cases. Typical ²⁹Si spectrum showed a broad line, around -95 ppm of the fly ash glass, and sharp resonance at -71.5 and -108 ppm belonging to silica in Ca₂SiO₃ and quartz, respectively. The quantitative data are presented. The specific surface area, measured by a nitrogen adsorption BET method, was estimated in wide range, 0.24 and 1.65 m²/g, for fly ash samples. The total pore volume (pore diameter, 3.4-20 nm) of different samples ranged from 0.1 to 1.9 mm³/g. Thus, the essential quantitative differences were observed between the oil shale ashes samples originated from combustion process.

Poster: DuWa-30

Fixation of dusting lands in mining industry: Complex chemical/biological solution

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Mining industry in Russia results in formation of 18,418 mln m³ of wastes annually, while existent 600 tailing and waste disposals occupy a surface about 18000 ha. However, forming dust contaminates wide adjoining areas that reach at least 55000 ha. Fixation of dusting surfaces on contaminated areas should be provided for prevention of spreading of toxic substances into environment. A proposed complex chemical/biological method of fixation includes treatment of surface by technical lignine sulfonate, sulfate soap and/or saponified tall pitch followed by seeding of some kinds of plants. Chemically fixed surfaces were found much more stable and significantly decreasing dusting. The highest strength was found for covers additionally treated by solution of CaCl₂. Application of chemical fixing agents allows saving soil humidity necessary for plant growth. Study of the effect of fixing compositions on different plants showed that sulfate soap and technical lignosulfonate did not affect growth of cereals

Poster: DuWa-31

Vegetable wastes as low-cost sorbents for Cr(VI) uptake

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Recently, the use of low-cost sorbents has been investigated as a replacement for current costly methods of removing heavy metals from solution. Natural materials or waste products from certain industries with a high capacity for heavy metals can be employed and disposed of with little cost. In this work, some waste products from industrial or agricultural operations (yohimbe bark, olive stones, grape stalks and cork) cut and sift to get the same particle size (1.0-1.5 mm) were used in batch experiments for the removal of Cr(VI) from aqueous solutions. Results showed that highest sorption capacities were registered at initial pH 2.0 for yohimbe bark and olive stones and pH 3.0 for grape stalks and cork. The presence of NaCl did not have any effect on metal removal by yohimbe bark and grape stalks but in the case of olive stones and cork, the removal efficiency decreased when increasing this salt concentration, due to Na⁺ competition for the active sites of the waste material. The experiment data were modelled by means of non-competitive Langmuir and Freundlich isotherms. When comparing the four materials, yohimbe bark waste was found to be the most efficient sorbent followed by grape stalks and cork that presented similar uptake values.

Poster: DuWa-32

Phytic acid: a green reagent for precipitation of metallic cations contained in liquid wastes

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Phytic acid is an important plant constituent. About 85 % of total phosphorus in cereals and vegetables is present on this form. The interaction between phytic acid and metallic cations (Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , Zn^{2+} ...) to form insoluble compounds could be used either remove heavy metals from industrial liquid waste or perform selective precipitation in different mixtures. This work is devoted to the study of selective precipitation of iron in FeIII-ZnII mixtures. Concerning metallic phytates, few thermodynamic data are available in literature. At first, chemical composition of both phytates was determined by chemical analysis and thermogravimetry leading to the following formulae: $\text{Fe}_2(\text{Phy}) \cdot 12\text{H}_2\text{O}$ and $\text{Zn}_3(\text{Phy}) \cdot 8\text{H}_2\text{O}$. Then aqueous solubilities of these compounds were measured. Solubility of iron phytate was found to be equal to $2.5 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ whereas zinc phytate has a solubility equal to $1.25 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. Finally, the separation of both metals was investigated using an experimental design. Three parameters were studied: iron concentration, pH of precipitation and stirring time. The results clearly show that selective precipitation of iron phytate is feasible using this green reagent. Iron is precipitated with a yield equal to 99.5% and its residual concentration in zinc solutions is only about $70 \text{ mg} \cdot \text{L}^{-1}$.

