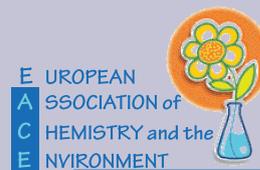




Environmental
Research Institute

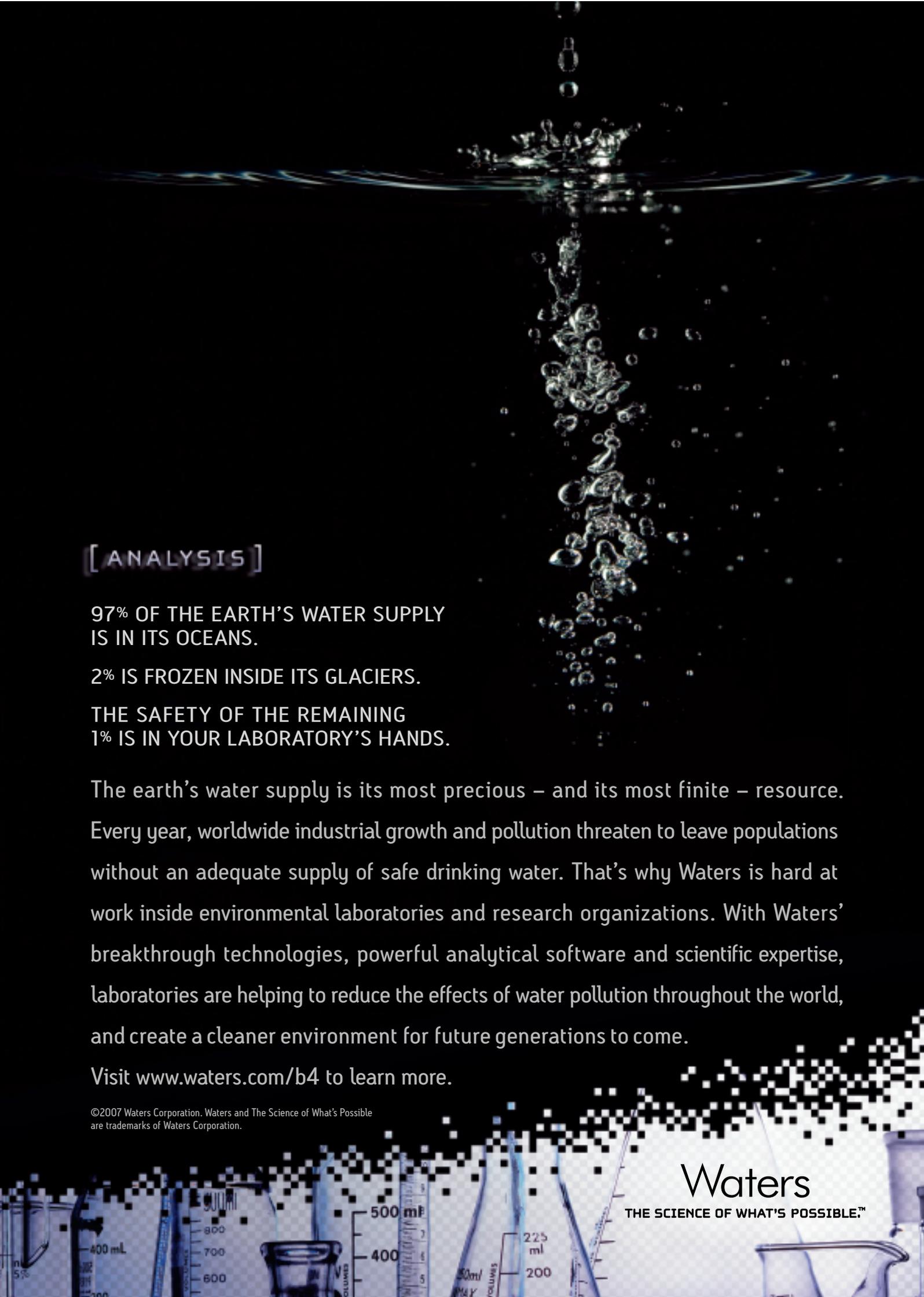


8th European Meeting on Environmental Chemistry (EMEC8)

Eden Court Theatre, Inverness, Scotland
5 - 8 December 2007



Book of Abstracts and Final Programme



[ANALYSIS]

97% OF THE EARTH'S WATER SUPPLY
IS IN ITS OCEANS.

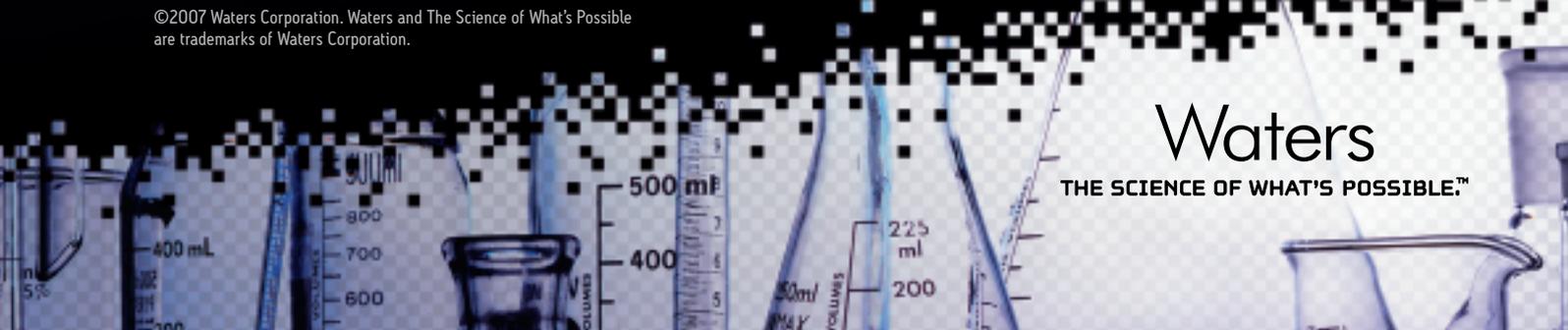
2% IS FROZEN INSIDE ITS GLACIERS.

THE SAFETY OF THE REMAINING
1% IS IN YOUR LABORATORY'S HANDS.

The earth's water supply is its most precious – and its most finite – resource. Every year, worldwide industrial growth and pollution threaten to leave populations without an adequate supply of safe drinking water. That's why Waters is hard at work inside environmental laboratories and research organizations. With Waters' breakthrough technologies, powerful analytical software and scientific expertise, laboratories are helping to reduce the effects of water pollution throughout the world, and create a cleaner environment for future generations to come.

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Local Organising Committee

Chairman	Dr. Stuart Gibb Environmental Research Institute North Highland College UHI Millennium Institute Stuart.Gibb@thurso.uhi.ac.uk
Vice-Chairman	Dr. Kenny Boyd Environmental Research Institute North Highland College UHI Millennium Institute Kenneth.Boyd@thurso.uhi.ac.uk
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Welcome



Dear Colleagues,

On behalf of the Organising Committee it gives me great pleasure to welcome you to the 8th European Meeting on Environmental Chemistry (EMEC8) and to Inverness. Although it is Scotland's smallest and newest 'city' (having been granted city status by the Queen in 2000), Inverness has been a natural focus for communication to and through the Highlands for most of the last two thousand years and is surrounded by some of the most unspoiled environments in Europe. We extend a warm welcome to all!

EMEC 8 is hosted by the Environmental Research Institute of the UHI Millennium Institute on behalf of the Association of Chemistry and the Environment (ACE). A full scientific programme of invited lectures, podium and poster presentations has been compiled which covers a broad range of issues in contemporary environmental chemistry. Our intention is to stimulate lively discussion and networking with colleagues from across Europe and further afield and perhaps instigate some new collaborations as well as refresh old ones.

The scientific programme will be based at the Eden Court Theatre on the banks of the River Ness. Eden Court has recently undergone an extensive refurbishment programme and we very much hope that this venue will provide an exciting setting for a stimulating and vibrant event.

In the traditions of Highland hospitality a full social programme has also been organised. This commences with a welcome reception at Eden Court on Wednesday evening and is followed on Thursday with a Civic Reception at the Town House kindly hosted by Highland Council. On Friday evening we travel to the nearby seaside town of Nairn, for the Conference Dinner at the Newton Nairn Hotel followed by a Ceilidh dance. We conclude with a post-conference tour on Saturday afternoon - sailing along the world-famous Loch Ness to visit the ruins of Urquhart Castle at sunset before a short visit to the Loch Ness 2000 Centre and finally returning to Inverness.

We sincerely hope that you will find the combination of scientific programme and social events to be rewarding and enjoyable from both professional and personal perspectives.

Very best wishes

Stuart W. Gibb
Chair, EMEC8 Organising Committee

Acknowledgements

The Organising Committee gratefully acknowledges the support of the following Exhibitors and Sponsors:

Sponsors



European Regional
Development Fund



Exhibitors



Bruker Daltonics is a leading manufacturer of mass spectrometry instruments and accessories for environmental research applications. Our products include a complete variety of MALDI-TOF, MALDI-TOF/TOF, FTMS, ESI-Ion Trap, ESI/TOF and ESI/QTOF systems, as well as a complete line of automated sample processing systems and productivity-enhancing software for all of your mass spectrometry needs. Our representatives will be on hand to discuss your requirements, please come and visit us at the stand.



Waters creates business advantages for laboratory-dependent organizations by delivering practical and sustainable scientific innovation to enable significant advancements in such areas as healthcare delivery, environmental management, food safety, and water quality worldwide. Bringing keen understanding and deep experience to those responsible for laboratory infrastructure and performance, Waters helps customers make profound discoveries, optimize lab operations, deliver product performance, and ensure regulatory compliance. Pioneering a connected portfolio of separation and analytical science, laboratory informatics, and mass spectrometry, Waters' technology breakthroughs and laboratory solutions provide an enduring platform for customer success.

General Information

Accompanying Persons

The accompanying person fee includes:

- Welcome Reception at the Conference venue on Wednesday 5 December
- Opening Ceremony at the Conference venue on Thursday 6 December
- Civic Reception at The Town House on Thursday 6 December
- Conference Dinner and Ceilidh at The Newton Hotel on Friday 7 December
- Closing Ceremony and refreshments at the conference venue on Saturday 8 December
- 1/2 day sight seeing tour
- Conference tour on Saturday 8 December (first come first serve basis)
- VAT @ 17.5%
- All tours will depart from Eden Court, Inverness

ACE AGM

The ACE AGM will take place on Thursday 6 December, 18.00 - 19.00hrs in the Office Suite, Third Floor, Bishop's Palace.

Badges

The name badge issued to delegates on registration serves as an admission pass to all scientific sessions, the exhibition and inclusive social events. Delegates are asked to ensure that they wear their name badges at all times.

Business Centre

There is no business centre within Eden Court, should you require photocopying, faxing, courier and freight solutions then please go to the EMEC 8 registration desk within Bishops Palace.

Car Parking

Delegates will be able to utilise the Eden Court car park. This car park is barrier operated and will be complimentary to delegates during the Conference however this will be subject to availability of spaces.

Cash Machines

There are no cash machines within Eden Court; the nearest cash machine is The Royal Bank of Scotland Plc which is situated on Tormnahurich Street.

Certificate of Attendance

A Certificate of Attendance will be available at the meeting. A voucher is included in your registration documentation and can be exchanged during the Conference for your certificate.

Cloakroom Facilities

There are cloakroom facilities next to the main ticket office within Eden Court; this service is complimentary to delegates throughout the Conference.

Credit Cards

Commonly accepted credit cards in hotels, restaurants and stores are American Express, Visa, MasterCard and Diners.

Dress Code

You may dress informally for the Conference. The dress code for the Civic Reception and Conference Dinner & Ceilidh will be smart casual.

Disclaimer

All best endeavours will be made to present the programme as printed. However, EMEC8 and its agents reserve the right to alter or cancel, without prior notice, any arrangements, timetables, plans or other items relating directly or indirectly to the conference, for any cause beyond its reasonable control. EMEC8 and its agents are not liable for any loss or inconvenience caused as a result of such cancellation. Delegates are advised to take out their own travel insurance and to extend their policy to cover personal possessions as the Conference does not cover individuals against cancellation of bookings or theft or damage to belongings. Tours run by third parties may be subject to cancellation should minimum numbers not be achieved.

Electricity

The voltage in the United Kingdom is 220-240V.

Exhibition

An exhibition of related products, services and technologies is being held concurrently with the Conference. The exhibition will be located within the Bishops Palace. The exhibition is open at the following times.

Wednesday 5 December	18.00 - 20.00
	<i>(Welcome Reception, Informal Poster Session & Exhibition Opening)</i>
Thursday 6 December	08.00 - 16.15
Friday 7 December	08.00 - 16.15
Saturday 8 December	08.00 - 14.00

First Aid

There are dedicated first aid trained staff within Eden Court to assist delegates if required. In the event of an emergency please contact either a member of Eden Court staff or Concorde Services staff.

Internet Facilities

There is Wifi access throughout Eden Court which will be available to delegates on a complimentary basis.

Information Desks

The main ticket office within the foyer of Eden Court also acts as an information desk should delegates require any assistance.

Kilt Hire

The EMEC 8 Committee offer the opportunity to all delegates to wear traditional Scottish dress for the Conference Dinner and Ceilidh on Friday 7 December at the Newton Hotel. The recommended Kilt Hire suppliers are detailed below:

Ben Wyvis Kilts
Highland Rail House
Station Square
Inverness IV1 1LE

Tel: +44 (0) 1463 715448
Web: www.benwyvis.co.uk

Boarstone Tartans
14 - 16 Victorian Market
Inverness IV1 1PG

Tel: +44 (0) 1463 239793
Web: www.boarstonetartans.co.uk

General Information

Language

The official language of the Conference will be English. No simultaneous translation will be available.

Lost Property

Enquiries regarding items lost or found can be made at the Registration Desk which is situated in the Bishops Palace. To minimise losses, please ensure that your Delegate Bag is labelled and that your name is written inside your copy of the combined Final Programme and Abstract Book.

Lunches and Refreshments

Coffee/tea and lunch will be served in the Bishops Palace.

Messages and Correspondence

Messages for delegates should be handed in at the Registration Desk in the Bishops Palace. Notification of messages will be displayed on the message board situated next to the registration desk. Please check the board daily and pick up your messages - they may be urgent.

Correspondence may be sent to delegates at the Conference and should be addressed as follows:

Delegate Name
EMEC8 Registration Desk
Eden Court Theatre
Bishops Road
Inverness IV3 5SA

Tel: +44 (0)1463 239841

Fax: +44 (0)1463 713810

Mobile Telephones

It should be noted that mobile phones must be switched off when delegates are in session halls.

Posters

Posters will be displayed in Bishops Palace. Posters should be assembled and dismantled at the following times:

Poster No.	Assemble	Dismantle
P01 - 06	Wed 5 Dec 12.00-17.00	Thurs 6 Dec 16.15-18.00
P07 - 12	Fri 7 Dec 07.30-09.00	Sat 8 Dec 14.00-16.00

Should you require information on when your poster should be displayed, please visit the registration desk. There will be an informal Poster session during the Welcome Reception therefore it is important that posters are installed by 17.00hrs on Wednesday 5 December. You are requested to be present at your poster during lunchtime for any questions.

Please note that the Organising Committee, EMEC8 or Concorde Services will not be responsible for posters which are not removed on time.

Public Telephones

There are no public telephones within Eden Court.

Registration Opening Times

The registration area in the Bishops Palace will be open at the following times:

Wednesday 5 December	18.00 - 20.00
Thursday 6 December	08.00 - 18.00
Friday 7 December	08.00 - 18.00
Saturday 8 December	08.00 - 13.15

Scientific Sessions

The Scientific Sessions will be held within the OneTouch Theatre.

Please refer to the venue orientation guide on page 6.

Smoking Policy

Smoking is not permitted within Eden Court. Should you wish to smoke then please do so outside the venue.

Speakers' Preview Room

The Speakers' Preview Room will be situated in the main Projection Room for the OneTouch Theatre which can be accessed from within the OneTouch Theatre. All speakers should report to this room two hours before their presentation time, even if they are not using any audio-visual material. The opening hours are:

Wednesday 5 December	17.00 - 20.00
Thursday 6 December	08.00 - 18.00
Friday 7 December	08.00 - 18.00
Saturday 8 December	08.00 - 13.15

Taxis

The telephone number for the local recommended taxi company, Highland Taxis is 01463 222222.

Value Added Tax (VAT)

Value Added Tax and similar taxes are charged on most goods and services in the United Kingdom. At the time of going to press, VAT in the United Kingdom is 17.5%.

VAT must be paid on goods or services at the point of sale

Business travellers within Europe, subject to certain conditions, may reclaim VAT for Conference registration fees, accompanying persons' registration fees etc. This applies to both non-European business travellers visiting Europe and to European business travellers to other EU countries. For further information please contact Customs and Excise on departure at the Airport.

Useful Websites

Visit Scotland (Inverness office) +44 (0) 1463 716996
www.visitscotland.com

Eden Court Theatre +44 (0) 1463 239841
www.eden-court.co.uk

Highlands & Islands Airports +44 (0) 1667 464000
www.hial.co.uk

Easy jet 0871 244 2366
www.easyjet.com

BMI Baby 0871 224 0224
www.bmibaby.com

Inverness Railway Station 0845 748 4950

National Rail Enquiries 0845 748 4950
www.nationalrail.co.uk

Scottish Citylink Coaches 0870 550 5050
www.citylink.co.uk

Stagecoach Inverness +44 (0) 1463 239292
www.stagecoachbus.com

Social & Tours Programme

Accompanying Person Tour

Included within the Accompanying Person fee is a half day sightseeing tour, for details regarding this tour please contact the Registration Desk within Bishops Palace.

Day/Date	Inclusive or Optional	Social Event	Tour Programme	Time
Wednesday 5 December	Inclusive	Welcome Reception & Informal Poster Presentation		18:00 - 20:00
Thursday 6 December	Inclusive	Opening Ceremony		09:00 - 09:45
	Inclusive	Civic Reception		19:00 - 20:30
Friday 7 December	Inclusive	Conference Dinner & Ceilidh		19:00 - 00:30
Saturday 8 December	Inclusive	Closing Ceremony		13:00 - 13:15
	Inclusive		Conference Tour	13:45 - 17:45

Welcome Reception and Informal Poster Presentation

All registered delegates and accompanying persons are invited to attend the Welcome Reception and informal poster presentation which will commence at 18:00 hours on Wednesday 5 December within the Bishops Palace at Eden Court. The Registration Desk will also be available during this period to allow delegates to register for the Conference.

Civic Reception

All registered delegates and accompanying persons are invited to attend a Civic Reception which will be held at The Town House within the centre of Inverness. The Civic Reception will commence at 19:00 hours, there will be no transportation as the venue is within walking distance of all city centre hotels.

Conference Dinner and Ceilidh

The Conference Dinner and Ceilidh will take place at The Newton Hotel, Nairn on Friday 7 December and all registered delegates and accompanying persons are welcome. There will be coaches organised to depart from Eden Court at 18:30 hours to take delegates to The Newton Hotel, and then there will then be a staggered departure of coaches to bring delegates back to Inverness at the end of the evening.