Poster: DuWa-33

A study of chromium(VI) sorption-reduction behaviour on modified rice husk sorbent and application for the remediation of chromium(VI) leachate from a chromium(VI) contaminated land

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Rice husk was used to prepare a carbonaceous sorbent using sulphuric acid treatment. The capability of the prepared sorbent to remove Cr(VI) from aqueous solutions was investigated by considering the various parameters: contact time, pH, metal ion concentration and sorbent status (wet and dry). The rate of Cr(VI) removal at pH 2 followed a first order rate expression approaching equilibrium within 50 hours. Sorption was highly dependent on the pH with reduction taking place in chromium solution with pH up to 7. At pH values ≤ 2 for 100 and 200 ppm of Cr(VI), complete reduction to Cr(III) was obtained with low sorption. Maximum sorption was found at pH range 2.4 -2.8 for both sorbents for 100-200 ppm. A contaminated soil with Cr(VI) concentration up to 15,000 ppm was washed with 0.1M citric, 0.1M acetic, 0.1M HCl, 0.1M sulphuric acid and 0.1M NaOH and hot distilled water. The leachate was acidified to pH 2 and reduced to Cr(III) using the carbonaceous sorbent. The carbon material seems cheap and efficient for Cr(VI) removal.

Poster: AfSR-1

Effect of rhamnolipids on the water solubilization and the mobilization of PAHs from contaminated soil

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Polycyclic aromatic hydrocarbons (PAHs) show limited natural attenuation in soils. These compounds are relatively immobile and are often not readily bioavailable. Tensioactive compounds (chemical or biological) have been shown to enhance the mobilization and flushing of PAHs from contaminated soils. Biosurfactants are particularly promising for soil decontamination purposes and groundwater protection because they are usually biodegradable and non-toxic. The objective of this study was to obtain experimental results to define and to predict the effective conditions for optimizing a soil remediation technology based on the injection of biosurfactants solutions in soil. The capacity of rhamnolipids to enhance the removal of pyrene, fluorene and fluoranthene from soil was investigated. The partitioning of PAHs between biosurfactant micelles and the aqueous solution was characterized by the mole fraction micelle-phase/aqueous-phase partition coefficient and the molar solubilization ratio. Single compounds and their binary and ternary mixtures were studied showing synergistic or antagonistic effects on the solubilization of the PAHs in static conditions. The K_m and RMS parameters easily obtained in static conditions were confronted with the results of PAHs mobilization observed from soil column experiments. The interest and the use of these parameters as predictive tools to evaluate soil remediation efficiency were investigated.

Poster: AfSR-2

A remedy to polluted grounds: a new in-situ approach

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The management of the polluted sites and grounds became one of the stakes of this new decade. This approach passes by a fine characterization of the sites and their pollutants, especially farmhouses to propose an adapted remediation. Accordingly, a new concept consists in an in-situ processing of the sites therefore limiting the costs and accelerating the possibility of making the site accessible. The goal of this study was to study, in laboratory, the sorption of various pollutants (heavy metals) present in a ground simulated on mineral phases. These minerals result from the degradation of an artificial glass in natural conditions. The first results highlight the development of porous mineral glass of zeolite types at the glassy surface, as well as a reduction in the ground contents. A finer study will make it possible to follow the processes of sorption and possible speciation of the pollutants, and will be supplemented by tests in real condition.

Poster: AfSR-3

Efficiency of meat and bonemeal combustion residue for lead immobilisation: kinetics and mechanism

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The presence of lead in aqueous effluents and the fate of meat and bonemeal stocks are two major environmental and health concerns. Among the different processes, valorisation of meat and bonemeal can be realised by a thermal treatment. During combustion, thermal energy is recovered and prion is destroyed. In our search for new materials to extract metal from aqueous effluents, we investigated the use of low risk meat and bonemeal combustion residues. We report here a study on their ability to uptake and immobilise lead. The thermal behaviour of crude meat and bone meal was followed by TGA. The resulting ashes were characterised by powder X ray diffraction (XRD), particle size, specific surface area (BET), and elemental analysis. Meat and bone meal combustion residues were found to be a natural apatite-rich substance. Mechanism and kinetics of lead removal by this bioinorganic material were investigated. Batch metal removal experiments were carried out and lead concentration, calcium and pH were monitored. The mechanism was compared to that occurring for pure apatite. Our results show that this natural apatite removes in a few minutes a large quantity of lead (275 mg/g capacity). Meat and bone meal combustion residues represent a valuable alternative apatite source for environmental application.

Poster: AfSR-4

Laboratory experiments with microbial mats: Biodegradation of petroleum model compounds and physiological response to pollution

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Microbial mats are able to thrive in heavily polluted environments and to degrade organic pollutants such as petroleum and pesticides. Aspects of biodegradation and the microbiological and physiological response of microbial mats to the addition of pollutants are addressed in frame of an interdisciplinary German-Palestinian-Israeli research project. Experiments were performed under field conditions in outdoor experimental ponds and in the laboratory with slurries and intact microbial mats. As pollutants we used n-octadecane, pristane, phenanthrene and dibenzothiophene. These model compounds represent bonds types present in major petroleum constituents. In order to achieve a close contact between the hydrophobic pollutants and microbes, model compounds were adsorbed to montmorillonite previously treated with benzyltrimethylammonium cations. The inoculation of a microbial community from Wadi Gaza (Palestine) under controlled laboratory conditions resulted in the development of a microbial mat with the capacity to biodegrade petroleum model compounds. In the laboratory, complete degradation of aromatic compounds was achieved within few days. Aliphatic compounds were partly preserved as an effect of incomplete bioavailability. The physiological response was monitored by microsensors techniques. A fast, strong decrease in oxygen concentration in the first week after addition of the pollutants was followed by a slow recovery over four weeks time.

Poster: AfSR-5

Using β -Cyclodextrin to enhance the bioavailability of soil adsorbed polyaromatic hydrocarbons - thermodynamic study of the environmental applicability

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The present work is concerned with increasing the bioavailability of hydrocarbons by using β -cyclodextrin. Hydrocarbons encountered in the environment are usually adsorbed on the solid particles or on the organic matter. The process of hydrocarbons desorption is a necessary step for their biodegradation. It may be facilitated by surfactants enhancing their solubilisation in the ground water and increasing their bioavailability. This however, could increase the risk of groundwater pollution so the surfactants replacement by biodegradable compounds such as β -cyclodextrin should be considered. It is known, that β -cyclodextrin may enhance the biodegradation of hydrocarbons using microbial colonies isolated from a petroleum polluted soil and effects on photodegradation of organophorus pesticides in humic waters. In this work we propose a tentative mechanism of formation of hydrocarbon- β -cyclodextrin aggregates in the complex aqueous environment. Aggregation phenomena were examined using surface tension measurements, UV-VIS absorption-photometry and of Dynamic Light Scattering of systems containing hydrocarbons. The mechanism based on experimental data was proposed to represent the processes of hydrocarbon desorption from the silica and the solubilisation with β -cyclodextrin. While, 1:1 complexes of β -cyclodextrin:hydrocarbon are formed in pure water, the formation of more complex aggregates may be observed in the aqueous environment containing certain polar compounds.

Poster: AfSR-6

In-situ chemical oxidation: determination of permanganate contribution for reducing perchlorethylene pools

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In-situ chemical oxidation is an emerging technology for destruction of chlorinated chemicals. In this study, we investigated the contribution of permanganate oxidation to free phase PCE removal, the effect of MnO_2 precipitation on the system permeability and the resulting mass flux after remediation. Column experiments were conducted in a 30 cm long borosilicate glass column of 5 cm internal diameter packed with well-characterized sand with free phase PCE in residual condition. During chemical oxidant flushing, the column effluent samples were analysed for pH and for $KMnO_4$ and PCE concentration to examine the removal processes occurring in the column. In addition, tracer studies were conducted to assess changes in the flow rate due to precipitation of MnO_2 . The mass transfer behaviour of PCE was also examined before and after chemical oxidation remediation. The results indicate that approximately 90% of PCE removal is due to dissolution and mobilisation of PCE and the remaining 10% to oxidation. By comparing the experimental results to the data available in the literature, the efficiency of chemical oxidation for free phase PCE remediation is discussed.