Conference Tour

The conference tour will depart at 13:45 hours from Eden Court, Inverness and will follow the schedule below:

- 13:45 Coach departs Eden Court
- 14:00 Depart Tormnahurich Bridge for charter on Loch Ness
- 15:30 Arrive at Urquhart Castle
- 16:15 Depart Urquhart Castle by coach for Loch Ness Visitor Centre
- 17:15 Depart Loch Ness Visitor Centre for Inverness

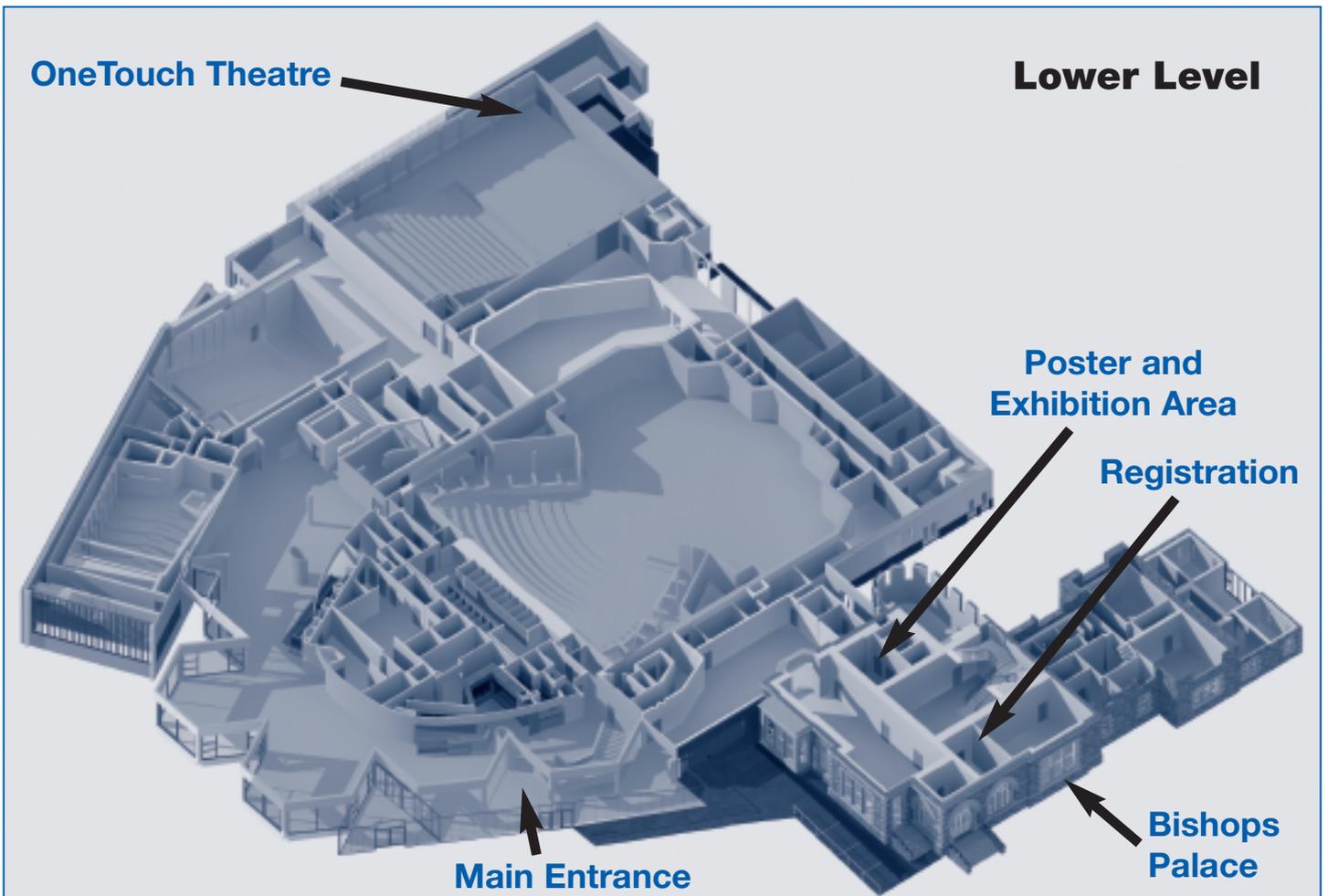
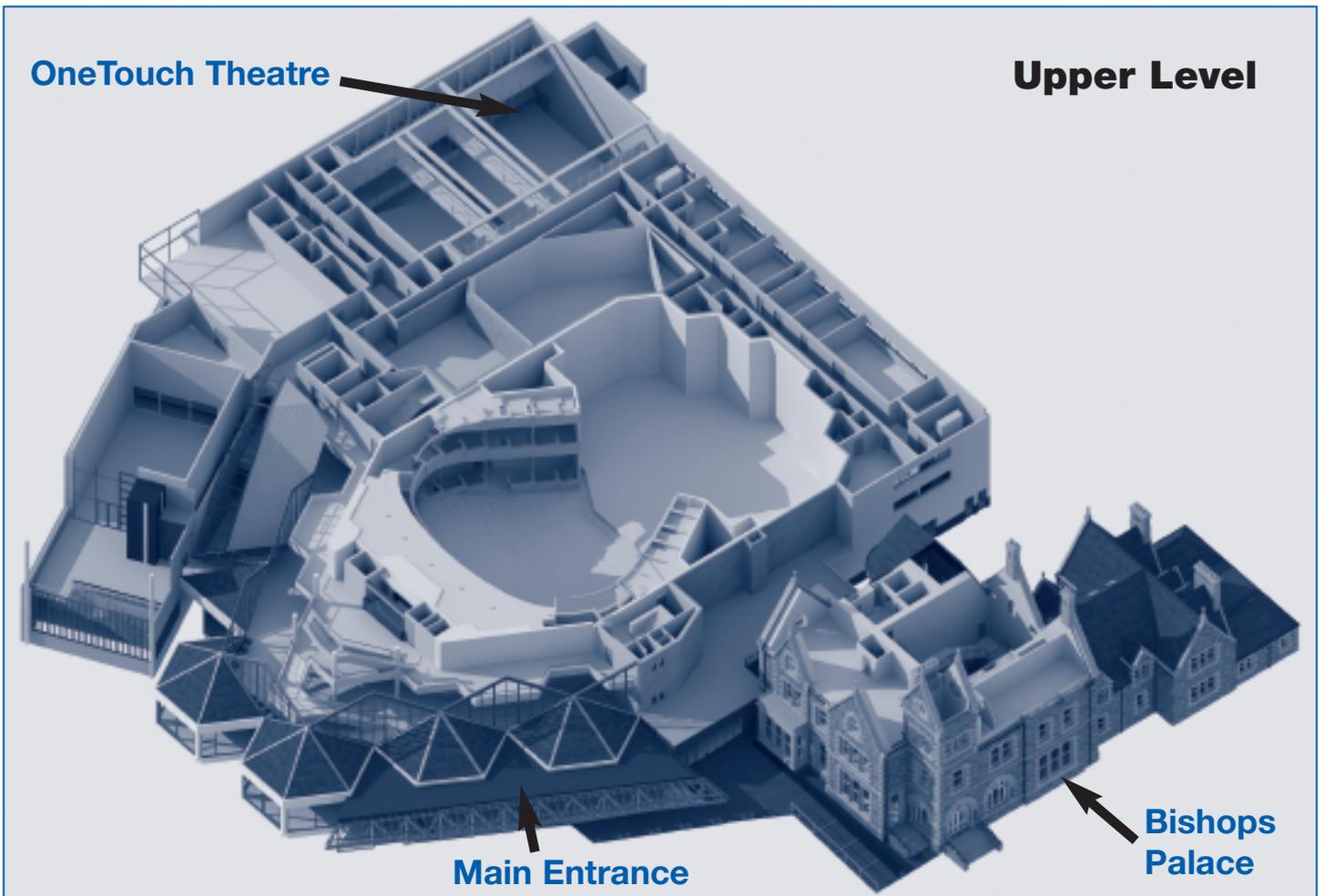
All delegates should bring the ticket for the conference tour which can be found within your registration documentation. Please note this tour had limited spaces and was allocated on a first come first served basis therefore the ticket is necessary to gain access to the tour.

Please note that if you indicated your attendance at social events on your registration form then delegates must wear their name badge to gain access. All appropriate information for each event will be found detailed within your registration documentation. If you have any queries please visit the Registration Desk.

If you have not indicated your attendance whilst registering online and you are interested in attending an event, please visit the Registration Desk to check availability.



Venue Orientation Guide



Map



Programme at a Glance

Time	Wednesday	Thursday	Friday	Saturday
08:00 - 09:00	Bishops Palace	OneTouch Theatre	OneTouch Theatre	OneTouch Theatre
AM	Arrival Coffee served in Bishops Palace (Registration, Exhibition and Poster Area)			
		<p>Welcome, Opening Ceremony Opening Address Professor Robert Cormack Principal, UHI Millennium Institute Chair: Stuart Gibb 09:00 - 10:00</p>	<p>Keynote Speaker Prof Paul Worsfold Introduction: Axel Miller 08:45 - 09:30 Page 9</p>	<p>Keynote Speaker Dr Valeria Dulio Introduction: Alistair Boxall 09:00 - 09:45 Page 9</p>
10:45 - 11:15		<p>Keynote Speaker Prof Alistair Boxall Introduction: Stuart Gibb 10:00 - 10:45 Page 9</p>	<p>Analytical Methods for Environmental Science Chair: Paul Worsfold FC4.1 - FC4.6 09:30 - 11:00 Pages 15 - 16</p>	<p>Biogeochemistry Chair: Axel Miller FC8.2 - FC8.4 09:45 - 10:30 Pages 20 - 21</p>
AM	Morning Coffee served in Bishops Palace (Registration, Exhibition and Poster Area)			
12:30 - 14:00		<p>Emerging Contaminants Chair: Alistair Boxall FC1.1 - FC1.5 11:15 - 12:30 Pages 11 - 12</p>	<p>Soil Chemistry Chair: Jan Schwarzbauer FC5.1 - FC5.4 11:30 - 12:30 Pages 16 - 17</p>	<p>Clean Technology and Green Chemistry Chair: Isabel Villaseca FC9.1 - FC9.5 11:15 - 12:15 Pages 21 - 22</p>
		<p>Buffet Lunch and Formal Poster Session in Bishops Palace (Registration, Exhibition and Poster Area)</p>		<p>Best Presentation Awards and Invitation to next EMEC ACE President: Stuart Gibb 12:15 - 13:00</p>
PM		<p>Invited Speaker Dr Ian Goodall Introduction: Kenny Boyd 14:00 - 14:30 Page 10</p>	<p>Invited Speaker Mr Adrian Shine Introduction: Stuart Gibb 14:00 - 14:30 Page 10</p>	<p>Closing Ceremony 13:00 - 13:15</p>
15:30 - 16:00		<p>Gas Exchange and Atmospheric Chemistry Chair: Anne-Marie Delors FC2.1 - FC2.4 14:30 - 15:30 Pages 12 - 13</p>	<p>Pollutant Chemistry Chair: Roland Kallenborn FC6.1 - FC6.5 14:30 - 15:45 Pages 17 - 18</p>	<p>Buffet Lunch in Bishops Palace (Registration, Exhibition and Poster Area) 13:15 - 14:00</p>
		<p>Afternoon Coffee served in Bishops Palace (Registration, Exhibition and Poster Area)</p>		
PM	<p>Registration Open and Welcome Reception 18:00 - 20:00</p>	<p>Water Treatment and Waste Management Chair: Jean-Claude Bollinger FC3.1 - FC3.7 16:00 - 17:45 Pages 13 - 15</p> <p>ACE AGM Office Suite, Third Floor, Bishop's Palace 18:00 - 19:00</p>	<p>Acquatic and Marine Chemistry Chair: Mark Fitzsimons FC7.1 - FC7.6 16:15 - 17:30 Pages 19 - 20</p>	

Keynote Speakers



Prof Alistair Boxall

KL1

Emerging Contaminants in the Environment: What should we be measuring?

Boxall, Alistair B

University of York/Central Science Laboratory, UK

In recent years there has been increasing concern over the so called 'emerging contaminants' such as degradates (formed in the environment and treatment processes), human pharmaceuticals, veterinary medicines, nanomaterials and personal care products. These substances have been shown to be released to the environment and in the few monitoring studies that have looked for them, they have been detected in surface waters, groundwaters and drinking waters. Whilst limited information is available on the potential impacts of these substances, there is some evidence that they may adversely affect human and environmental health. For example, many degradates of pesticides are potentially more toxic than the parent compound, selected adjuvants are suspected endocrine disruptors and there is concern that long-term exposure to antibacterial pharmaceuticals may be contributing to the development of resistant bacteria. It would therefore be prudent to 1) develop a better understanding of which emerging contaminants are likely to contaminate the environment, 2) determine what are the potential risks of these to environmental and human health; 3) develop analytical methodologies for substances identified as high risk; and 4) expand current monitoring programmes to quantify those emerging contaminants that are likely to pose the greatest risk to environmental and human health. This presentation will provide an overview of our current knowledge of emerging contaminants and of how they enter and behave in the environment. Approaches

(including in silico methods) for identifying those emerging contaminants that are likely to pose the greatest risk to the environment and human health will be illustrated. Major research challenges will be highlighted.



Prof Paul Worsfold

KL2

Flow injection techniques for investigating the biogeochemistry of dynamic marine environments

Worsfold, Paul

University of Plymouth, UK

Instrumental analytical techniques are critical for improving our fundamental understanding of environmental processes. In addition to the challenge of environmentally relevant detection limits is the need for high temporal and spatial resolution measurements. In this context there is a growing need for rapid and reliable but relatively low cost techniques that can be remotely deployed to provide high quality environmental data. This presentation describes the evolution of flow injection (FI) based instrumentation for aquatic environmental monitoring. FI techniques now impact on a wide cross section of analytical chemistry activities, providing imaginative and practical solutions to challenging analytical problems and contributing to the improvement of data quality. Key aspects of field based FI systems will be discussed, including reaction chemistry, detector design, analytical performance, sample presentation and data processing. Two examples will be used to illustrate the impact of FI techniques at the interface between environmental analytical chemistry and biogeochemistry. The first is the determination and cycling of phosphorus species in catchments and estuaries. Novel solid state detection coupled with on-line photochemical oxidation of dissolved organic phosphorus in natural waters will illustrate the potential of FI techniques for gathering high temporal resolution data for catchment management. A more complex FI manifold coupled with sequential enzymatic hydrolysis will be shown to identify individual classes of organic phosphorus species in the

Gippsland Lakes (Australia) and the Tamar Estuary (England). These results will demonstrate the potential importance of the organic phosphorus fraction (which is often overlooked) as a bioavailable source of phosphorus in aquatic systems. The second is the determination and biogeochemistry of iron in the open ocean. An FI with chemiluminescence detection (FI-CL) will be described for the determination of iron in remote, open ocean environments. As a rate limiting nutrient, iron plays a key role in ocean productivity and climate change. Data from real time monitoring of picomolar concentrations of Fe(II) and Fe(II+III) in the Atlantic and Southern Oceans will be presented and the biogeochemical cycling of iron discussed. The Atlantic Ocean data show the power of FI-CL for global scale spatial mapping of sub-nM surface iron concentrations and the Southern Ocean results demonstrate the ability to provide high temporal resolution data from truly remote locations. The procedure used for the collection of a bulk (1 L) low level (< 1 nM Fe) Atlantic Ocean sample for the preparation of a CRM and results from shipboard and global laboratory intercomparison exercises for low level iron in seawater will also be presented to emphasise the importance of 'clean' analytical protocols.



Dr Valeria Dulio

KL3

NORMAN FP project – Network of Reference Laboratories, Research Centres and Related Organisations for Monitoring and Bio-monitoring of Emerging Environmental Substances

Dulio, Valeria

INERIS - Direction Scientifique, France

Background: Emerging substances are of increasing concern to scientists, regulators and the public. They are not necessarily new chemicals and some of them have often long been present in the environment, but their presence and significance are only now attracting closer attention.

Objectives: The main goal of the NORMAN project (Co-ordination Action funded under the EU 6th Framework Programme - Contract N° 018486 - website <http://www.norman-network.net>) is to promote the creation of a permanent network of reference laboratories and research centres, able to ensure, in collaboration with competent authorities, industry, standardisation bodies, NGOs, etc.:

A more rapid and wide-ranging exchange of data and information on emerging substances;

Better data quality and comparability via validation and harmonisation of common measurement methods and monitoring tools.

Among the results already achieved by the NORMAN network it is worth mentioning:

Three databases: (i) EMPOMAP: a database of experts, organisations and projects dealing with emerging substances, (ii) EMPODAT: a database of geo-referenced monitoring and occurrence data accompanied by the ecotoxicological information from bio-assays and biomarkers and (iii) EMPOMASS: a database of mass spectrometric information on provisionally identified and unknown substances.

A common European framework for the validation of methods for the monitoring of emerging pollutants. The protocol has been tested in different interlaboratory studies. On the basis of the results, the protocol will be improved and proposed for implementation in the field of European Legislation and Standardisation (e.g. at CEN level).

Four workshops on various topics in the field of emerging pollutants.

The NORMAN newsletter which contains critical reviews of recent scientific publications in the field of emerging pollutants. Conclusions and future perspectives: The experience during the NORMAN project shows that there is a clear need at the EU level for an independent and competent forum facilitating the technical/scientific debate on the issues related to emerging substances. NORMAN is now preparing the follow-up of the NORMAN project, with the creation, starting from September 2008, of a non-profit association open to all interested stakeholders dealing with emerging substances - whether in analysis of their occurrence and effects, risk assessment or risk management. A written proposal and a call for expression of interest are available.

Invited Speakers



Mr Adrian Shine

Adrian Shine is the leader of the Loch Ness & Morar Project and has been engaged in fieldwork in the Highlands since 1973 collaborating on projects involving workers from some 20 universities and academic institutions within the UK and overseas. Adrian has used the Loch Ness Monster controversy as a vehicle for interpreting the dynamics and diversity of deep lakes. In the course of hundreds of TV, radio and video appearances Adrian's stance has always been to use media interest in all things "Nessie" to question, challenge and stimulate serious enquiry but also to popularise subjects people may not immediately consider interesting. He has published over a dozen scientific papers and articles on Loch Ness and has initiated collaborations developing innovative new sampling equipment and techniques.

Loch Ness; Indirect Chemistry

The larger oligotrophic Scottish lochs present some difficulty in detecting long term trends and changes, since they are unlikely to present visible or sometimes measurable water quality changes. This may be due to a lack of previous monitoring, chemical fluctuations or to nutrient levels lying near to detection thresholds. The historical diatom record locked in the sediments reveals changes in Loch Ness which could be seen as precursors to a degree of enrichment.

In a similar indirect manner, the living zooplankton communities may provide clues to a "productivity paradox" whereby the greater nutrient inputs to the northern basin are not reflected in the distribution of biomass which may owe more to allochthonous DOC.



Dr Ian Goodall

Ian gained a degree in Natural Sciences at Cambridge, and followed this with a PhD in Chemistry at the University of East Anglia. His PhD looked at how the analytical profiles of carbohydrates could be used in food authentication, particularly that of orange juice, and was based at the MAFF Food Science Laboratory. From non-alcoholic beverage research, Ian progressed to spirit drinks, with a move to the Scotch Whisky Research Institute (SWRI) in 1996. The SWRI is sponsored by most of the major whisky distilling companies in Scotland and carries out non-competitive research on behalf of its members. Ian was initially involved in distillation research, studying the effect of whisky still design on the flavour of the final spirit. However, with the development of the information provision that the SWRI offers its members, he became involved in developing its technical Help Desk and communication resources. Ian is now the Senior Scientist at the Institute responsible for Product Protection research and Bottling issues.

Scotch Whisky Production - Using Science to Add Value to the Product, and the Environment

The Scotch Whisky Research Institute provides a centre of scientific excellence dedicated to the needs of the whisky industry and the distilled beverage industry in general. Its aim is to assist its member companies in improving their products and processes and to maintain the position of Scotch whisky in world markets. To put the importance of the Scotch whisky industry to the UK in perspective, it is directly responsible for over 10,000 jobs in Scotland and supports 65,000 jobs throughout the UK, and, as one of the top five export earners, the annual export earnings of the industry are in excess of £2 billion a year.

This presentation will provide an overview to the Institute and its operations. Examples will be taken from all stages of the whisky production process to illustrate how the scientific research work of the Institute supports its members, adding value to their products and ensuring the industry has a sustainable future. Core research elements that will be discussed will include the development of new cereal varieties for distilling, understanding flavour development during distillation, studying alcohol losses during maturation and protecting the integrity of Scotch whisky by identifying counterfeit products.

In recent years, the sustainability remit of the Institute research has expanded to cover an increasing array of areas and new technologies. The impact of the industry on the environment, and conversely, the environment's impact on the industry is becoming a more integral part of the Institute's research programme. This presentation will highlight a number of areas in which the Institute is developing its experience in environmental chemistry to support the needs of the industry and the environment that supports it.

Oral Presentations

Emerging Contaminants **FC1.1 - FC1.5**

Gas Exchange and
Atmospheric Chemistry **FC2.1 - FC2.4**

Water Treatments and
Waste Management **FC3.1 - FC3.7**

Analytical Methods for
Environmental Science **FC4.1 - FC4.6**

Soil Chemistry **FC5.1 - FC5.4**

Pollutant Chemistry **FC6.1 - FC6.5**

Aquatic and Marine Chemistry **FC7.1 - FC7.6**

Biogeochemistry **FC8.2 - FC8.4**

Clean Technology and
Green Chemistry **FC9.1 - FC9.5**

FC1.2

Selected Musk Compounds in Waste Water and Sewage Sludge
Vavrova, Milada; Caslavsky, Josef; Masova, Michaela; Mares, Jan
Faculty of Chemistry, Brno University of Technology, Czech Republic

Synthetic musk compounds are fragrance substances commonly used as fragrant constituents of detergents, cleaning and washing agents, and cosmetics (creams, perfumes, deodorants). At present, there are more than three thousands of synthetic fragrances being used for perfuming commercial products. However, some musk compounds have proved to accumulate in the environment as well as in tissues of human body, and hence they are classified as persistent organic pollutants. Due to increasing consumption of these compounds their input into various environmental compartments becomes a serious problem. The main route of this process is via wastewaters because their elimination in the wastewater treatment plants is often insufficient. This thesis was focused on some synthetic fragrances produced by the AROMA Prague Co. The aim of this study was to perform a method optimisation for the determination of selected fragrances in wastewaters and sewage sludge. Two passive techniques were used for the isolation and preconcentration of target analytes from waters; solid phase microextraction and semipermeable membrane devices. Different extraction techniques for the separation of studied compounds from sewage sludge and solid matrices were compared - classical extraction, microwave extraction and solid phase extraction. The identification and quantification of analytes was carried out by HRGC/MS. Optimized method was used for the determination of target analytes in real samples of wastewaters and sewage sludge from the Brno city Wastewater Treatment Plant (WWTP) and from smaller WWTP situated in University of Veterinary Medicine in Brno.

Detection limit was calculated for each analysed compounds. We succeeded in monitoring of all analysed compounds using the optimised method. The results obtained from both wastewater treatment plants were comparable. Arocete and Arofire compounds were found at the highest levels.

Acknowledgement: This study was supported by the Project OC- 183, COST Action 636.

FC1.1

Oestrogenic Endocrine Disruption in Wild Atlantic salmon (*Salmo Salar*) Parr in Scotland

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Effluents from wastewater treatment works (WWTW) often contain compounds that are oestrogenic. In England, and a number of other developed countries, oestrogenic exposure of wild freshwater fish populations appears to be widespread and primarily related to WWTW discharges. Effects observed in male fish include abnormal reproductive development and impaired sperm quality. Male production of the egg yolk precursor protein vitellogenin (Vtg) is now routinely used as an indicator of oestrogenic exposure. Here we present the first evidence that fish in Scotland may also be exposed to oestrogenic compounds, and the first report of oestrogenic effects in wild Atlantic salmon. In a small scale study conducted in autumn 2006, free ranging Atlantic salmon parr were collected from upstream and downstream of two wastewater treatment works in south west Scotland and concentrations of Vtg were determined in blood plasma using a homologous enzyme linked immunosorbent assay (ELISA). Vtg concentrations were found to be elevated in male salmon parr caught immediately (<500 m) downstream of one WWTW, but not in fish caught approximately 2 km downstream of the other. Mean plasma Vtg concentration was approximately 30-times higher downstream (925±1072 ng/ml) of the first WWTW than upstream (33±23 ng/ml). This degree of Vtg induction is comparable to that observed in rainbow trout caged in English rivers for three weeks, but lower than has been seen in other studies of wild fish.

FC1.3

Degradation Products of Synthetic Polymers: Potential Threat for the Environment

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Background: Synthetic polymers are widely used due to their excellent properties which can be "tailored" with respect to their planned use. The total amount of synthetic polymers is constantly increasing. At the end of their life cycle great part of the polymer containing products is disposed on the waste dumps, where they remain usually for quite a long time. To solve this problem biodegradable polymers are proposed and synthesized. It is necessary to evaluate the possible environmental effects of their degradation products.

Objectives: The main aim of this study was the identification of degradation products of synthetic polymers of polyurethane type, modified by several additives improving their biodegradability under environmental conditions.

Methods: The polyurethane foams (PUFs) were synthesized by the reaction of 2,4-toluene diisocyanate and polyether polyol. Carboxymethylcellulose, cellulose acetate, acetylated potato starch, 2-hydroxyethylcellulose and hydrated wheat protein were used as additives in amounts ranging from 1 to 30 % w/w of the polymer. PUF without additive was used as the reference. The first set of PUFs was hydrolysed by refluxing in water; the second one was subjected to the degradation under simulated natural conditions. The third experimental set was prepared by deposition of PUF extracts on the soil and weathering. The duration of the experiment was from 3 week to 2 months. Degradation products were extracted and identified by GC/MS, HPLC/MS and MALDI-TOF MS.

Results: In extracts of weathered PUF benzenediamine derivatives were identified. In hydrolysed PUFs the presence of phenol, 5-octadecene and 1-nonadecene was proved, as well as benzene-propanoic acid.

Conclusion: Products of the degradation of polyurethane foams with biodegradable additives were identified. In future experiment, longer weathering period will be used and also the ecotoxicological tests of the degradation products will be employed.

Acknowledgement: This work was supported by the grant MSM 0021630501 from the MSMT of the CR.

Oral Presentations

FC1.4

Presence of estrogenic compounds and betablockers in influent and effluent of six wastewater treatment plants

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This study is part of a national project, which aims at quantifying micropollutants in domestic waters (dissolved and solid phase) and evaluating the performance of different WWTP technologies. Investigated molecules include the 33 priority substances of the Water Framework Directive and pharmaceuticals from several therapeutic groups. Between January 2007 and June 2008, 16 WWTP representative of the main conventional treatment plants found in France, will be studied.

We will present the results obtained in the dissolved phase for 6 WWTP (mostly activated sludge process). Daily average samples were collected on the water treatment line (for 3 successive days) and on the sludge treatment line. We analysed 5 hormones, including conjugated forms (estrone, a and b-estradiol, estriol and ethynilestradiol) and 10 betablockers (oxprenolol, metoprolol, timolol, propranolol, nadolol, betaxolol, bisoprolol, acebutolol, atenolol, and sotalol). The analysis of hormones consists in a solid phase extraction (Oasis HLB cartridge), a purification with florisil and an analysis by LC-MS/MS. For betablockers, the extraction is performed on MCX cartridge and followed by LC-MS/MS analysis. The synthetic hormone, ethynilestradiol, was never detected. Estriol showed the highest hormone concentrations in influents (50 to 400 ng/L), but was below detection level in effluents. Total hormone concentrations were generally below 14 ng/L in effluents. Three betablockers were rarely detected either in influent or in effluent: timolol, oxprenolol and betaxolol. All other betablockers were generally present and their concentration could reach more than 2000 ng/L in influent and 1000 ng/L in effluent. The comparison of concentrations measured in dissolved phase of influents and effluents showed that elimination is more efficient for sotalol, atenolol and propranolol than for acebutolol and nadolol.

FC2.1

Release of Greenhouse Gases (Ghg) from Surface Waters in Mer Bleue Peatland, Canada: Sources of Dissolved Gaseous Carbon and Diurnal Cycles

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Background: Peatlands represent a huge global store of carbon. As the climate warms and rainfall patterns change, the fate of this carbon is uncertain and if released to the atmosphere may represent an important positive feedback to global warming. Studies have shown that surface waters draining peatlands are permanently supersaturated with CO₂ and CH₄ with respect to the atmosphere, suggesting they may act as important pathways for the release of carbon to the atmosphere.

Aims/Objectives: Until now studies have relied on a small number of isolated measurements to calculate long-term evasion rates. Here we try to capture diurnal fluctuations in gas concentrations. We also aim to relate the diurnal variation in CO₂ in the water column to similar cycles in other parts of the peatland ecosystem.

Methods: CO₂ probes were encased in a water tight gas permeable membrane and submerged in a beaver pond at Mer Bleue peatland, part of Fluxnet Canada. Measurements were made continuously throughout July and August 2007.

Results: The study revealed large diurnal fluctuations in dissolved CO₂ with a range of approximately 8000 ppmv. Concentrations of CO₂ in the surface water (10cm) reached >30000 ppmv and >90000 ppmv at depth. (70cm). CH₄ supersaturations (using headspace analysis) reached >7000 and >16000 times atmospheric concentrations at 10 and 70 cm depth respectively.

Discussion: Using this concentration data, gas exchange across the water-atmosphere boundary will be calculated, and the contribution of CO₂ and CH₄ evasion to the net GHG balance of the peatland discussed. Diurnal cycles in concentration and evasion rates are compared to both CO₂ cycles in the soil, and Net Ecosystem Exchange. This provides important information about the main drivers and controls on surface water gas concentrations.

FC1.5

On the Fate of Macrolide Antibiotics in Water/Sediment Systems

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"Background": Lately, macrolides have been regarded as one the most frequently detected class of antibiotics in environmental waters (1,2). However little is known on the fate of these chemicals in water/sediment systems.

"Objectives": Major objectives of this work were to investigate the reactivity of macrolides upon direct and indirect photochemistry and in presence of different model clays and manganese oxides. For this purpose, anhydroerythromycin, roxithromycin and clarithromycin, three representatives of the macrolide family were investigated.

"Methods": water and solid samples were analysed for macrolides and their degradation products at selected time by high-performance liquid chromatography (HPLC) and UV detection at 205 nm, with product identification confirmed by HPLC-mass spectrometry.

"Results and Discussion": The aqueous speciation of the selected macrolides was dominated by association with iron(III) ions and with dissolved organic matter (DOM) resulting in a strong increase in water solubility of macrolides which might explain their high occurrence level in environmental waters. Under simulated sunlight, macrolides were relatively stable except in ultrapure water. A sensitization effect was also observed in presence of iron(III) ions accounting for an increase in the pseudo first order rate constant. Sorption on clays appeared to be the major factor influencing the loss of macrolides. However, the presence of large amount of DOM was also found to decrease the sorption of macrolides to clay suggesting that DOM may increase their mobility in the environment. Clays catalysed the macrolide degradation by the hydrolysis of sugar moieties and the multiple dehydrations. The surface acidity of clay enhanced the rate of clay-catalysed degradation of macrolides providing a mechanism for detoxification of these chemicals in the environment.

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FC2.2

NitroEurope - Greenhouse gas fluxes from Auchencorth Moss

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NitroEurope addresses the major question: What is the effect of reactive nitrogen (N) supply on net greenhouse gas (GHG) budgets for Europe? One of the objectives is to establish robust datasets of N fluxes and net GHG exchange in relation to carbon (C) and N cycling of representative European ecosystems, as a basis to investigate interactions and assess long-term change. This is met by a programme that integrates observations of N fluxes and pools. Here results from Auchencorth Moss are presented. The site is located 17 km south west of Edinburgh and comprises a 335 ha peatland catchment. The vegetation is dominated by *Calluna vulgaris*, *Juncus effusus*, grassy hummocks and hollows.

Net ecosystem exchange of CO₂ was measured continuously by eddy covariance and soil fluxes of N₂O, CH₄ and CO₂ were measured every fortnight using conventional chamber methods. Temporal variations in these fluxes were compared with variations in mineral NH₄ and NO₃ concentrations, soil moisture, water table, soil and air temperature and the concentration of CO₂, CH₄ and N₂O in soil air.

Mean N₂O-N fluxes from nine chambers from May 2006 until August 2007 were 0.31 (-63 to 62) µg m² h⁻¹ and mean CH₄ fluxes were 35 (-180 to 1280) µg m² h⁻¹. Soil respiration was generally between 0.15 and 0.4 g m² h⁻¹. GHG fluxes at this site were dominated by CO₂ exchange, being responsible for >90% of the total GHG budget. CH₄ and N₂O fluxes at this site are very low. There seemed to be a trend for high CH₄ and N₂O fluxes with high water table and soil uptake during dry periods.

It is important to measure these low fluxes of N₂O as it is an important GHG and measured fluxes might therefore be more relevant in context with the total GHG budget rather than the total N budget. Moreover, it is important to understand underlying processes and interactions to better quantify net GHG exchange. Measurements are ongoing and will be compared with other sites across Europe and produce robust data sets for the whole of Europe.

Oral Presentations

FC2.3

Hydrogen Peroxide in Natural Cloudwater: Sources and Photoreactivity

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Hydrogen peroxide is known to be an important oxidant in cloudwater, controlling the liquid phase oxidation processes and thus influencing the oxidizing capacity of the atmosphere. Hydrogen peroxide in cloud droplets originates both from gas-to-liquid partitioning of H₂O₂ and HO₂• (very soluble species) and aqueous-phase photoproduction. The first way has traditionally been considered as the predominant source, while more recent studies support the hypothesis that light absorbing compounds present in cloud droplets can initiate aqueous phase photochemical reactions resulting in H₂O₂ formation. In order to factorize between gas phase and liquid phase photochemical reaction we compare in-situ diurnal and seasonal variation in natural cloudwater and the behaviour of H₂O₂ during irradiation experiment in which real cloud samples are irradiated with light similar to solar spectrum in a hermetic photoreactor free from the gas phase transfer. We collected 94 samples from 30 cloud events at puy de Dôme summit along different seasons and the whole day duration; additionally 7 high volume samples were used for irradiation experiments. Hydrogen peroxide was revealed sensitive to solar radiation: its concentration in cloud droplets shows diurnal trend (photoproduction) depending on air mass pollution degree. On the contrary during irradiation experiments of the cloud aqueous phase, the concentration shows a regular decreasing with an average half-life time of 3.1 hours. The linking of these results leads to conclusion that photochemical production of H₂O₂ has priority in gaseous phase and photoformation of hydrogen peroxide in marine cloud water is negligible in a free tropospheric site.

FC3.1

Compound Orientated Prediction for Long-term Behaviour of Organic Contaminants in Solid Waste and Seepage Water of a Deposit Landfill

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Background: In the past landfills have been used intensively as final waste deposits. Due to insufficient bottom sealings and as a result of treated effluent emissions they have affected frequently ground and surface water. In 2005 this kind of waste management was stopped in Germany. But as a consequence of their potential to harm the environment the deposits have to be controlled in the future. However, there is very limited knowledge on the long-term behaviour of the contamination within the waste.

Aim: This study tried to provide a first prediction of the long-term behaviour of relevant organic contaminants in waste and corresponding seepage water of a German waste deposit considering transport and degradation processes as well as toxicological properties.

Results: Based on qualitative analysis, literature enquiry as well as former investigations, (revealing information on the composition of seepage and leakage water, the impact on ground water as well as on transfer processes between seepage water and particulate matter within the deposit) a compound specific system has been developed to categorize 84 selected pollutants. This system classified 13 substances as long-term persistent and for 8 compounds a high risk potential for the aquatic environment was defined. Further on, an experimental set up was designed to estimate the long-term leaching of semi-polar compounds, in detail bisphenol A and phthalates.

Conclusion: Our study led to a compound related base for a monitoring set up controlling ground and riverine water affected by a waste deposit landfill. Further on, a minimum observation time of ca. 30 years for the deposit itself has been pointed out. Principally, this work can act as a model study for developing compound orientated monitoring systems for enclosed waste deposits.

FC2.4

Atmospheric Long Range Transport of Persistent Organic Pollutants: A Circum-arctic View

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The present levels of persistent contaminants found in the Arctic environment can not be related to known use and release from potential sources within the Arctic, and can therefore only be explained by long-range transport from lower latitudes. Today, atmospheric long-range transport is known to be one of the most important sources for the presence of many persistent organic pollutants in the Arctic environment. Within the past decade, international regulation measures were initiated in order to restrict or prohibit the direct release of persistent pollutants. As surveillance tool, long-term monitoring of atmospheric POP transport into the Arctic is an important tool to control the effect of such regulatory measures. Under the umbrella of the Arctic Monitoring and Assessment Programme (AMAP) circum Arctic Monitoring of POPs have been performed. This circum-Arctic effort has provided impressive evidence for the regional effect of globally emitted anthropogenic pollution. Institutes from Canada, Iceland, Norway, Canada and Russia) have performed comprehensive monitoring of long-range transported organochlorines like polychlorinated biphenyls (PCB) and chloro-pesticides as well as their transformation products. The Norwegian national atmospheric monitoring station "Zeppelin mountain" in Ny-Ålesund (Svalbard) is one of the most important contributors to this long-term monitoring effort. A first assessment of time trends and fate of conventional chlorinated compounds like hexachlorocyclohexane (HCH), chlordanes and selected PCBs will be presented mainly based on the data from the Zeppelin station as well as the Canadian (Alert) station. Information from the Icelandic (Storhofdi), Finnish (Pallas), and Russian sites (Amderma) will also be included. Spatial and temporal trends as well as environmental implications and consequences will be discussed in the presentation.

FC3.2

Labile, Dissolved and Particulate PAHs and Trace Metals in Wastewater: Occurrence and Removal in Treatment Plants.

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Eleven wastewater treatment plants (WWTPs) collecting various types of wastewaters (combined and separate sewers, household and industrial wastewaters) have been studied from 2005 to 2007. At each plant, labile, dissolved and total trace metals were sampled (24 hour composite samples) and analyzed (ICP-AES), at the inlet and at the outlet. Special emphasis was given to three plants, on which exhaustive sampling campaigns were conducted: labile, dissolved and total Polycyclic Aromatic Hydrocarbons (PAHs) and trace metals were sampled and analyzed at every stage of the treatment. Labile fractions were obtained by deploying respectively Semi-Permeable Membrane Devices and Diffusion Gradient in Thin films for PAHs and metals. The data allow to quantify PAHs and metals fluxes at the inlet and outlet of the WWTP and to evaluate their significance regarding environmental fluxes. Moreover, the efficiency of each treatment stage will be discussed, depending on the various species. Special emphasis will be given on the fact that labile and dissolved forms of contaminants are much less retained in the plants by conventional treatments than particulate ones. Moreover, as far as metals are concerned, some additional tertiary treatments (used for flocculating suspended matter) constitute a significant source of dissolved metals. These results are likely to stimulate the discussion on the ecotoxicological impact of treated wastewaters on aquatic ecosystems, in so far as labile contaminants are thought to be the most bioavailable –and possibly toxic– ones.

Oral Presentations

FC3.3

Leaching Behaviour of Oil Shale Semicoke

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Background: Production of oil from oil shale in vertical retort process results in large amounts of solid waste – semicoke - which is classified as hazardous waste in Estonia. The composition and properties of semicoke depend on the composition of oil shale and on the conditions of retorting process. The high temperature during retorting results in considerable changes also in the mineral part of oil shale and increases the content of potentially leachable components in the solid residue. Leaching of different compounds and ions from wastes is considered the main environmental issue with respect to future utilization or disposal of wastes.