Poster: AfSR-7

Residual effect of compost on sorption and availability of heavy metals in soil

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The sorption properties of a soil which has been treated 15 years ago with high rate of composted sewage sludge have been investigated to evaluate the residual effect of compost addition on the soil sorption capacity. Zn and Cd sorption showed that also after 15 years the addition of compost affected markedly the sorption. After compost the soil solid phase showed a greater affinity for the metals, since the amounts sorbed are higher than in the original untreated soil at every concentration used. The isotherm, indicated a great affinity between the metal ions and the sorbing surfaces which selectively favours heavy metal sorption in the respect to alkaline ions. A possible explanation for these findings is that new sorbing sites become available on the solid phase of the soil following compost addition, and that these sites are still active 15 years after the cessation of compost addition to soil. Compost can contribute for a long period to the retention of heavy metals, influencing their distribution between the soil solid and liquid phases. However, since the sorption capacity is inversely related to the amount of metal sorbed, only "low metal" compost can provide new sorbing sites free of heavy metals.

Poster: AfSR-8

A comparison of natural and commercial sorbent materials for the removal of copper from aqueous media

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Recent research has demonstrated the potential of certain natural materials for detoxification of metal bearing waters i.e. to function as biosorbents. Here we report results of an evaluation of two biosorbents, mechanically milled crabshell (MMC) and cryogenically milled crabshell (CMC) for the removal of copper (Cu^{2+}) from aqueous solutions over a range of concentrations. Their performance was compared to Darco®, Nortit® activated carbons and a Dowex® 50W strong cation-exchange resin. Both crabshell materials removed up to 99.5% Cu^{2+} from 1–1000 mg/L solutions. This compared favourably to the most efficient commercial material, Dowex® 50W (> 99.8% Cu^{2+} removal from 1–1000 mg/L solutions). While the activated carbons removed >99.5% Cu^{2+} in the 1–50 mg/L range, they were less efficient at more elevated concentrations. Results indicated removal to be a rapid process which proceeded via a complex range of mechanisms including ion-exchange, adsorption, absorption and precipitation depending on contact time, solution pH, initial copper concentration and adsorbent used. Although MMC was marginally less efficient in removing Cu^{2+} than CMC, its production costs from raw crabshell are significantly lower. Since crabshell is an environmentally benign, waste-material, we conclude that MMC constitutes a viable low-cost biosorbent for removing Cu^{2+} from aqueous media.

Poster: AfSR-9

Study of the possible treatment of peasant well water of Abidjan (Ivory Coast) by TiO₂ photocatalysis

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The presence of chlorinated phenols and chlorinated pesticides in peasant well water of the city of Abidjan is a big problem of public health in Ivory Coast. Most of these recalcitrant compounds are considered toxic or potentially carcinogenic and mutagenic to mammalian, aquatic life and are listed among the priority pollutants by US EPA. Advanced oxidation destructive processes, such as TiO₂ photocatalysis, have been shown to be an effective alternative, especially at low contaminant concentrations. For our study, we chose to degrade the 4-nitroacetophenone (4-NAP) because this molecule has a structure which one finds in many pesticides. The influence of the photocatalyst concentration on the mineralization kinetics of 4-NAP has been investigated employing different concentrations of Degussa P25 varying from 0.1 to 2 g/l. For higher concentrations of TiO₂, the removal efficiencies decreased with increasing amount of TiO₂. These results show that the optimum amount of TiO₂ is 1 g/l. The pH has an important effect on the photomineralization of 4-NAP. It is necessary to work at acidic (or neutral) pH, because at basic pH there is much repulsion of 4-NAP by negative TiO₂ surface. We have also tested different photocatalysts