Aims: The objective of this work was to study leaching behaviour of oil shale semicoke and predict changes occurring during its weathering.

Methods: Evaluated testing methods- batch tests and a percolation test – were used to study the leaching behaviour of oil shale semicoke. The changes in leaching after carbonation in laboratory experiments were investigated.

Results: The results confirmed that leaching of heavy metals is not problem in case of oil shale semicoke and different inorganic components in eluates of semicoke showed lower values than leaching limits set for hazardous waste at a landfill for non-hazardous waste. Very high pH (12-13) of the leachate of fresh semicoke and its changes with time as well as possibility that sulphur can leach in different forms depending on conditions must also be considered important.

Discussion: The fresh oil shale semicoke contains chemically active compounds, which undergo different chemical reactions when in contact with air and water. The possibility of sulphur speciation depending on conditions must be taken into account in order to find out appropriate technology for semicoke disposal or possible reuse. The performed study also showed the crucial importance of careful sampling and sample storage as well as selecting of right analytical methods in order to properly characterize the hazardousness of this type of waste.

FC3.5

Arsenic Removal from Water by Sorption onto a Metal (Hydr)Oxide Waste Entrapped in a Calcium Alginate Gel Matrix

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Background: Iron oxy(hydr)oxides, either natural or synthetic, have shown a good arsenic sorption capacity.

Objectives: A solid waste by-product of an electroplating industry has been investigated for As(III) and As(V) sorption. This sorbent, mixture of metal (hydr)oxides, has been used in native and entrapped in calcium alginate form. Effect of gel matrix, oxide concentration in the bead, pH, contact time and arsenic concentration have been studied.

Results: A 10% (w/v) of (hydr)oxide was found to provide spherical beads and good sorption performance. Solution pH was found to exert a stronger influence in As(V) than in As(III) sorption. The optimum pH range resulted to be within 5-10 for As(III) and 5-9 for As(V). pH 8 was chosen for further sorption experiments. Equilibrium was reached after 48 hours. Kinetics data of As(III) and As(V) sorption onto native waste oxide (O) and entrapped in calcium alginate beads (O-CA) were modeled by non-linear regression according to pseudo-first and pseudo-second order model.

Equilibrium data were evaluated by Freundlich and Langmuir models, obtaining their characteristic parameters by non-linear analysis. Langmuir Qmax for As(III) were 77.4 and 126.5 mg/g for O and O-CA, respectively and for As(V) were 26.8 and 41.6 mg/g for O and O-CA, respectively.

Cu, Ni, Fe and Ca release from the sorbents as a consequence of arsenite and arsenate sorption at different pH values was evaluated. A significant ion release from the sorbents was observed at acidic pH, consequence of oxide solvating. The amount of metal ion released was lower in the case of O-CA; the gel matrix acts as a barrier by ion exchange of the released cations with Ca²⁺.

Conclusion: This waste is an effective sorbent for As(III) and As(V) and its entrapment in calcium alginate makes it a potential candidate for industrial wastewater treatment.

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FC3.4

Effect of pH Control and Temperature on Cr(VI) Removal by Using Grape STALKS Wastes in a Batch Reactor

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University of Girona, Spain

Background: Recently, grape stalks waste has been reported as a low cost sorbent capable to adsorb Cr(VI) and to convert hexavalent ions into the less toxic trivalent ions^[1].

Objective: In this work, grape stalks wastes have been used to remove Cr(VI) from aqueous solutions in a batch reactor. The effect of pH control, temperature and initial metal concentration on Cr(VI) adsorption and Cr(VI) reduction to Cr(III) was evaluated.

Methods: Experiments were carried out with and without pH control, temperature and metal initial concentration. were varied within the range 5-50°C and 5-20 mg/L, respectively. In all the experiments 4 L of Cr(VI) solution were contacted with 10g of grape stalks (0.25-0.56 mm) under continuous agitation (250 rpm) until equilibrium was reached. A PLC (Programmable Logic Controller) with a set point pH 3.0±0.2 was used for the automatic pH control. Temperature control was assured by an external water recirculation system.

Results and Discussion: The results showed that the control of pH and the increase of the temperature and initial metal concentration led to an increase of the rate of Cr(VI) adsorption-reduction. During the process, Cr(III) appeared in solution achieving a maximum concentration value after 10-15 minutes and further decreasing until reaching an equilibrium value. After 2 hours of operation an initial solution of 20 mg/L Cr(VI) solution was converted into a 4.7 mg/L Cr(III) solution which implies 100% and 76% of Cr(VI) and total chromium elimination, respectively.

The proposed process appears to be very promising for the detoxification of aqueous effluents containing Cr(VI).

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FC3.6

Priority Pollutants (Hg²⁺ and Cd²⁺) Removal from Water by ETS-4 Titanosilicate

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Background: The microporous titanosilicate material ETS-4 has been used for the removal of Hg²⁺ and Cd²⁺ from water. Both mercury and cadmium are classified as priority substances by the European Water Frame Directive. They are among the most toxic pollutants present in aquatic systems where may persist for decades after the source of pollution is stopped.

Objectives: The objective of this work was to evaluate and compare the ability of ETS-4 titanosilicate for the decontamination of two priority substances, Hg²⁺ and Cd²⁺, from water.

Methods: All experiments were isothermally (295 K ± 1) carried out in batch conditions in 2 L volumetric flasks. Mercury and cadmium solutions were prepared daily by diluting the corresponding stock solution to the desired initial concentrations ([Hg²⁺] <0.25 µmol L⁻¹ and [Cd²⁺] < 30 µmol L⁻¹) in high purity water (18 MΩcm). Known masses of ETS-4 (between 1.5 and 100 mg) were added to the corresponding metallic solution and this time was considered the starting point of the experiment.

Results and Discussion: It has been demonstrated that ETS-4 has a great affinity for both these metal cations even when their initial concentrations are low. The uptake rates for both Hg²⁺ and Cd²⁺ were fitted to the pseudo-second order which confirmed that the kinetics of the removal of Cd²⁺ is faster than that of Hg²⁺. However, at the equilibrium, ETS-4 has a higher capacity for Hg²⁺ than for Cd²⁺. Adsorption isotherms for both Hg²⁺ and Cd²⁺ were well fitted to Langmuir isotherm and the corresponding monolayer capacities of ETS-4 are 0.432 and 0.239 µmol mg⁻¹, respectively, which are quite well consistent with those predicted by the pseudo-second order equation.

Conclusions: The contribution of this work is to support the use of this material for the removal of Hg²⁺ and Cd²⁺ from water since the results obtained show that ETS-4 titanosilicate is a very promising material for environmental remediation.

Oral Presentations

FC3.7

Removal of Arsenic by Chemical and Electrochemical Processes: Optimization and Comparison

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Since January 2006, because of the high toxicity of arsenic, many regulating agencies have decided to reduce the maximum contaminant level of arsenic in drinking water from 50 to 10 µg/L. Development and optimization of innovative processes allowing the effective removal of arsenic are required. Among the physico-chemical processes already existing, the most commonly used is the coagulation/flocculation process with iron or aluminum salts.

During this coagulation/flocculation process, the addition of a cationic coagulant, provides positive electric charges which reduce the negative charges of the colloids and neutralize the forces that keep them apart. This neutralization leads to a destabilisation of the colloids. However, the addition of chemical reagent and the need for high size contact tank involve the development of an alternative process: the electrocoagulation process, in which cations are produced by the electrodisolution of metallic anodes. As a consequence, the objectives of the present work are to implement, optimize and compare these two processes as for the removal of arsenic.

The optimization of the chemical process, on a synthetic groundwater with the same characteristics as water coming from granitic areas, with addition of ferric chloride, allowed determining the optimal treatment dose (100 mg/L of FeCl₃) and the optimal coagulation pH (pH > 6,0). These optimal conditions were tested on different arsenic concentrations (20, 100 and 500 µg/L), added as As(III), as As(V) or as a mixture of the two inorganic species. The same treatment dose was used in electrocoagulation in order to compare the two processes.

The results underline: i) a complete removal of As(V) during the two processes; ii) a removal of As(III) up to 96% during coagulation/flocculation and up to 98% during electrocoagulation; iii) no change in arsenic speciation during chemical process. However, the adaptability of the processes and the optimal conditions must be confirmed for surface water with high organic matter concentrations.

FC4.2

Canada's New Chemical Management Plan and the Impact on the Analytical Chemist

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Environment Canada, Canada

The Canadian Environmental Protection Act, 1999 is one of the main laws governing chemical substances in Canada. Under CEPA the Ministers of Environment and Health were required to categorize all 23,000 substances on the Domestic Substances List. Categorization identified substances that are inherently toxic to humans or to the aquatic environment and are persistent and/or are bioaccumulative.

Approximately 4300 substances that meet the categorization criteria are being considered for screening assessment to determine if they pose a risk. Approximately 200 substances of highest concern are currently being addressed through the Challenge under the Chemicals Management Plan.

Where the screening assessment determines that the substance poses a risk, then the risk management objective is the elimination of releases of measurable quantities of (virtual elimination -VE). This requires that an established reference analytical method be available to measure the substances at low levels in environmental media. This reference method is used to define a Limit of Quantification (LoQ), enabling the establishment of a baseline against which progress towards VE can be measured. Various substances have been subject to this process including 2378, TCDD/F in pulp and paper mill effluents, hexachlorobenzene (HCB) in solvents, HCB and dioxins in soil, hexachlorobutadine and chlorinated benzenes in chlorinated solvents.

The process to establish a LoQ will be presented and discussed in terms of the above examples. Currently analytical methods and LoQs are being established for chlorinated paraffins and 2-methoxy and 2-butoxy ethanol. The results of this work will be presented.

Also, there will be some discussion of challenges to the analytical chemist of the substances in the first batch of substances released under the Challenge.

FC4.1

New Analytical Methodologies for the Study of Emerging Contaminants in the Context of the European Water Framework Directive (WFD)

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For more than a half-century, a general awareness of the impact of human activities on the environment has emerged and is nowadays a common project for political authorities, scientists or citizens. As aquatic systems are the final receptacles of anthropogenic waste, a strong interest is focused on these systems. In the late 1990's, analytical technologies (chromatography coupled to specific detector: mass spectrometry) have achieved a sufficient high performance level to detect, identify and quantify polar organic compounds which were ignored before. Thus, an important and widespread contamination of aquatic systems by this kind of compounds has been highlighted. In Europe, the implementation of the Water Framework Directive marks a strong standpoint. Two classes of organic compounds have retained specific attention: non ionic detergents such as alkylphenol-polyethoxylates (APEO) that are ubiquitous in the environment and pharmaceutical substances among while more than 120 different compounds have been detected in aquatic systems (2006).

The presented work deals with the development of analytical methodologies for the study of both classes of analytes: APEO breakdown products and various classes of pharmaceutical substances for human uses and their application to the analysis of complex aquatic matrices.

First analytical methodologies (conservation, extraction, purification) regarding complex sample treatment, for aqueous samples as well as for solid ones, are exposed and discussed. Then, advantages and drawbacks of analytical developments on ULPC@-MS-MS are exposed and compared to more conventional approaches (LC-MS, GC-MS). Applications of these analytical methodologies to the study of Waste Treatment Plant samples (dissolved phase, suspended matter and sludge) are presented to illustrate their interest. Finally, a discussion on the implementation of the developed methodologies in the context of the WFD are exposed.

The authors acknowledge financial support from the ANR PRECCOD AMPERES and ORQUE Program

FC4.3

Environmental Reference Materials: Examples Of New Developments For Organic Analysis

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"Background:" Certified Reference Materials (CRMs) play a fundamental role in quality assurance (QA) and quality control (QC) measures to ensure reliable measurement results. In the environmental field, the analysis of organic pollutants still poses considerable challenges, in particular in view of the envisaged legally binding monitoring duties imposed on the Member States by the Water Framework Directive (WFD) (2000/60/EC). In this respect, the European Commission has recently proposed Environmental Quality Standards (EQSs) for the priority substances listed as an annex to the WFD. The EQSs are at present exclusively designed for the water compartments, but it is likely that they will be transposed to sediments and biota, as being part of aquatic ecosystems. These very low EQSs represent a significant analytical challenge, because sound monitoring will require the appropriate quality of the analytical data. The use of appropriate CRMs will therefore be necessary in guaranteeing the required accuracy and will also help evaluating measurement uncertainties properly.

"Aim(s)/Objectives(s):" the growing demand for CRMs to cover different environmental matrices and contaminants, particularly in the field of organic analysis, is only partially met by the materials at present offered by the various RM producers. In trying to reduce this gap, the Institute of Reference Materials and Measurements (IRMM) is currently devoting efforts in establishing new strategies for the development of RMs for environmental organic analysis.

"Discussion:" novel approaches dealing with different aspects in the analysis of priority pollutants will be presented. For example, the preparation of a RM for polyaromatic hydrocarbons (PAHs) in water, the development of a standardised method for quantifying short chlorinated chain paraffines (SCCPs) in sediments and the investigation on an alternative matrix preparation for polychlorobiphenyls (PCBs) in fresh fish will be discussed.

Oral Presentations

FC4.4

ESI-TOF Technology Enabling Screening of an Unlimited Number of Known and Unknown Compounds in Different Matrices

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Classical target pre-selected LC-MS analysis in MRM mode allows the screening of only a limited number of targets simultaneously. All possible targets must be taken into account when setting up the experiment, and retrospective screening for fresh targets after the run is not possible. Since the number of targets is increasing continually, alternative approaches for non-presumptive screening are desirable without making compromises in sensitivity. An ESI-TOF mass spectrometer is presented which fulfils all these criteria. This new generation of ESI-TOF instruments combines this advantage with a high sensitivity in the sub-ppb to low ppb range. The mass accuracy (3-5 ppm) and resolution (15000) of such a device permits highly discrete separation of a target from matrix, using extracted ion chromatograms with a tolerance as exacting as 2 millidalton. As full scan spectra are acquired, the information of an unlimited number of targets is always available. Information on unknown species is also obtained and data can be retrospectively interrogated for new components.

In addition to the high mass accuracy, the use of the precise isotopic pattern (True Isotope Pattern; "TIP") gives a high confidence in the characterization of a compound. The isotopic pattern is characteristic for every molecular formula. In combination with high mass accuracy, even unknown compounds can be identified with a high certainty.

Finally, the data-rich files obtained must be handled and interpreted to give useful results. To achieve this, a purpose-designed software package, TargetAnalysis™, has been created. The process and output of this package will be described, showing a complete multi-target screening solution.

Data will be presented from LC-MS analysis of spiked matrix extracts containing pesticides of interest in concentrations from 5 to 1000 mg kg⁻¹, demonstrating dynamic range and sensitivity. The importance of True Isotope Pattern as an independent tool for assigning identity will be discussed. Analysis of a real-case sample (oranges) and the detection of pesticide residues of interest will be shown.

FC4.6

Enhanced Separation and Detection of Tetrabromobisphenol-A and Hexabromocyclododecane Isomers Using UPLC®/MS/MS

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The analysis of Tetrabromobisphenol-A (TBBPA) and Hexabromocyclododecane (HBCD) isomers using HPLC MSMS has been widely reported^{1,2}. Whilst HPLC offers a good robust method, advantages can be gained by the use of Ultra Performance Liquid Chromatography™ (UPLC®), enhancing both the chromatographic resolution and throughput of the analytical method³. The shorter residence times can also minimize the potential for on-column adsorptive and degradative losses during the separation. The optimized separation resulted in a method run time of 10 minutes, with TBBPA and 5 HBCD isomers analysed (α , β , γ , δ , ϵ) being separated to <10% valley. Comparability of the data for real samples, to that run using a standard HPLC MSMS system is excellent with a variation of approximately 20 percent between the two sets of data, whilst offering a time saving of >15 minutes from injection to injection, improving the throughput capability of the analysis by >200%.

FC4.5

Mass Spectrometric Fingerprints of Dissolved organic matter in riverine and coastal waters

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Dissolved organic matter (DOM) constitutes a substantial pool in the global carbon cycle. While the vast majority of this is present as refractory material in the deep ocean, thought to derive mostly from marine primary production, marine surface waters and riverine systems also represent significant reservoirs. DOM comprises a complex mixture of largely uncharacterised material. Contained within this mixture, however, is potentially valuable information concerning the source of the carbon and any transformation processes to which it has been subjected. Given its inherent complexity, isolation and rigorous structural characterisation of the individual compounds in a DOM sample is clearly impractical.

Analytical fingerprinting is a generic term describing any technique (eg. IR, NMR, MS) whereby multiple samples can be screened rapidly, each generating a unique signature spectrum. Here we describe a fingerprinting method for DOM using solid phase extraction and time-of-flight mass spectrometry followed by Chemometric data analysis. Samples were collected across a salinity gradient from freshwater to marine from the River Thurso, Scotland, UK. Qualitative differences were observed providing a basis for the further development of this application. Changes along the transect highlight the potential of this technique to shed further light on the transport, processing and fate of terrestrial carbon in the marine environment.

FC5.1

Bioremediation of Petroleum Polluted Soil (Oil Refinery in Pancevo, Serbia)

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Background: Experiments of bioremediation offered the opportunity to gain the fundamental knowledge on the fate of pollutants in the environment, but also to assess to what extent bioremediation as a technique may be applied to refine the polluted water, soil or sediments.

Objective: The present investigation was focused on transformation of oil type pollutants during 6 months ex situ bioremediation of soil (Pancevo Oil Refinery, Danube alluvion, Serbia).

Methods: The pollutant changes were monitored by analysis of the soil samples taken in time intervals of two weeks (12 samples: P1-P12). Organic substance was extracted by Soxhlet's method. Fractions of alkanes, aromatics, alcohols and fatty acids were isolated by column chromatography. Gas chromatographic-mass spectrometric technique was applied for analysis of some compounds.

Results: More significant changes in the composition of the oil pollutant occurred in particular during the last phases of the experiment (P8-P12). The activity of microorganisms was reflected in the increase of quantity of the polar fractions. The quantity of total eluate increased, and the insoluble residue was reduced to minimum. n-Alkanes in alkane fractions have not been detected. In P1 only marginal amounts of pristane and phytane have been detected. They occurred in sample P8, and in even higher quantities in P12. The proceeding bioremediation process was accompanied by the decrease of the amounts of hopanes. In the initial sample P1 the distribution of steranes follows a pattern, which is characteristic for crude oils. Their identification was not possible in samples P8 and P12.

Conclusion: In performed experiments the oil pollutant was transferred to a form which can be removed more efficiently from the soil. The observed changes in the alkane fractions' compositions may be considered as atypical, referring to the fact that during oil biodegradation under natural conditions, the order of decomposition normally follows: n-alkanes > isoprenoids > polycyclic alkanes.

Oral Presentations

FC5.2

Remediation Strategies Based on Bioavailability at a Former Manufactured Gas Plant Site

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The knowledge of the processes of bioavailability can be used in remediation strategies, both in the selection of appropriate technologies, and in the evaluation of the soil quality after treatment. The aim of the paper is to compare, on the basis of bioavailability results from three different remediation strategies: phytoremediation, soil washing and thermal desorption. The site Manufactured Gas Plant utilized for over eighty years (1908–1994) with production of large quantities of wastes: organics, arsenic and heavy metals. Soil samples for this work were collected at various depths in “hot spot” zones. Chemical and biological(microcosm scale) tests were used to characterize heavy metals forms in order to select the liquid phase for the washing process, to evaluate the potential bioavailability of metals for phytoextraction and to estimate the effect on heavy metal mobility after thermal treatment. Soil washing Data from chemical extraction strongly addressed to the use of water in the washing process. Treatability test, showed that the concentration of contaminants as decreasing the particle sizes. After the treatment the washing waters were always free of metals. Phytoremediation In this case, bioavailability was estimated by coupling chemical approach with bioassay, performed with plants growing in the contaminated soil. Following indication from bioavailability tests, “assisted phytoextraction” was selected. Chemicals added promoted the uptake of Pb and As uptake and greatly increased the efficiency of the technology . Thermal desorption treatment was carried out at 500 °C to remove the organics present in same soil. After the treatment coupling chemical extraction and biological tests, a remarkable increase in the mobile and plant bioavailable fraction of heavy metals was discovered, ascribable to the destruction of organic matter. These last results highlight unforeseen effects that remediation technologies may have on bioavailability in the case of complex contamination.

FC5.4

Pesticide Transfers From Soil To Subsurface Waters, Impact On Earthworms

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Background: For many years it has been known that pesticides cause environmental risks and severe damages in agricultural soils and subsurface waters because of their large use, particularly in viticulture.

Aim(s)/Objective(s): Actually, the aim of this study is to quantify the influence of agricultural practices on pesticide transfer to drainage waters, in the Gaillac vineyard (South West of France).

Methods: The identification and the quantification of pesticides from the different biological matrices are performed by HPLC/UV, GC/MSn, and polarography. The effects of a mixture of insecticides and/or fungicides at different environmental concentrations are investigated on earthworms in a laboratory experiment in order to reproduce the Gaillac vineyards conditions. Neurotoxicity, metabolisation and oxidative stress' enzymes (cholinesterase (ChE), glutathion-S-transferase (GST) and catalase (CAT)) are studied as biomarkers on earthworms after short-term exposures in terrariums. The purpose is neither to focus on each isolated biomarker variation, nor on each molecule impact but to observe the global effects of pesticide exposure as it could occur in a vineyard.

Results: Results show that chemicals can be detected with multi-residue analysis in soils (Limit of Detection (LOD): 12.5 to 0.55 ng.g⁻¹ of wet soil according to the molecule and the analytical technique) and in subsurface waters (LOD: 5 µg.L⁻¹ to 120 ng.L⁻¹). Pesticides are neurotoxic for earthworms: ChE activity is inhibited for only a few days of exposure. They are metabolised (increase in GST activity) that induced the production of free radicals (significant increase in CAT activity). After a long period of exposure, invertebrates cannot cope with severe toxicity (cellular dysfunction, protein catabolism). Pesticide concentration in soil decreases in presence of earthworms (compared with terrarium without invertebrates). Then, the study suggests that earthworms play a key role in soil detoxification.

FC5.3

Arsenic and Heavy Metals Mobility in Mining Soils: Sequential Extractions and Kinetic Approaches

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Background Heavy metals in mining areas may cause environmental concerns for their high concentration levels and consequently suitable tools are needed for evaluating their mobility. Sulphide oxidation is the main process promoting system acidification and metals release. Selective dissolution is an useful method to study metal scavenging as Fe and Mn oxy-hydroxides. Many leaching protocols have been proposed to provide rapid screening texts (single extractant) to define metals mobility, but, owing to the complexity of the studied environment, dissolution kinetic tests and sequential extraction procedures (SEPs), adapted to soil mineralogy, seems to be more adequate. Aim The aim of this study is to compare different extraction methods and suggesting reliable procedures to assess the mobility and the potential hazard of metals, getting a basic information on the solubility rate of the associated mineral phase. Methods Two sequential extraction (the standard BCR and a 9 steps one) procedures and a kinetic approach (30 ml EDTA 0,05M pH 6.5; 3g sample, extraction time 15' to 48h), have been applied in soils from the mining district of Baccu Locci, Sardinia, Italy (As up to 3300, Pb up to 1600 and Cd up to 24 mg/kg, respectively). Results SEPs and kinetic extraction evidence a general low metal mobility in these samples however strongly related with Mn and Fe oxyhydroxides (redox conditions). A good agreement with the kinetic study has also been found: this permits to better quantify the easily mobile fraction, possibly representing an environmental risk. The proposed 9 steps SEP evidences the importance of the extractant selectivity overall when organic matter is not completely destroyed. Conclusion In Mediterranean mining areas, characterized by a dry climate and scarce water circulation, SEPs adapted to soil mineralogy are useful tools to evaluate the potential risk of metal mobilization in mining soils and the kinetic approach, independent from mineral phase, may represent a simple method as well.

FC6.1

Photochemical Degradation of Persistent Organic Pollutants under Arctic Conditions

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The polar night at 80° northern latitude lasts from October until March and changes within few weeks into the midnight sun. This extreme change in overall light conditions has a tremendous effect on the photochemical degradation of some persistent pollutants. Due to the lack of photochemical degradation processes, long-range transport of certain high volatile organic compounds is only observed during the winter (e.g., non-methane volatile organics).

Indications for a seasonal dependent photochemical degradation were also found for persistent pesticides like trans-chlordane in atmospheric samples from the Zeppelin Mountain monitoring station. The presence of modern currently used pesticides (CUPs) in Arctic ice samples has been confirmed in earlier studies (Hermanson et al. 2005). Most of these chemicals are sensitive to photochemical degradation processes (confirmed in laboratory studies). Therefore, the environmental stability (persistence) of these contaminants in the Arctic environment is surprising and contradictory to the established scientific opinion that only semi-volatile, persistent contaminants are present in polar environments. The here presented study will focus on the evaluation of the environmental stability and photo-reactivity of CUPs under Arctic environmental conditions.

Reaction pathways and potential transformation products will be elucidated. A first review on potential photochemical transformation processes under Arctic conditions based upon literature information as well as own laboratory and field experiments will be given.

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Oral Presentations

FC6.2

Application of Advanced Oxidation Processes (Aop) for the Removal of Selected Metabolites of Organophosphorous and Neonicotinoid Insecticides

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Background: Organophosphorous (OPs) and neonicotinoid compounds are used in agriculture as insecticides. Diazinon and chlorpyrifos are typical representatives of OPs, while commercially important neonicotinoids are imidacloprid and acetamiprid. Official food and drinking water monitoring programme provides the analytical measurements only for only parent pesticides, but the fate of metabolites formed after the application is still unknown.

Objectives: The goal of our research was to develop a new HPLC-DAD method for simultaneous and fast detection of selected metabolites in aqueous samples and to implement this method in different processes for their removal.

Methods: The examined compounds were: IMP (2-isopropyl-6-methyl-4-pyrimidinol), which is the metabolite of diazinon and was one of the most applied OPs in the past; TCP (3,5,6-trichloro-2-pyridinol), which is also from the OPs group and it is the metabolite of chlorpyrifos, and 6CNA (6-chloronicotinic acid), which is the metabolite of acetamiprid and imidacloprid and belongs to the neonicotinoid group. In order to determine the possible harmful effects of metabolites we examined their toxicity with luminescent bacteria *Vibrio fischeri* and calculated EC50 values for each metabolite in water solution. Our further research was focused on photodegradation of metabolites under natural sunlight and the removal of those compounds with different AOPs, such as ozonation, UV photolysis and TiO₂ photocatalysis. Samples were taken from the solution in different time intervals and analysed using HPLC-DAD technique. The influence of pH on the degradation process is investigated, too.

Results: The results from all studies were compared in terms of kinetics, formation of degradation products and mineralization. The ozonation and photocatalysis express higher degradation efficiency in terms of kinetics and mineralisation compared to photolysis. Toxicity tests showed TCP the most toxic one.

Conclusion: Applied methods are effective for the removal of those metabolites.

FC6.4

Comparison of Fenuron Degradation by Hydroxyl and Carbonate Radicals in Aqueous Solution

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Background: Hydrogencarbonate and carbonate ions are among ubiquitous scavengers of hydroxyl radicals generated in water treatment process or natural waters. These ions react with hydroxyl radicals with second-order rate constants of 8.5×10^6 and $3.9 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$, respectively, leading to the formation of the carbonate radical, CO₃•⁻. The reactivity of this radical is only partly understood and little is known concerning its reactivity with organic contaminants e.g. pesticides.

Objectives: In this work, we investigated and compared the degradation of a phenylurea pesticide Fenuron, by hydroxyl radicals and carbonate radicals in aqueous solution. Competitive kinetic experiments were performed with atrazine used as the main competitor for both processes and degradation products were identified by LC-MS.

Results: The second-order rate constant of reaction between fenuron and carbonate radical was found to be $(7 - 12 \pm 3) \times 10^6 \text{ M}^{-1}\cdot\text{s}^{-1}$ [$(7 \pm 1) \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$ for hydroxyl radical]. The formation of degradation products was studied by LC-MS in the two cases. The reaction with carbonate radical leads to the formation of a quinone-imine derivative which appears as the major primary product together with ortho and para hydroxylated compounds. These two compounds represent the major products in the reaction with hydroxyl radicals. The reaction of both radicals also leads to the transformation of the dimethylurea moiety. An overall comparison of degradation products will be presented during the conference.

Conclusion: In this study, we have clearly shown that carbonate radicals may generate more degradation products than hydroxyl radicals do in our experimental conditions. The involvement of carbonate radical is relevant for water treatment and environmental processes. Therefore, experiments dealing with the identification of degradation products need to be performed with major pollutants and especially with those whose reaction with CO₃•⁻ occur with a rate constant of $10^8 - 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$.

FC6.3

Nitrate Induced Photodegradation of Chlorotoluron: Chemical Evidence and Ecotoxicological Effects

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Surface waters are frequently contaminated by nitrates and pesticides due to agricultural activities. As nitrates constitute a major source of radicals through photochemical reactions, they might induce pesticide phototransformation and such process could lead to noxious derivatives constituting a potential risk for aquatic biota [1]. Such reactivity was shown to occur on phenylurea herbicides in conditions simulating solar irradiation [2]. The present study aimed at assessing the photoprocess and evaluating its ecotoxicological impact under real solar light. For this purpose, experiments were carried out in Rennes, France, using 24 3-m diameter aquatic mesocosms that included sediments and organisms representative of pond biotopes. These were contaminated with chlorotoluron in the presence or not of nitrate at various concentrations. Monitoring of the herbicide disappearance and by-product formation by LC-MS-MS led us to demonstrate the existence of the photodegradation process. Some of the biological effects regarding organisms representing three trophic levels will be presented.

[1] Bonnemoy F., Lavédrine B., Boulkamh A., Chemosphere 54 (2004), 1183-1187.
[2] Shankar M.V., Nélieu S., Kerhoas L., Einhorn J., Chemosphere 66 (2007), 767-774.

FC6.5

Mercury Contamination from Various Anthropogenic Sources in Korea

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Background:
In spite of significant concerns about mercury contamination and its toxic impacts in the environment, limited studies have been carried out in Korea.

Objective:
The objectives of this study are to investigate the extent and degree of mercury contamination in soil, dust, sludge and marine sediments from various anthropogenic sources in Korea and to understand the distribution patterns of mercury concentration in studied area.

Method:
The anthropogenic sources of mercury contamination were divided into five major sources such as by-product from abandoned Au-Ag mines, coal combustion, cement production, industrial process, and urban discharges. Various types of samples including soils, dust, sludge and marine sediments in the contaminated areas from the five anthropogenic sources were taken and analyzed for Hg by Cold Vapor Atomic Absorption Spectrometry (CVAAS) after acid digestion.

Results:
Mercury concentrations in the samples were in the range of 6.0~21,100 ppb in soil from the vicinity of the abandoned Au-Ag mines. In the vicinity of coal-burning power plants, mercury concentrations were in the range of 11~192 ppb in soil, 44~559 ppb in dust. In addition to samples from cement production areas and metal smelting industry the concentrations of mercury were in the range of 15~960 ppb in soil and 99~671 ppb in dust and 67~686 ppb in soil, respectively. The mercury concentration from urban and industrial discharge ranged from 808 to 2,540 ppb, and 31 to 935 ppb for mercury was found in marine sediments.

Conclusion:
According to the chemical results, it can be seen that Hg levels in dust samples tend to be higher than those in soil samples. Furthermore, most of samples contained relatively higher concentrations of mercury compared with the ocean dumping levels and the NOAA guideline.

Oral Presentations

FC7.1

Evaluation and Method Development of Solid Phase Adsorbents for Phycotoxins in the Marine Environment

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Solid-phase adsorption toxin tracking (SPATT) was recently developed to facilitate monitoring of lipophilic shellfish toxins (LSTs) in shellfish harvesting areas. SPATT for LSTs was founded on the observation that when low levels of toxin-producing algae were present in the water column significant amounts of toxins were dissolved in seawater. A lag between detection of dissolved toxins adsorbed onto porous synthetic resin, phytoplankton peak cell densities and highest toxin concentrations in shellfish was demonstrated, suggesting that SPATT technology could be a useful predictive tool for the onset of a toxic event. It is envisaged that early warning will allow improved decision making; avoiding harvest of contaminated shellfish stock. In this study, we have sought to further evaluate adsorbents that could be applied to SPATT for hydrophilic phycotoxins including paralytic shellfish poisoning (PSP) toxins and domoic acid (DA), associated with amnesic shellfish poisoning (ASP). Using laboratory-scale experiments, we investigated the removal of two PSP toxins (neosaxitoxin, NEO and saxitoxin STX) from seawater using computationally designed polymers (CDPs). An ethylene glycol methacrylate phosphate (EGMP) based polymer was able to adsorb both PSP toxins completely. To optimize toxin recoveries, a variety of extraction procedures were examined and a protocol developed enabling the recovery of 97% of NEO and 92% of STX from the CDP. An additional CDP and a variety of adsorbents (activated glass beads, resins and zeolites) were assessed for the adsorption and recovery of DA from seawater. The best adsorbent was found to be Amberlite®XAD761 which demonstrated nearly 100% binding of available DA. We aim to validate the use of these adsorbents for use in shellfish monitoring programmes and assess their potential as an early warning technology for the aquaculture industry.

FC7.3

New Global Pollutants Derived from Marine Debris Plastic

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Plastic wastes are generally disposed off underground and find their way into the environment through careless littering. They may also be carried by water into the ocean with consequently very wide distribution. Plastics constitute the main content of garbage present in marine debris. Since the late 1980s, certain pollutants such as phthalic acid esters (PAE) and bisphenol-A(BPA), a typical additive or raw material for polycarbonate, both of which may possibly be eluted from plastic products, have often been detected in rivers and oceans. But the sources and elution pathways of these compounds have yet to be clearly elucidated. Still, polymer degradation in nature remains but little understood. At present, no kinetic data on polymer degradation in daily life situations or the natural environment are available. Polystyrene (PS) was found to undergo degradation at 30°C. Possibly, PS degradation occurs gradually in water bodies or along sea shores with consequent release of various pollutants such as BPA. This process is expatiated by low environmental temperature at which plastic decomposition can occur, as has been confirmed by the presence of degradation products in nature. Simulation study has indicated that low molecular weight pollutant elution from PS will come to be in excess 30 thousand tons a year within the next 100 years. Thus, plastic waste in the environment will certainly constitute a new source of global pollutants for long into the future.

FC7.2

Combined Effects of Salinity and Temperature on the Solubility of Organic Compounds. Thermodynamic Bases. Application to an Example

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Background: Solubility behaviour of a large variety of compounds is of paramount importance in many natural or accidental environmental processes. Since long, attention has been focused as well on the solubility of gases like carbon dioxide or dioxygen in natural fresh or salted waters as on the dissolution and re-precipitation of solid compounds as calcium carbonate (calcite, aragonite ...) between rocks and water. Recently, attention has been also focused on the physical becoming of the accidentally spilled cargos during ship-wreck or other sea-events.

Aim: Does such or such part of the cargo dissolve? In which quantity? Does this quantity depend on temperature and/or water salinity and of their variation in time? An attempt will be made here to elaborate a comprehensive view about the conjugate effect of temperature and salinity on solubility.

Methods: The fundamental laws ruling dissolution phenomena are thermodynamical in nature. The analysis of the temperature effects on these particular phase changes are founded onto the Gibbs-Helmholtz (or Van't Hoff) relation. The salt effects are described through the Setchenov formula,; no true demonstration of this relation has never been made although many studies about a wide variety of compounds exist; some among these studies deal with the effect of temperature on the Setchenov coefficient but no comprehensive view about the conjugate effect of temperature and salinity on solubility has been elaborated until now at our knowledge.

Results: Here the study is applied to equilibria between partially soluble solids in a given solvent. The formulation found may be applied to scarcely soluble liquids and is confronted with experimental data concerning dimethyldisulfur (DMDS) solubility in water obtained at four salinity values and four temperatures. Indeed DMDS is an industrial compound widely transported by sea.

Conclusion: The major effect found both thermodynamically and experimentally is an unexpected damping of temperature effects by salinity.

FC7.4

Bioactive Peptides Secreted by Skin Glands of Ranid Frogs. Mass Spectrometric Approach for the De Novo Sequencing

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Amphibians have rich chemical arsenals that form an integral part of their defense systems, and also assist with the regulation of dermal physiological action. In response to a variety of stimuli, host defense compounds are secreted from specialized glands onto the dorsal surface and into the gut of the amphibian. Many of these peptides exhibit either potent vasodilator, antifungal, anticancer or antimicrobial activity.

Complexity of skin secret of genus Rana frogs makes classic sequencing technique (Edman degradation) impossible. Usually peptide mixtures contain several dozens peptides in femtomole to nonomole quantities. Additional problems deal with various peptide length (10-50 residues) and the presence of C-terminal disulphide cycle. Thus mass spectrometric approach becomes more efficient.

The following approach was developed. Matrix assisted laser desorption/ionization (MALDI) spectrum of the raw secret allows detecting the principal components of the peptide mixture. Separation of the main components is achieved by high pressure liquid chromatography (HPLC). HPLC chromatogram accompanied by MALDI spectrum characterizes each frog species. It reflects variability of the species depending on the climatic conditions of its habitat.

Mass spectrometric sequencing involves electrospray ionization (ESI-MS-MS) experiment with the HPLC separated fractions using two modes of fragmentation activation. This experiment allows determination of the primary structure of the major components (complete or up to C-terminal bridge). Accurate mass measurements allow differentiation between lysine and glutamine, while secondary fragmentation processes permit distinguishing isomeric leucine and isoleucine.

HPLC-ESI-MS-MS experiment in nano spray mode results in detection of the minor ingredients of the secret. The search for peptides belonging to the families of bradykinines, tachykinines and temporines may be realized detecting characteristic ions. S-S bonds may be modified by carboxamidomethylation for ESI or oxidation for MALDI experiments.

The proposed approach allows significantly increase the efficiency of the analysis in terms of the detection of the known peptides and structural elucidation of the new ones.

Oral Presentations

FC7.5

Withdrawn

FC7.6

Aluminium: An Easy To Measure Oceanic Water Mass Tracer

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Background

Profiles suggest that aluminium (Al) is a good oceanic water mass tracer, with concentration profiles mimicking those of temperature, salinity and other chemical tracers. Although Al has been flagged in the literature as a potential tracer, only one published study has used it in this way (Measures et al., 1988, JGR, v93, 591). Al is easy to determine in seawater by the lumogallion method, refined by Hydes et al. (1976, Analyst, v101, 922). Despite this, full depth measurements of Al away from continental shelves are spatially sparse, possibly because of the perceived difficulties in measuring this trace metal at sea.

Aims

We show that seawater Al samples can be collected using routine sampling equipment and frozen with integrity for analysis on land, thus removing the need for clean room facilities onboard the ship.

Methods

Tests were carried out to determine whether unmodified rosette bottles alter the Al concentration in seawater during sample collection. Additionally duplicate samples were compared to determine the effect of freezing on Al levels in seawater.

Results

A slightly elevated Al concentration (0.34nM) was found in seawater after being in contact with the rosette bottle for two hours. However this is within the precision of the method. A 1:1 relationship was found between samples (r 0.90) that had been analysed immediately and after being frozen. A paired t-test showed no significant difference between frozen samples and those analysed fresh (t 0.074, $t(0.025,51)$ 2.008).