Poster: AfSR-10

The study of photocatalytic activities of titania and titania - silica aerogels

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Titanium dioxide appeared to be a subject of great interest concerning its photocatalytic activity that follows decontamination ability. Although, particularly, TiO₂ P25 Degussa is still commonly used in the photocatalytic processes the new ways of refined Titania photocatalysts production have been investigated. The research can be split, at least, in three directions: firstly catalyst doping using transition metal ions following that band gap of the semiconductor decreases, secondly size lessening of the single particle resulting in the increase of the oxidizing power of the excited electron holes and finally increasing the adsorption capability of the catalysts. In the present studies second and third way of the catalyst improvement has been undertaken. Titania and titania-silica aerogels have been prepared. Their photocatalytic activities were determined and extensive structure research was carried out.

Poster: AfSR-11

Thermodynamics of hydrocarbon complexation by β -cyclodextrin in aqueous environment

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The release of hydrocarbons into the environment, whether accidental or due to human activities, is a main cause of water and soil pollution. Many bioremediation technologies have been developed to remove these contaminants. Several petroleum aliphatic and polycyclic aromatic hydrocarbons can act as source of carbon and energy for the growth of soil microorganisms. Their hydrophobicity and low water solubility mean that hydrocarbons pass very slowly from a non-aqueous to the aqueous phase liquid in which they are metabolised by microorganisms. Moreover, in the soil they are adsorbed to clay or humus fractions. β -Cyclodextrin may enhance solubilization and removal of contaminants. Biodegradation is also enhanced due to increased bioavailability of pollutants. This work considers thermodynamic and kinetic aspects of hydrocarbon complexation with β -cyclodextrin in aqueous solutions and in adsorbed state. The influence of the composition of the aqueous phase and of the presence of polar organic compounds on the mechanism of complex formation was taken into account. Data obtained with differential scanning calorimetry were used to calculate the standard entropy, enthalpy and Gibbs energy of the inclusion reaction. Calorimetric experiments were also performed to determine the activation energy of the hydrocarbon complexation.

Poster: AfSR-12

Phytoextraction capacity of trees growing on a metal contaminated soil

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Phytoremediation is an innovative biological technique to reclaim land contaminated by heavy metals or organic pollutants. It aims to select the appropriate plant species to decontaminate polluted areas by contaminant extraction. In the present work, we studied the ability of five woody tree and shrub species to extract heavy metals from a polluted soil to their superior parts. The metal content in leaves and twigs was determined. *Salix* and *Betula* extracted heavy metals from the contaminated soil and transferred them to their superior tissues. On the other hand, *Alnus*, *Fraxinus* and *Sorbus* excluded them from their superior tissues. In a phytoremediation approach of soil contaminated by heavy metals, the plants must be chosen among the species that are able to grow on contaminated soils. This is true for phytoextraction and phytostabilisation. When they can also take up large quantities of heavy metals through high concentrations in their shoots and/or a high biomass production, then phytoextraction can be considered. Ultimately, the option to be taken will depend on the physico-chemical characteristics of the soil to be decontaminated as well as on local laws and further use of the soil.

Poster: AfSR-13

Influence of catalyst type, temperature and grain size on contact precipitation of fluoride

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In the northern region of Thailand, groundwater in several parts contains fluoride exceeding the 1993 WHO guidelines (1-1.5 mg/l). This has caused the fluorosis problem-a serious bone disease-among local people. Thus, suitable solution must be created. Contact Precipitation is a relatively new method. It has been tested in field only for a short period in Tanzania (Dahi 1997) and in lab in Thailand (Albertus et al 2000). It requires low operations and maintenance cost, low daily working load, and no risky chemicals. As the result, it gives high removal efficiency. Therefore, it might be an appropriate method for defluoridation in Thailand. Study on factors that influence on the process's efficiency and the reaction will lead to optimization of this method. This study was divided into three parts. First study, influence of catalyst type, was conducted in Jar test. Three different types of bone char (from Kenya, Thailand and Scotland) and two types of activated carbon (from Thailand and Scotland) were tested. Second study was to investigate the influence of temperature. Experiment was carried out in both chemostat system and jar test simultaneously. Considered temperatures were 15, 20, 25, 30 and 35 °C. The third study was to investigate the influence of grain size. This experiment was carried out in columns.