Conclusion

Contamination free seawater samples for Al analysis can quickly and easily be collected on routine oceanographic cruises with only basic contamination controls such as the use of gloves. This greatly increases the opportunity for the measurement of this metal and its future use as a water mass tracer.

FC8.1

Withdrawn

FC8.2

Do Arsenic Profiles in Ombrotrophic Peat Bogs Reflect Depositional History or Biogeochemical Mobility?

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Dated cores of sediments from freshwater lakes and of peat from ombrotrophic bogs have been used successfully to reconstruct deposition histories of some potentially harmful trace elements, such as Pb, that have been released to the environment by anthropogenic activities. In lake sediments, however, the post-depositional diagenetic mobility of As, in conjunction with that of redox-sensitive Fe, can result in a significant natural enrichment of As in near-surface layers, often perturbing the historical pattern of As deposition. In ombrotrophic bogs, where there may be fluctuating water table depths and varying redox conditions, there is potential for vertical mobility of As, although the bulk peat matrix, almost exclusively organic in nature, is obviously different from that of typical lake sediments. The aim of this study was to determine and compare peat profiles of As with those of Pb and Sb, two elements considered to be essentially immobile in peat, and those of redox-sensitive, potentially mobile elements such as Mn, Fe, P and S in three Scottish ombrotrophic bogs.

Peat cores were collected from bogs in west-central, east-central, and north-east Scotland. Air-dried peat sections were subjected to microwave-assisted nitric/hydrofluoric acid digestion and subsequently analysed for a range of elements (e.g. As, Pb, Sb, Mn, Fe, P, S) and Pb isotopic composition by ICP-OES and ICP-MS as appropriate. For quality control purposes, reference materials were analysed along with the samples. Upper sections of the cores were ²¹⁰Pb-dated using gamma spectrometry.

Concentration profiles of As in the uppermost sections of the cores from each of the sites were indeed similar to those of Pb and Sb rather than to those of the biologically essential and redox-sensitive Mn, Fe and S. These observations suggested that As was not subject to significant post-depositional remobilisation and that As may be considered immobile in ombrotrophic peat bogs. Calculated As, Pb and Sb depositional fluxes were at a maximum (up to 0.6, 40 and 0.8 mg m⁻² y⁻¹, respectively) during the industrial period (between the 1910s and 1960s) at each of the sites. Results (concentrations, fluxes, inventories, elemental ratios etc) will be discussed further in terms of comparative historical trends in sources and emissions of these elements to the environment.

Oral Presentations

FC8.3

Microbial Chlorination of Organic Matter in the Forest Soil

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In nature, chlorine does not occur only as chloride or bound in substances of anthropogenic origin in the polluted environment but also in many hundreds of compounds of natural origin. Chloride deposited in the forest ecosystem from the atmosphere reacts with soil organic matter (SOM) under the mediation by enzymes and/or microorganisms (to a lower degree also abiotically), forming chloroacetic acids (CAA), chloromethane, chloroform, other aliphatic and aromatic compounds and chlorinated humic substances. Chloride, to which coniferous trees are sensitive, is thus mostly blocked in organochlorines, which even prevail over chloride in soil and are involved in SOM degradation, leading to smaller SOM decay products and finally to their mineralization. The aim of our investigations was to explore and consider the role of chlorine in coniferous forest ecosystems. Radiotracer methods were used with advantage. The results showed that chloride is not conservative, that it is reactive and forms intermediates like chloroacetic acids or chloroanisoles, which are further biodegraded and mineralized. As responsible microorganisms are considered e.g. basidiomycetes known as producers of chloroperoxidases and called "litter decomposers". Soil samples were analyzed by traditional extraction methods: direct extraction of chloride with water, extraction of chloride contained in microorganisms after their destruction by freezing and finally by alkaline extraction of chlorinated humic substances (HS). However, in our experiments the alkaline extract after acidic precipitation of HS afforded only chloride. One possible explanation is cleavage of C-Cl bond, another is further extraction of chloride remaining in microorganisms. Our investigations with fermentation horizon of forest soil showed an increase of chlorination with chloride content and time and only low abiotic chlorination. Part of the chlorine may be released as volatile chlorinated compounds into the atmosphere, part in the run-off. The chlorine level in the forest ecosystem may thus be conserved.

FC9.1

The Effect of *Eisenia fetida* Earthworms on the Redistribution of Residual Pb, Zn and Cd in Soil after Remediation with EDTA Soil Leaching

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"Background" Using soil washing remediation techniques, only the labile heavy metal (HM) species are removed from the soil, leaving the residual ones in non-bioaccessible forms. Remediation processes thus disturb the chemical equilibrium among different species of HM in the soil. Re-establishing of such equilibrium shifting HM back to more bioaccessible and mobile chemical forms should be expected after exposing the remediated soil to environmental factors. Earthworms are considered to be an important biological soil factor, changing with their activity the accessibility/mobility of HM after soil washing with EDTA.

"Aim" The aim of this study is to investigate whether the impact of earthworms can be reduced by intensive chelant soil leaching.

"Methods" Contaminated soil from a smelter site (Pb 4602 mg/kg, Zn 1826 mg/kg, Cd 30.4 mg/kg) was washed with increasing EDTA concentrations (2.5, 5.0, 10.0, 20.0, 40.0 and then 4-times with 40.0 mmol/kg EDTA). Fractionation with a 6-step sequential extraction, mobility (Toxicity Characteristic Leaching Procedure), plant accessibility (extraction with DTPA) of Pb, Zn and Cd and Pb oral bioavailability (Physiologically Based Extraction Test) were determined for the soil, for soil processed by *Eisenia fetida* and for *E. fetida* casts produced in these soils.

"Results" A gradient of removed HM was reached: 6.0, 13.0, 41.0, 45.0, 54.0, 73.0% of initial Pb, 3.0, 4.0, 13.0, 15.0, 20.0, 23.0% of initial Zn and 17.0, 33.0, 54.0, 61.0, 66.0, 74.0% of initial Cd were removed, respectively. *E. fetida* activity increased Pb, Zn and Cd mobility in all soil treatments. Concentrations of HM in the carbonate fraction increased in casts, but decreased in processed soil indicating the possibility of a time-dependent complexation of HM to carbonates favored by earthworms gut processes.

"Conclusions" Results indicate that *E. fetida* activity changed the accessibility/mobility of residual HM in all leaching treatments. The transition of residual HM in time (ageing) should be considered.

FC8.4

Muddy Waters: The Role of Particles in the Estuarine Cycling of Organic Nitrogen

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Background Globally, total nitrogen (TN) loadings to estuaries are increasing due to changes in urbanisation etc. Organic N (ON) constitutes >50% of the TN input to estuaries, but its speciation, reactivity and fluxes are poorly quantified.

Hypothesis The reactivity and flux of organic nitrogen (ON) in turbid estuarine systems is significantly controlled by interaction with suspended particle material (SPM).

Aims (1) to fractionate estuarine SPM on the basis of particle settling velocities. (2) to characterise the particle fractions (physico-chemical and biological properties) in relation to their ON loading. (3) to determine the reactivity of the particle fractions to ON in relation to particle characteristics for contrasting seasons.

Methods Water Samples were collected from the Tamar Estuary (SW England). Suspended particulate Material (SPM) was fractionated and the water and particles characterised. Incubations using ¹⁴C-labelled amino acids (AA) as ON proxies examined SPM-water partitioning. The particle concentrations used for incubation experiments were those measured in the estuary.

Results The results under the two conditions employed ("live" and "dead" particles) were considerably different. Under dead conditions there was only negligible binding of the AA to the particles and most remained in the water. The results were similar regardless of the AA chemical structure. Under live conditions, uptake of the AAs onto particles was rapid, with 80-90% removed from solution over 24 hours.

Discussion The results indicate that the AA uptake onto particles was controlled by bacteria, which used the AAs for cell growth. The results were unexpected as the research literature suggests that the compound chemistry controls its attachment to particles and we used a range of compounds to test this.

Conclusion The broad conclusion to be drawn was that bacterial uptake of AAs is much more rapid and quantitatively important than any other type of physico-chemical binding. Our findings contradict the idea that particle-associated ON is protected from bacterial degradation, and it appears that assumptions on the behaviour of ON in aquatic systems will need to be revised.

FC9.2

The Use of Speciation Modelling in Chemically Enhanced Phytoextraction of Metals from Contaminated Soils

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Chemically enhanced phytoextraction of metals from contaminated soils is a fast emerging technological approach used in soil remediation. The use of plants with high biomass yields together with mobilising agents, such as chelants (e.g., EDTA, EDDS), can be effective especially in low-moderately polluted soils. However, the main drawbacks remain the environmental fate of the mobilising agents and the competition of other metals present in soils (e.g., Fe, Ca) at high concentrations which lowers the extraction of the target metals. This study focuses on phytoextraction of Pb (as the main contaminant) from agricultural soils originating from the mining and smelting area of Pořbram, Czech Republic. Batch incubation experiments and speciation modelling (PHREEQC-2) were performed in order to evaluate the extracting efficiency of the tested mobilising agents (EDTA, EDDS, NH₄Cl) and the possible competition of other metals present in the soils. The results showed that Fe influenced greatly the extraction of Pb using EDTA, due to the ability of EDTA to slowly dissolve soil Fe-(hydr)oxides and to form stable Fe(III)EDTA complexes. The main competing cations during EDDS extraction of Pb were Cu, Zn and Fe. The addition of chlorides led to an increase in the mobility of Cd and Zn, mainly because of the formation of CdCl⁺ and ZnCl⁺ complexes. However, Pb was present predominantly as PbCl₃⁻, which led to sorption of the complex at low pH. The results obtained were in good agreement with plant experiments. Therefore, speciation thermodynamic modelling together with batch experiments proved to be efficient tools for understanding the extraction process during chemically enhanced phytoextraction of metals from soils.

Oral Presentations

FC9.3

Cement Obtained from Rice Husk Ash Doped with Commercial Battery Rejects

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Rice husk (RH) is an agricultural residue containing about 10-30% of silica (SiO₂). Usually this material is burned at rice fields. This practice may cause respiratory and environmental problems.

Portland cement is one of the most consumed materials in the world. The traditional method used for the production of cement is based on solid-state reactions at temperatures around 1450 C. Portland cement is a complex material, composed basically by calcium silicates, calcium aluminates and calcium aluminoferrites, among others. The calcium silicates, Ca₃SiO₅ and α -Ca₂SiO₄, account for nearly 75% of ordinary cement. The cement industry generates about 6% of total CO₂ emission

This work presents the synthesis of β -Ca₂SiO₄ doped with manganese and zinc, extracted from commercial batteries. The main idea is to use cement derived from RH to encapsulate heavy metals in order to minimize environmental contamination.

Rice hull ash was heated at 600oC. After this thermal treatment, it was obtained a white powder, identified as cristobalite. Rejects of zinc-coal battery were separated from commercial batteries and, after simple physical treatment were used as dopant in the synthesis of β -Ca₂SiO₄.

The solids were mixed in stoichiometric proportions, in order to render hybrid calcium silicates having a general formula given by: (Ca_{1.96-x}ZxBa_{0.04})SiO₄, where "Z" corresponds to the cation inserted and "x" its substitution level. After mixing the solids, water was added (30:1, water: solids) and the suspension was sonicated for 60 minutes (Thornton, 25 kHz). After drying, the solids were grounded and heated up to 800oC. The overall process was followed by FTIR spectroscopy (Perkin-Elmer, Spectrum One) and x-ray diffraction (Shimadzu).

The release of zinc and manganese were also studied by atomic absorption (Perkin-Elmer) and preliminary results show that zinc and manganese are stabilized into cement matrix.

FC9.5

Biomethanol Production from Biomass, Organic MSW, Communal Wastewater Sludge and Reduction of CO₂, CH₄ Emission

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Background Europe has become more dependent on external energy sources in the last decades. This dependence is more problematic since most of the fossil energy sources are in non-allied countries; moreover there have been conflicts in those countries for a long time now.

It is proved that as a result of the excessive use of fossil fuels, the CO₂ content of the atmosphere is growing. The growing CO₂ level, along with other greenhouse gases, cause climate change. Additionally, the growing volume of agricultural (especially forestry) waste, municipal solid waste and industrial waste generate other environmental problems. It is obvious, that these problems are the results of human activity. Besides, the present waste treatment methods contribute to the increase of greenhouse gas emission as well.

The syngas production from biomass has already been realized in many countries. The syngas is used either in gas engines for electricity production or producing Fischer-Tropsch fuel and sometimes methanol. The raw material is usually primer biomass from forests, such as wood logs.

There are some syngas producing plants, which utilize the packaging waste from mixed MSW. These plants have one major thing in common: they mainly use external energy source, which come from the electric grid.

Method Our fundamental assumption is that the organic parts of MSW and communal waste water sludge can be excellent raw materials. Additionally, utilizing them instead of land filling can decrease their contribution to greenhouse effect, which is a very positive effect.

Syngas production is making an exothermic reaction of clean oxygen. The heat then is used in an endothermic reaction, blowing in vapor, blue gas reaction results in CO and hydrogen.

Because of the investment costs, energetic reasons and to maximize efficiency we intend to use so called one-step syngas production in shafted layout. We also intend to examine and compare to the optimums of other methods. After separation of vapor and tart, feeding back to the combustion zone solves the residue problem. The separations of these components are also for the protection of the catalyst of methanol production.

The CO₂ is not washed out from the system. It can be stored periodically and can be used in methanol production utilizing wind and solar energy as well.

Results We developed a new methanol manufacturing technology from waste with renewable energy using.

FC9.4

Influence of Membrane Preconditioning Method on Proton Exchange Membrane Fuel Cell Performance

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Depletion of fossil fuels and environment degradation are two of the most important problems related to energy production. The need to find an efficient and no-polluting energetic source has resulted in increased attention to the fuel cells. Inside these, proton exchange membrane fuel cells (PEMFC) are regarded as a possible alternative power source for stationary and mobile applications.

In the PEMFC performance, the membrane-electrode assembly (MEA) plays a very important role. A significant element of the MEA is the ion exchange membrane which is the element that conducts the protons from the anode to the cathode. One of the first steps in the MEA manufactured processes is the membrane preconditioning method to improve chemical and physical characteristics of the polymer.

In this work it has been studied the influence of the different preconditioning methods used in the performance of the PEMFC. With this purpose, they have been carried out 10 different preconditioning methods in which the final state of the polymer changes. Finally, these membranes were hot-pressed with the electrodes to form the different MEAs.

All these MEAs were tested in a PEMFC working with 5 cm² electrodes. The polarization curves and the cyclic voltammeteries were the MEAs characterization methods. The supplied gases were hydrogen and oxygen, both dry and the operational temperature was 80°C. Analysing the results, it can be seen that the best results were obtained with the MEAs preconditioned in H⁺ form.

Poster Presentations

Atmospheric Chemistry	P01
Aquatic and Marine Chemistry	P02
Soil Chemistry	P03
Soil - Water - Atmospheric Systems	P04
Biogeochemical Cycling	P05
Ecotoxicology	P06
Pollutant Chemistry	P07
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Clean Technologies and Green Chemistry	P10
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P01.02

Air/Water Interface Effects Relevant to the Photochemistry of Atmospheric Droplets

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Background. Photochemical processes in the atmospheric aqueous phase are involved in the transformation of organic and inorganic compounds, some of which have an impact on global climate [1,2]. The elevated surface-to-volume ratio of atmospheric water enables interface processes to play a considerable role [3]. **Aim(s)/Objective(s).** The present work studies the combined surface effects of the coadsorption of organic compounds and inorganic ions [4] and of the photolysis quantum yields on the rate of photochemical reactions at the air/water interface. The photolysis quantum yields are increased at the droplet surface, where the solvent cage is incomplete and recombination processes are much less effective [3,5].

Methods. The solvent-cage effect on nitrate photolysis was assessed by the addition of radical scavengers and the monitoring of nitrite photogeneration. Surface coadsorption of nitrate and benzene was evaluated with the Wagner-Onsager-Samaras approach.

Results. We show that solvent-cage recombination decreases the quantum yield of nitrate photolysis by a factor of around 6.5. Nitrate photolysis could thus be 6.5 times more effective at the air-water interface than in the solution bulk. **Discussion.** If both photolysis quantum yield and surface coadsorption are taken into account, in a 1 μm water droplet over 50% of the total photochemical conversion of benzene into phenol upon nitrate photolysis would take place in a surface layer that accounts for just 0.15% of the volume. Other photochemical reactions (e.g. the photolysis of FeCl_2^+) could undergo an even higher surface enhancement. These findings could substantially modify the current knowledge concerning multiphase atmospheric chemistry.

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P01.01

Development of Biomarker Protocols for the Assessment of Environmental Air Quality Changes Using the Reindeer Lichen *Cladonia portentosa*

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The deposition of atmospheric pollutants is now recognized as a major driver of biodiversity changes at mid to high latitudes. Understanding at what levels and how these atmospheric pollutants affect vulnerable organisms will enable more accurate predictions of the consequences of future changes in climate pattern and pollution. Detecting specific biochemical signatures of such pollutants in organisms is a key step in this process. These so called "biomarkers" will be unique and can thus be related to the overall health of the environment. Identifying the abundance or state changes of biomarkers will provide the basis for rapid, broad-spectrum, effects-based monitoring systems, which can be applied for the early detection of atmospheric pollution. As lichens are well known for being indicators of air quality, we investigated the affects of the major pollutant wet-nitrogen and other trace chemical deposition in the UK on the metabolic response of the reindeer lichen *Cladonia portentosa*. This was achieved by correlating data from high-throughput biochemical methods and atmospheric data (from the UK Air Quality Archive and the Centre of Ecology and Hydrology) using multivariate modelling techniques. As a first step, models were constructed from chemical composition information identified via Fourier Transform Infrared Spectroscopy which was correlated to wet deposition data. The calculated models showed good potential for detecting biological responses occurring in relation to deposition gradients. Data confirming the responses of the lichens and identifying key biomarkers will be presented. Although FT-IR is an excellent tool for a broad metabolite analysis, yet more sensitive analytical techniques such as mass spectrometry have to be applied for the identification of specific compounds, produced due to increasing nitrogen deposition from the atmosphere. The latest data from this analysis will also be presented.

P01.03

Atmospheric Bulk Deposition and Active Biomonitoring of Trace Elements in Belgrade Urban Area

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Active biomonitoring by moss bags has been used to examine atmospheric deposition in urban area of Belgrade (Serbia). The study aimed at testing element accumulation capability of moss *Sphagnum girgensohnii* Russow., collected from an unpolluted pristine wetland area (Dubna, Russian Federation), in relation to atmospheric bulk deposition. The moss was exposed in bags to atmospheric deposition at three representative urban sites, in parallel with bulk collectors, for 3-months period from July 2005 to October 2006. The concentrations of Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb in the samples were determined by INAA and AAS techniques.

Significant enrichment of examined elements in exposed moss bags was obtained in relation to the initial moss content. A parallel moss survey carried out with bulk deposition collectors gave similar results in terms of time deposition and spatial distribution patterns for some of the investigated elements. Significant correlations between moss elemental contents and total atmospheric deposition were found for. Seasonal variation was observed for V and Ni for both types of monitoring techniques, as the ambient concentrations were elevated in winter. The correlation template between some of analyzed elements for moss and bulk deposition was similar. The concentrations of V, Fe, Ni, Cu, and Zn in *S. girgensohnii* significantly reflect their atmospheric deposition and recommend moss bags for trace elements monitoring in urban area.

Poster Presentations

P02.01

The Concentration of Contaminants in Mussels Collected from Intertidal Locations in Scotland

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Background: The Scottish Environment Protection Agency (SEPA) analyses contaminants in mussels to assess compliance with the Shellfish Growing Waters Directive and the standstill clause of the Dangerous Substances Directive. Bioaccumulation of contaminants in mussels facilitate detection of substances that would not be detectable in waters due to their low concentration in waters.

Methods: Mussels of a specific size are collected annually during Winter. The samples are depurated and freeze dried prior to analysis for trace metals and trace organic compounds. Samples for trace metal analysis are digested in nitric acid in sealed containers. The metals in the digest are determined by ICP/MS (or cold vapour atomic fluorescence). Trace organic compounds are extracted into a solvent and determined by GC/ECD or GC/MS.

Results: External quality control is provided by participation in the QUASIMEME Laboratory proficiency test scheme. The laboratory has UKAS accreditation and uses validated material as an internal check on the quality of the results. The results will be displayed and assessed against available criteria (e.g. OSPAR background/reference concentrations)

Discussion Contaminant concentrations are generally low throughout Scotland but tend to be higher in the more densely populated and industrialised areas

P02.02

Halogenated Aromatics and Aliphatics in Ground Water Highly Contaminated by Industrial Activities

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Background: Halogenated compounds are important anthropogenic, mostly xenobiotic contaminants in groundwater systems, in particular as the result of industrial emissions. They are of high environmental interest due to their high environmental stability, their bioaccumulation tendency and the frequently observed ecotoxicological and toxicological effects. However, the information on the environmental fate of halogenated aromatics and alicyclic compounds in ground water systems especially with respect to their transformation is still limited.

Aim: Therefore, we investigated two huge contaminated ground water systems using traditional organic-chemical analysis and partially compound specific stable carbon isotope analyses. Both ground water zones are not only characterized by high concentrations of a wide variety of contaminants but also by a long-term contamination. The studies focused on the qualitative and quantitative detection of the pollutants but also on the identification of metabolites and their isotopic signature in order to get information on the transformation behaviour of the contaminants.

Results: Firstly, we investigated the emission of chlorinated naphthalenes caused by chemicals continuously used for wood impregnation. Since various substances with related structures were emitted simultaneously, it was able to observe differences in the environmental behaviour (especially related to transformation/degradation) caused by small modifications of chemical structures. The second study dealt with a ground water contamination dominated by HCH and DDT-related compounds emitted by a chemical plant. Within the wide spectrum of contaminants also several metabolites were identified reflecting partially unusual transformation behaviour in this aquifer.

Conclusion: In summary, this contribution will reflect and discuss in detail the environmental behaviour of numerous halogenated aromatics and aliphatics in ground water systems on a structure-chemical level.

P02.03

DDA Related Compounds In Environmental Samples

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Background: DDA appears in the environment as one of the main DDT metabolites, but has been neglected in contamination studies so far. However, due to its risk potential this polar metabolite needs to be considered in the assessment of DDT contamination in soils, rivers and groundwater. Aim and scope: Since DDA is due to its carboxylic group the best water soluble DDT metabolite, this study focussed on the environmental pathway of DDA in surface and ground water as well as in corresponding riverine sediments. Results: For this purposes water and sediment samples were investigated derived from locations nearby an industrial point source, where DDT has been produced over decades and, consequently, a huge long-term emission was evident. Qualitative and quantitative GC/MS analysis of free and sedimentary bound DDT residues considering all known metabolites as well as isotopic analysis of DDA in ground and surface water revealed insights into the potential of DDA formation and degradation as well as into the transport processes distributing DDA within the aquatic system. This is of special interest with respect to the infiltration of riverine contamination in corresponding ground water that is destined for drinking water production. Conclusion: This study claimed to regard the importance of DDA as water related contaminant and as long-term impact of DDT pollution on the aquatic environment.

P02.04

New Global Pollutants Derived From Marine Debris Plastic

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Plastic wastes are generally disposed off underground and find their way into the environment through careless littering. They may also be carried by water into the ocean with consequently very wide distribution.∞@Plastics constitute the main content of garbage present in marine debris. Since the late 1980s, certain pollutants such as phthalic acid esters (PAE) and bisphenol-A(BPA), a typical additive or raw material for polycarbonate, both of which may possibly be eluted from plastic products, have often been detected in rivers and oceans. But the sources and elution pathways of these compounds have yet to be clearly elucidated. Still, polymer degradation in nature remains but little understood. At present, no kinetic data on polymer degradation in daily life situations or the natural environment are available. Polystyrene (PS) was found to undergo degradation at 30 ∞C. Possibly, PS degradation occurs gradually in water bodies or along sea shores with consequent release of various pollutants such as BPA. This process is expatiated by low environmental temperature at which plastic decomposition can occur, as has been confirmed by the presence of degradation products in nature. Simulation study has indicated that low molecular weight pollutant elution from PS will come to be in excess 30 thousand tons a year within the next 100 years. Thus, plastic waste in the environment will certainly constitute a new source of global pollutants for long into the future.

Poster Presentations

P02.05

Oil Spill Source Investigation: The Depuration of Triterpanes and Steranes Biomarkers from Mussels (*Mytilus edulis*)

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To unambiguously identify spilled oils and petroleum products and to link them to sources is extremely important in settling questions of environmental impact and legal liability. In recent times, geochemical biomarkers have played an important role in the chemical fingerprinting of oils, e.g. in the Nordtest system. Specific triterpane and sterane ratios have been successfully applied by geochemists to investigate and correlate spilled oil in sediments and water phases to their sources. Geochemical biomarkers bear intrinsic fingerprints of their source rocks. They are resistant to photochemical and microbial degradation (Peters & Moldowan, 1993) and therefore have the potential to retain these fingerprints after spillage. However, to date, little is known about the fate and degradation characteristics of these hydrocarbons in aquatic organisms.

This study investigates the changes in specific triterpane and sterane ratios currently used by Nordtest for oil spill identification, in naturally incurred mussels. The data are used to investigate the stability of the diagnostic ratios over time, and hence their reliability in oil spill source identification.

The study was carried out in both a laboratory flow through system and in a field depuration experiment. Concentration of individual triterpane (m/z 191) and sterane (m/z 217) compounds were estimated by Gas Chromatography–Mass Spectrometry (GC-MS) and ratios calculated. There was little change in the triterpane ratios with time confirming the stability of these compounds in mussels. The sterane ratios $29aaS = (29aaS/29aaR)$ and $29bb = [29bb(S+R)/29aa(S+R)]$, investigated showed significant decreases with depuration time.

The stability of these ratios over time is being further investigated in a laboratory experiment using mussels artificially contaminated with oils of known geological origins. The data from these studies will contribute to an assessment of the implications of using biomarker ratios in contaminated organisms in oil spill identification.

P02.07

Degradation of 2,4-dichlorophenol photoinduced by Fe(III) polycarboxylate complexes

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Background: Iron is the most abundant transition metal in natural aquatic environments. The polycarboxylate groups are one of the most common functional groups of the dissolved organic compounds in natural waters. These acids are chelating agents which form complexes with metal ions.

Aim: In this work, the impact of photolysis of Fe(III)-pyruvate, citrate and tartrate complexes on the fate of pollutants in environment was studied. 2,4-Dichlorophenol (2,4-DCP) was used as model compound for its high toxicity and as the key intermediate in the synthesis of the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid). First the characterization of iron complexes was done by spectrophotometric methods.

Methods: The degradation of 2,4-DCP photoinduced by Fe(III)-carboxylate complexes was studied under 365 nm which is a wavelength representative of the solar emission. The quantum yield of Fe(II) formation and 2,4-DCP disappearance were studied in order to discuss the initial period of the process. The influence of the most important parameters, such as pH, initial concentration of the 2,4-DCP, Fe(III) and carboxylate acids on the photodegradation rate of 2,4-DCP were systematically investigated.

Results and conclusion: All these complexes produce, by photoredox, reaction reactive species which are able to degrade pollutants. The photodegradation rate of 2,4-DCP is strongly influenced by pH. The mechanism of the formation of reactive species, such as hydroxyl radicals, is discussed. For longer irradiation time, a total disappearance of 2,4-DCP was obtained.

P02.06

Withdrawn

P02.08

The Assessment Of The Bioaccumulation Of Selected Halogenated Xenobiotics In The Aquatic Food Chain

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Background

Halogenated compounds as polychlorinated biphenyls (PCBs) or pesticides (DDT or hexachlorocyclohexanes HCH) are the main representatives a large group of xenobiotics called persistent organic pollutants (POPs) which were once (or still are) used in many applications, but were early recognised as serious threat to the environment. These chemicals tend to persist in the environment for a long period of time and accumulate in the food web with a high resistance to be metabolised and excreted.

Aim(s)/Objective, Methods

The aim of this study was to assess the degree of contamination in the aquatic food chain by using selected fish and bird species as bioaccumulation markers (bream, pike-perch, perch, tench; cormorant). The samples of prepared fat tissue (from skin, muscle and viscera) from caught individuals were analysed by means of high resolution gas chromatography by both electron capture and mass detectors.

Results and Discussion

Based on the results, the levels of monitored pollutants corresponded very well with a position of given species within the food chain and reflected its feed habits. The concentrations of 7 major PCB congeners and pesticides (DDTs, HCH and HCB) in water and sediment samples were mainly units or tenths of ppb whereas the levels in phytophagous fish were approx. hundredfold higher and in predatory fish and birds reached the values of units and even tens of ppm. The results clearly illustrate the process of bioaccumulation of these pollutants through the aquatic food chain and follow interspecies differences. The comparison between more sampling areas (polluted and relatively unpolluted) and species was made as well.

Poster Presentations

P02.09

Optical Signatures of Marine and Terrestrial Colloids in the River Thurso Estuary

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Aquatic colloids are usually defined on the basis of size, i.e. chemical and biological entities having at least one dimension between 1 nm and 1 μ m. In natural waters they constitute a major and highly variable fraction of the dissolved organic matter (DOM) reservoir, whose distinct optical properties interfere significantly with light propagation in surface waters. These properties and their short-term variability may explain why remote sensing data in estuarine and coastal waters cannot always be related to bulk water quality parameters such as chlorophyll a or dissolved organic carbon.

In this study, the first critical steps were taken towards interpreting the optical signature of colloidal matter in a black water river. The UV-visible absorption coefficient measured at 355 nm, which is conventionally used as an index of coloured DOM (CDOM) abundance, decreased linearly with salinity ($a(355)=18.5 \text{ m}^{-1}$ at $S=0.1$; $a(355)=2.5 \text{ m}^{-1}$ at $S=33.8$), indicating that terrestrial humic substances behaved conservatively during estuarine mixing. The spectral slope (320-520 nm) also decreased with salinity. These results can be explained if small colloids aggregated during estuarine mixing to form larger entities that were still of colloidal size so that, overall, no net CDOM removal was detected.

EEM fluorescence enabled three fluorophores to be clearly identified: fulvic-like (F), humic-like (H) and protein-like (P). Primarily of terrestrial origin, fluorophores F was associated with the colloidal fraction (NMW>5 kDa) of CDOM throughout the estuarine mixing zone while H switched from colloidal to soluble forms (NMW<5 kDa) at an early stage of mixing with seawater ($S \geq 4.0$).

These results reveal that the optically defined fractions of DOM in estuarine waters are found in distinct size ranges but that these ranges shift across the salinity gradient, which contributes to the highly variable optical signature reported in these waters.

P02.11

Major and Trace Elements Distribution in Sediments of Itea Gulf, Greece

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Background: Over the last 34 years a bauxite beneficiation plant is located in the region of Fokida prefecture, central Greece. Bauxite, the main product of this mining company, is being transported abroad by cargo ships. These activities take place just two kilometers from the seaside town of Itea. As a result, bauxite dust is released to the atmosphere and deposited to the vicinity area.

Aim: Scope of this study is to investigate the environmental impact of these activities to the coastal environment.

Method: Sediment core samples at five sites on the seafloor of the Gulf of Itea and five surface soil samples along the beach were collected, during January 2007. Moreover, two bauxite samples were also collected from the plant area. The length of the sediment cores ranged from 8 to 16 cm and two to three sub-samples from each core were selected for analysis. All samples were subjected to major and trace element determination by ICP-MS. Prior to analysis, samples were air-dried, crushed to fine powder and homogenized. Acid digestion of the samples was carried out by using the combination of $\text{HNO}_3 + \text{HClO}_4 + \text{HF}$. To confirm the accuracy of the method two different standard reference materials (IAEA soil-7 and IAEA-405) were digested and analyzed simultaneous with the samples.

Results/Discussion: Nineteen different elements (Ag, As, Ba, Cd, Co, Cr, Cu, Fe, Ga, Mn, Mo, Ni, Pb, Sb, Th, Ti, U, V and Zn) were determined in all sediment, soil and bauxite samples. One-way analysis of variance (ANOVA) was performed to assess spatial differences in elemental concentrations. Multivariate statistical analysis was also performed in order to identify the natural and potential anthropogenic sources of the elements in the study area.

P02.10

Characterization of Dissolved Organic Matter in Lake Sediment Pore Water Samples by Spectroscopic Methods

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"Background" Lake sediment pore water dissolved organic matter (DOM) plays a significant role in aquatic ecosystems having influence on nutrients and carbon cycling as well as on the availability of different contaminants. Thus, the investigation of the distribution of pore water biomolecules can be useful for the evaluation of environmental conditions in aquatic system. Pore water DOM consists mainly of humic substances, proteins, carbohydrates and other non-humic macromolecules.

"Aim(s)/Objective(s)", "Methods" The objective of this research was to characterize temporal changes in DOM content in Lake Rõuge Tõugjärv, South-Estonia using fluorescence and UV-VIS spectrometry. The sediment core was dated using several methods (210Pb, varvochronology) and the analyzed period covered last 150 years (from 1852 to 2005). Pore water samples were extracted by centrifugation.

"Results", "Discussion" Fluorescence spectrometry revealed the presence of two fractions. Excitation/emission wavelength maximums of the peaks corresponded to humic substances (with excitation in range 325-340 nm and emission maximum at 410-425 nm) and proteinaceous matter (with excitation in range 275-290 nm and emission maximum at 300-330 nm). The content of DOM in analyzed period showed a slight decreasing trend. The ratio of the fluorescence intensities for humic and protein fractions $F(H)/F(P)$ which in water studies indicates biological activity varied insignificantly. The type of sediment pore water was evaluated by calculating the ratio of absorbances obtained at 254 to 360 nm and comparing the obtained values with the fluorescence maximum intensity results.

P02.12

The Role of Two Sediment Dwelling Invertebrates on the Mercury Transfer from Sediments to the Estuarine Trophic Web

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Background: Estuarine sediments are essential for the biogeochemical cycle of contaminants, acting as source, sink and transformation center. Benthic organisms in direct contact with sediments are exposed to these contaminants, and in the case of toxic heavy metals such as mercury (Hg), may bioaccumulate and promote its transfer to estuarine food webs. *Scrobicularia plana* and *Hediste diversicolor* are common estuarine benthic species, with worldwide distribution. Both are essentially deposit feeders and important prey items to higher trophic levels, and thus must play an essential role in the mobilization of Hg from sediments to biota.

Aims: Assess the annual total and organic Hg bioaccumulation pattern of *S. plana* and *H. diversicolor*, to evaluate the potential Hg transfer from contaminated sediments to food webs.

Methods: Hg was quantified by thermal decomposition atomic absorption spectrometry, using a LECO AMA-254. Dissolved Hg and suspended particulate matter (SPM) Hg analyses were performed by cold-vapor atomic fluorescence spectrometry (CV-AFS). Organic Hg determinations were determined through digestion with KBr, followed by extraction into toluene.

Results and Discussion: *S. plana* accumulated more total Hg than *H. diversicolor* in contaminated areas, with a maximum of 0.20 mg kg⁻¹ y⁻¹, while for organic Hg the annual accumulation was similar between species and below 0.045 mg kg⁻¹ y⁻¹. The higher organic Hg fraction in *H. diversicolor* is related to the omnivorous diet of this species, but both species increase organic Hg bioavailability, by burrowing activities and uptake in anoxic sediment layers. Integrating the annual biological production of each species revealed Hg incorporation rates up to 28 μ g m⁻² y⁻¹, and to extract 12 g Hg y⁻¹ (of which 90% with *S. plana*) in the contaminated basin, that can be transferred to higher trophic levels. *S. plana* is therefore an essential vector in the mercury biogeochemical cycle, by increasing its bioavailability and, by predation, to transfer it to economically important species.

Poster Presentations

P02.13

Metals Content in Different Size Classes of Edible Species in a Wetland Area (Italy)

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Background: Marine organisms accumulate contaminants from the environment therefore have been extensively used in marine pollution monitoring programmes. Heavy metals are an important group of chemical contaminants and the food is the major vehicle of incoming in the human system.

Aim: Hg, Cd, Pb, As, Cr and Ni were determined in two fish species, *Dicentrarchus labrax* and *Spaurus aurata*, collected in a wetland area (near Venice lagoon) in the autumn of 2005. All metals were monitored in muscle tissue and liver, so as to identify the organs responsible of accumulating mechanisms. The metals accumulation was investigated in two different size classes. The concentrations of the priority substances were evaluated respect the threshold uptake for human fish consumption fixed by Regulation (CE) N. 466/2001.

Methods: The analyses were performed by a graphite furnace atomic absorption, for Cd and Pb; Direct Mercury Analyser, for Hg; ICP-OES, for As, Cr and Ni. The analytical procedures were tested using CRM (DORM-2, DOLT-3); all samples run in triplicate.

Results: A progressive increase of Cd and Hg concentrations was found in tissues at different sizes; Cd was principally accumulated in the liver while Hg was principally accumulated in the muscle tissue. Cr was accumulated, for both species, in the muscle tissue but it didn't show increase of concentration with different fishes sizes. Ni and Pb were accumulated only in the *Spaurus aurata* liver, while As only in the *Spaurus aurata* muscle tissue.

Discussion: The results of this study supply valuable information about organs responsible for metals accumulation. Cd, Ni, Pb were principally accumulated in liver while Hg, Cr and As in muscle tissue. In general all metals, except Hg, were accumulated more in the *Spaurus aurata* than in the *Dicentrarchus labrax* tissues. In the majority of the analyzed samples the metal concentrations, recorded in the muscle tissue, were well within the prescribed threshold uptake (Regulation CE N. 466/2001) and then considered safe for human consumption.

P02.15

Developments in Automated Nutrient Analysis

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Background: Anthropogenic activities have resulted in an increase of nutrient inputs, especially nitrogen and phosphorus, to the marine environment. Nutrients can enter the marine environment from domestic & agricultural wastes and atmospheric discharges. In coastal areas, enrichment of nutrients can result in the reductions in water quality associated with eutrophication. Monitoring of nutrients in sea water is required under the Oslo and Paris Commission Strategy to Combat Eutrophication. Automated analysis has long been necessary to provide high precision and high sample throughput required on research vessels at sea. Recently, we replaced a Bran+Luebbe Autoanalyser 3 (AA3) with a Bran+Luebbe QuAAtro capable of analysing for nitrite (NO₂), silicate (SiO₄), ammonium (NH₄), phosphate (PO₄) and TOxN (NO₂ + NO₃) simultaneously. Adoption of new instrumentation required validation of the methods for analysis of nutrients aboard research vessels. Aims: To validate the QuAAtro for use aboard research vessels and to apply the methods to the analysis of Scottish coastal waters. Methods: Nutrients were determined using the QuAAtro, using standard methods. Results: The QuAAtro methods were successfully validated for use onboard FRV Scotia with limits of detection (LOD) comparable to those for the AA3 for PO₄ and TOxN (0.01 μM), and half the existing LODs for NO₂, SiO₄ (QuAAtro 0.01 μM; AA3 0.02 μM) and for manual NH₄ determination (QuAAtro 0.09 μM manual method 0.19 μM). The precision of the methods has been further improved from the AA3 to the QuAAtro, generally by factors of 1.5 – 3. The two autoanalysers were used in parallel on FRV Scotia in January 2007. Samples were collected every fifteen minutes for the duration of the cruise and analysed within 10 hours for all nutrients. 400 samples were analysed using both instruments. The data were compared and gave correlation coefficients of greater than 0.9 for PO₄, TOxN and SiO₄. Overall there was no evidence of nutrient enrichment in Scottish offshore or coastal waters.