Poster: AfSR-14

Column studies for assessment of PAH biodegradation kinetics in polluted soils

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Polycyclic Aromatic Hydrocarbons (PAH) are present in numerous petroleum hydrocarbons pollutions of soils. These compounds show a particular resistance to the endogenous micro-flora biodegradation for essentially two reasons: their weak bio-availability and their toxicity for some bacteria. Current researches have to improve the knowledge of these parameters in order to accelerate the bioremediation processes of such polluted soils. A laboratory scale pilot plant allowing the systematic study of these factors before their extrapolation at full scale has been designed. Several soils samples from a former gasworks site containing a lot of PAH strongly adsorbed on ground particles have been laboratory tested. A study protocol already defined by the Biobasic Environnement company for the implementation of biodegradability studies has been used. The scope of this work is to determine the biodegradation rates in a specific case of soil contamination by PAH, in order to assess the technical and economical feasibility of an in-situ bioremediation treatment. The stoichiometric equation for bacteria growth and pollutant biodegradation has been established, allowing the determination of mass balances. Biodegradation monitoring is achieved continuously by an on-line measurement of carbon dioxide production and intermittently by analysing residual hydrocarbons. Results lead to the knowledge of biodegradation rates which allow to determine the treatment duration and cost.

Poster: AfSR-15

Removal of heavy metals by modified zeolites

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Introduction Natural, synthetic or modified zeolites can be used for the immobilisation of heavy metals in solutions and soil. The aim of this work is to evaluate new tailoring substances that enhance the capacity and selectivity of the zeolite material for certain heavy metals. Suitable tailoring molecules, like cysteamine, with its positively charged amino group and a thiol group can serve as bridging molecules between the zeolite and mercaptophilic heavy metal cations. Methods The zeolite in its natural and sodium form was shaken with cysteamine solutions for one day. After three-fold washing with water, the zeolite was mixed with lead nitrate solution. Results and Outlook The natural zeolite adsorbed cysteamine up to 11.7% of its CEC, the sodium zeolite up to 21.3%. The desorption tests with water showed that only a minor part of the cysteamine could be released. The adsorption tests with lead indicated that the treatment with cysteamine did reduce the adsorption capacity of the zeolite. This phenomenon can be explained by competition for adsorption sites between cysteamine and lead. However, the mercaptophilic cysteamine should show a distinct enhancement towards adsorption of cadmium and mercury cations.

Poster: AfSR-16

Problem based learning (PBL) technique applied for basic sciences education chemistry and the environment

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Problem Based Learning (PBL) is currently applied for the teaching of Chemistry and Environmental Sciences. PBL allows students to propose solutions for specific problems. These are selected and designed in order to demand from the student acquisition of critical knowledge, problem solving proficiency, self-directed learning strategies, and team participation skills. Students assume increasing responsibility for their learning, giving them motivation and feelings of accomplishment. Faculty in turn become resources, tutors, and evaluators, guiding the students in their problem solving efforts. The importance of the environment and its protection is taken into account on each part of the course. Each problem usually consists of everyday issues such as air pollution caused by chemicals emitted from automobiles and industrial processes. Students are required to propose a solution based on their knowledge of Chemistry and the Environment. The success in applying PBL is monitored by evaluating the students knowledge of basic theory in chemistry and environmental issues and its application to solve specific problems assigned during the academic period. Furthermore, designing problems concerning pollution and environmental impacts caused due to the presence of specific chemicals, allows the student to understand the behavior of these substances within the environment

Poster: Teac-1

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