P02.14

The Anti-Oxidant Properties of Scottish Seaweeds

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Although there has been interest in the natural products found in seaweeds since the late 1970s much of the work focused on the isolation and characterisation of novel natural products with little attention being paid to the bioactivity of the isolated compounds. More recently interest in the bioactivity of these natural products has grown focusing on both ecological and biomedical roles. Here, the antioxidant activity of 13 locally sourced seaweed species is investigated. Antioxidants are important in combating the effects of reactive oxygen species (ROS) which can be generated in both plants and animals, usually by exposure to ultraviolet light or pollutants or as a result of dietary deficiencies. The ROS can interact with DNA, proteins and lipids resulting in damage at a cellular and genetic level. Extracts of the 13 algal species were separated according to their polarity using solvent partitioning. The antioxidant activities of the resulting fractions were assessed using the DPPH radical scavenging and ABTS radical cation decolourisation assays. The amount of phenolic compounds contained in each of the fractions was additionally determined using the Folin-Ciocalteu method. From the results obtained it is evident that many species contain a significant amount of antioxidants. It is also clear that brown algae contain either larger amounts of or more effective antioxidants compared to red and green algae. A direct comparison of the amount of phenolics in extracts of *Fucus* species suggests that shore location may be an important factor in determining the amount of phenolic compounds present in the plants. *Fucus vesiculosus*, commonly found high on the shore, contains four times the amount of phenolics compared to *Fucus serratus*, which is commonly found in the low intertidal zone. The increased phenolic content of *F. vesiculosus* may be a consequence of the fact that this species is adapted to spend more time directly exposed to sunlight and desiccation whereas *F. serratus* spends the majority of its time submerged.

P02.16

Mercury Accumulation in Liza Aurata along an Estuarine Contamination Gradient

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“Background:” Contamination by heavy metals is a widespread threat to aquatic environments. In particular, mercury (Hg) acts as a major pollutant with high toxicity to humans, ecosystems and wildlife. The most toxic form is methylmercury, which is readily bioavailable and accumulating in food webs due to bioconcentration and bioamplification. Fish, as top predators, are a powerful tool to assess the impact of contaminants in aquatic environments.

“Aim(s)/Objective(s):” The aim of this work was to contribute for a better understanding of how a field exposure to an anthropogenic mercury aquatic gradient influences metal accumulation in a fish species (golden grey mullet, *Liza aurata*), namely its distribution among the main target tissues.

“Methods:” Total mercury concentrations were determined in water column, sediment and fish collected at three different locations: a highly contaminated area, an intermediate contaminated area and a mercury-free area (control area). Juvenile specimens of golden grey mullet were collected and blood, gills, brain, muscle, liver and kidney samples were taken.

“Results:” The total mercury concentration varied according to the tissues examined, ranging from 0.008 – 1.2 μg/g wet weight (blood < gills < brain < muscle < liver < kidney). Total mercury concentrations in water ranged from 8.3 – 20.8 ng/L and in sediments from 0.01 – 4.5 μg/g dry weight. The highest concentrations were found in the most contaminated area. Comparing the control with the most contaminated area, Hg concentrations duplicated for gills and kidney, and all the other organs revealed higher increments: muscle increased 3.5 fold, liver 4 fold and brain almost 5 fold. In control and intermediate area, positive correlations were found between liver and muscle Hg concentrations

“Conclusion:” Brain seemed to be the most sensitive organ and the high content of mercury in liver is a good indicator that a chronic exposure occurred since this organ is responsible for metal metabolism.

Poster Presentations

P02.17

Distribution of Lithogenic and Biogenic Fractions of Seston in Shallow Estuarine Systems: Influence of Resuspension and Implications for Sampling

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Background: The knowledge of the partition of biogenic and lithogenic material in plankton net material is essential to accurately quantify pollutant incorporation, bioavailability, bioaccumulation and bioamplification in plankton communities.

Aims: Study the influence of tidal resuspension on the seston lithogenic and biogenic partition, ii) Achieve useful knowledge for optimization of sampling procedures regarding plankton research.

Methods: Suspended particulate matter (SPM) and seston (63 and 200 µm nets) samples were collected hourly over a semi-diurnal spring tidal cycle. Water intensity current, water column height, salinity and pH were measured and carbon content (%C) and aluminium content (%Al) were quantified both in SPM and in seston.

Results and Discussion: The tidal variation of environmental parameters (water velocity, salinity, pH and water height) reflected the characteristic traits of mesotidal systems, and resulted in marked variations in suspended particles concentrations and origin. The %C in the plankton nets was negatively correlated with both the water velocity and the amount of SPM, suggesting an influence of resuspension on the composition of collected material. In addition, %C and %Al in seston showed a highly significant negative correlation, reflecting the opposite behaviour of these biogenic and lithogenic tracers during the tidal cycle. The biogenic fraction ranged from 27 to 91% in the 63 µm net and between 45 and 95% in the 200 µm net, the highest observed in slack periods.

Conclusion: Tidal resuspension was considered one of the most important forcing functions regulating the composition of seston and the partition of suspended biogenic and lithogenic particles, with important implications. For environmental research focusing on transport of contaminants, trophic transfer and plankton bioaccumulation it will be essential to minimize sampling bias by aiming sample collection at slack periods, when resuspension is minimal and the biogenic fraction of seston close to 100%.

P02.19

Physicochemical Behaviours during an Accidental Discharge at Sea. Dissolution, Adsorption, Spreading out. Dimethyldisulfide (DmDS) Case-Study

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BACKGROUND. Maritime traffic of chemicals is in constant expansion which implies an increase of spillover risks of more and more important and diverse cargos. Then, the operators in charge of the response after an accident must face more and more difficulties related to the behaviour at sea of these products after release. Available data are often incomplete and don't take into account the specificities of the marine environment. DMDS is a chemical whose use is developing in several industrial fields. Its very high vapour pressure is known, but numbers of uncertainties about its behaviour at sea typically persist; consequently it was worth studying its solubility limits, spreading ability, sedimentation process and chemical stability all factors important in spillovers.

METHODS. Solubility was studied by determining DMDS solution contents by chromatography under several conditions of salinity and temperature. Spreading properties on water and silica were studied by tensiometry and imaging. Sedimentation was studied by the use of the unique 5 meter high column of water, the Cedre Experimental Column (C.E.C). The molecular stability was studied by NMR techniques.

RESULTS. Solubility limits (S) were studied on temperature (T) and salinity (sal) ranges of 10 to 25°C and 0 to 34‰, respectively. Dissolution kinetics was fast (saturation after one hour) and the solubility was low (≈ 2 g L⁻¹). A statistical treatment of the data gave the expression: $SDMDS = 2.04 - 0.021 (sal) - 0.008 T$. The sedimentation study showed that when injections were performed in the C.E.C. under the water surface (because DMDS density is higher than water one), a loss of 10% in volume occurred during the sedimentation process and when they were made just above the water surface, DMDS formed a thin slick before its sedimentation; this entailed the evaporation of a part of the injected quantities. It was not possible to detect any molecular degradations under test conditions during two months.

CONCLUSION. In conclusion, DMDS is a volatile product denser than water which could generate a toxic cloud in case of release at the sea surface. This should be taken into account by the responder team. The part of the product which would sink could accumulate because of the weak solubility and could persist on the sea-floor especially in the absence of water agitation.

P02.18

Distribution and Desorption of HCB and Other Chlorinated Benzenes from Sediments and SPM of the Rhine and Elbe River

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Background: HCB is despite the ban in the 1980s still a problem in sediments and SPM of the Rhine and Elbe River systems. Within the framework of the Environmental Specimen Bank (ESB) sediment and SPM samples were analysed for HCB and other chlorinated benzenes. A contamination level of up to 300 ng HCB g⁻¹ d.w. was detected in SPM samples and up to 700 ng HCB g⁻¹ d.w. in sediment samples in 2005, respectively.

Aim and Scope: Since 1981 HCB is banned in Germany as a pesticide and it is included in the "dirty dozens" of the Stockholm Convention of POPs. The concentrations exceed by far the preliminary guideline values of the WFD. This study focuses on the distribution of HCB in different grain size fractions of a dated sediment core from the Rhine River and on a contaminated SPM sample from the Rhine River and the Elbe River in 2005, respectively. The analysis was performed by means of GC/MS in the SIM and scan-mode. Additionally, Tenax® desorption studies were undertaken to analyse the sorption behavior of HCB.

Results: The distribution of CBs within different grain sizes and the relative contribution of HCB to the sum CB illustrates a retarded degradation. Detailed screening of the sediment samples revealed no other degradation products of HCB like chlorinated anisols, anilines or phenols. The first results on the desorption experiments indicate a quite different release of CBs for the sediment and SPM samples from the Rhine River compared to the Elbe River.

Conclusion: This study illustrates the residual background concentration of an old contaminant and refers to the persistence and limited bioavailability of these compounds. Therefore, monitoring programs should still include the old chlorinated pesticides. The reference on a selected grain size (e.g. < 63 µm) has to be questioned.

P02.20

Estimation of Trace Metal Bioavailability in Streams using Diffusive Gradients in Thin Films (DGT) in the vicinity of Distilleries

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Background Spey. Failure to meet the Environmental Quality Standards (EQS) for copper has been recorded in certain minor water bodies associated with whisky distilling in the Spey catchment. The work described arose out of an action plan aimed at achieving a better understanding of the sources of copper and of its consequential environmental impact.

Under the Water Framework Directive (WFD) water bodies which fail to achieve good ecological status as a result of discharges of chemical substances may be identified for remedial action. It is important that this action is both prioritised and appropriate to the risks involved. An EQS is derived in such a way as to ensure an adequate level of protection in sensitive environments, thus minimising the possibility of false negatives. One consequence of this is that failure to meet an EQS does not necessarily imply that unacceptable effects will occur in the water body. The measurement of more ecologically relevant forms of trace elements could lead to an improved understanding of the risks posed at individual sites and provide better information on which to base decisions in respect to the most appropriate courses of action.

The technique of diffusive gradients in thin films (DGT) involves the diffusion of metal ions from the water source through a hydrogel membrane backed by a layer containing ion exchange resin (Chelex). The sequestration of metal by the resin creates a concentration gradient in the gel and given a known diffusivity, the time weighted average concentration of metal may be calculated.

The study showed that the DGT labile (bio-available) concentrations of copper were consistently lower than dissolved copper concentrations by varying degrees, and in a number of cases were below the established EQS where the dissolved copper measurement indicated otherwise.

Poster Presentations

P03.01

Withdrawn

P03.02

Application of Principal Component Analysis (PCA) for Determination of Background Concentrations of Metals in Sediments

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Background

In the interpretation of the geochemical data, choice of background values play important role. The problem concerning natural background levels of heavy metals is the central issue in all projects dealing with the case of sediments as pollution indicator.

Objectives

The objective of this paper was to definition of background concentrations of the metals in the sediments from the Tisa River and its tributaries using the Q-mode of PCA.

Discussion

For the determination of background concentrations of the investigated metals, the Q-mode of PCA was applied onto normalized metal concentrations. AI was used as a grain-size proxy. A plot of scores, which gives the positions of the samples in the coordinates of the principal components, isolated the 8 samples of the tributaries into one group and rest of the samples representing river sediments (surfaces and lower laying) into another. The mean values the concentrations of the metals for these samples were defined as the background values for the Tisza River sediments. The calculated background concentrations (in mg kg⁻¹) were: Cu (41.9), Cr (11.37), Zn (127.3), Pb (19.13), and Ni (42.27). These values are similar to the values for other localities (Ria de Vigo, coastal sediments, NW Spain), sedimentary rock and continental crust. The background level for Cr in one of the Tisza River sediments is low and differs from the other ones, probably because of the specific geological and morphometrical features of the basin itself.

Conclusion

This paper illustrates the utility of Q-mode of PCA for determination of background concentrations of metals in river sediments. The calculated background concentrations of the Cu, Zn, Pb, and Ni in the Tisza River sediments are similar to the values for other localities, and the background level for Cr is low and differs from the other ones.

P03.03

Nitrogen-15 Natural Abundance of Alpine Plants as Indicator of Nitrogen Nutrition Features in Mountain Ecosystems

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Mountain ecosystems sensitively react to disturbance and climate change, especially with respect to nutrient cycles. Within nitrogen cycle, different organic and inorganic N compounds with different ¹⁵N natural abundance are formed, being in general more ¹⁵N enriched with N cycle becomes more open. We have studied the change of ¹⁵N natural abundance of plant species as influenced by different N sources in four representative alpine ecosystems of the Northern Caucasus. The aim was to estimate, how leaf $\delta^{15}N$ can reflect the change of ¹⁵N enrichment of N sources. Nitrogen isotopic composition of alpine plant species demonstrated significant response to input of different N sources with different ¹⁵N enrichment into the soil. All investigated species showed increase of leaf $\delta^{15}N$ (by 1.0–9.8‰) when ¹⁵N enriched NO₃–N (+9.5‰) was added. Using isotopic mass balance we quantified NO₃–N contribution to mixed plant nutrition from natural soil and artificial NO₃– sources. All grasses and sedges demonstrated lower NO₃–N uptake (20–40%) relative to all other species (40–60%) of corresponding community, with exception of two ericoid mycorrhizal and N₂-fixing species (10–30%). Decrease of leaf $\delta^{15}N$ following treatment with ¹⁵N depleted NH₄⁺–N (–8.0‰) was less pronounced. In all communities significant $\delta^{15}N$ decrease (by 2.0–4.9‰) was observed for grasses and sedges only. Less pronounced response on ¹⁵N depleted source can be connected to its transformation in rather more ¹⁵N enriched form as a result of increasing N transformation activity in the N supplied soil. Therefore nitrogen isotopic composition of alpine plants well reflects the increase of ¹⁵N enrichment of soil N sources.

P03.04

Experimental Analysis of Sorption of Environmental Chemicals to Soil Organic Matter

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Sorption of environmental chemicals to soils and sediments affects their mobility and fate. For organic compounds, the organic carbon (OC) fraction (f_{OC}) of the solid matrix is the predominant sorbent phase. Normalization of the solid-liquid partition coefficient of the solute, K_d, to the OC content of the matrix results in K_{OC} = (1/f_{OC}) * K_d as often used quantitative measure of the sorption process. The goal of our project is to determine the impact of pH on the sorption of organic compounds to soil organic matter. To this end, sorption isotherms have been determined for both neutral and ionogenic sorbates, keeping in mind that for a given soil type, the degree of dissociation of humic and fulvic acids as major OC components depend on pH. Starting point for the experimental setting was the OECD guideline 121, which was adapted for the present purpose in order to control different predefined pH values for the measurements. The new experimental data are compared with literature values, and discussed from the viewpoint of compound-matrix interaction forces that govern the sorption process.

Keywords: soil sorption, pH dependence, humic substances, HPLC

Poster Presentations

P03.05

Mesurement of Gas Adsorption and Mercury Intrusion as Quantitative Characteristic of the Efficiency of an Acid Activation on Smectic Clay Minerals

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Acid activated clay minerals are used as catalysts in the desulphurization of crude oil or as catalyst carrier, as drilling mud, as bleaching earth etc. The aim of this work was to study few Goshica's clay parameters and the possibility of changing this parameters through acid activation using sulfuric acid.

The efficiency of the acid activation can be described in two ways. As increase of the surface and as increase of the cumulative pore volume after the activation. In different samples of the clay mineral the activation was done with different sulfuric acid concentrations for two and three hours. Afterwards the specific surface was measured by means of nitrogen adsorption. All the measured isotherms belong to the pseudo-two kind. After the activation the surface enhanced from around 100 m²/g to 180 m²/g. The mesopore distribution is calculated out of the hysteresis between adsorption-desorption isotherms of the nitrogen. It is shown that the activation increases significantly the amount of mesopores which is reflected in the cumulative volume.

The macropore volume of the clay samples were measured by means of mercury intrusion porosimetry for pore sizes up to 320 nm. The volume of the macropores results to an increase up to two times after the activation. The cumulative volume of all the pores is shown like a good parameter of the efficiency of the acid activation.

The measurements were fulfilled in the newly equipped laboratory of the surface characterizations of the Tirana University. These analysis are of big interest for the industry in Albania and Kosova.

P03.06

Adsorption of Lead and Cupper by Goethite in the Presence of Oxalic Acid *Peregomov, Leonid*¹; *Violante, Antonio*²

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Soil organic matter affects chemical and biochemical reactions on soil minerals. Oxalate, one of the most abundant low molecular-weight organic anions present in the soils, is secreted by plant roots and produced by bacteria and fungi and is often a product of decomposition of leaf litter. The aim of this work was to study the adsorption of lead and cupper on a synthetic goethite in the presence of oxalic acid, as affected by pH and oxalate concentration. The sorption experiments were carried out by adding solutions Pb and Cu as nitrates with initial concentration of metals 25 mkM/l to 0.02 g of synthetic goethite. The samples were kept for 6 h at a constant pH by adding HNO₃ or KOH. The range of experimental pH was from 3 to 5.5 and used oxalate/metal molar ratios were from 0, 1, 2, 4, 8 and 10. The relative affinity of Cu for goethite without oxalic acid was higher than one of Pb, that is in accordance with works of Kinniburgh and Jackson (1976, 1981). In the absence of oxalate pH₅₀ values of Cu and Pb were 4.7 and 5.1 respectively. Adsorption of both elements was low at pH 3 and 3.5 and reached 20 mkM/g for Pb and 25 mkM/g for Cu at pH 5.5. At constant pH (4.5) in the presence of oxalic acid adsorption of Cu on goethite surface increased up to oxalate/metal molar ratio 2 and then slowly decreased. Adsorption of Pb by the mineral rised up to molar ratio 6 and at ratio 8 and 10 slightly decreased. It is known that organic ligands adsorbed on the surfaces of metal oxides decrease their point of zero charge (Huang and Violante, 1986). Therefore, the fixation of certain amount of oxalate has increased the number of negatively charged sites and adsorption of Cu and Pb. However, at relatively high oxalate concentrations, opposite phenomena, which prevent metals adsorption, occurred. Large amount of oxalate may either occupy many adsorption sites, which are then not available for Cu and Pb or may favor metal desorption relative to ternary complex formation. The research was supported by Grant INTAS N 06-1000014-6126

P03.07

P04.01

Withdrawn

Withdrawn

Poster Presentations

P04.02

Opposite Behaviours of Organics and Salts at Different Interfaces. Possible Impact on the Environment.

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Background: Desorption from soil particles may feed surface adsorption, bubbling and, by way of consequence, the formation of polluted aerosols.

Aim: In this report, we consider the co-adsorption behaviour of carbofuran and lead salt both on silica beads as model of sand and at the free surface of water, together with de-sorption kinetics data in order to evaluate the possible impact of adsorption on sediments on the air pollution. Indeed, despite its extremely weak adsorption at the water/silica interface, carbofuran can, however, induce the coadsorption of metallic salts like, for example, lead nitrate, and thus enhance its adsorption.

Methods: After comparison of the data obtained by a depletion method in the case of the solid/liquid interface and by tensiometry for the atmosphere/liquid interface, we tried to find a relationship with kinetic measurements about adsorbant desorption from a silica surface.

Results: At the water/atmosphere interface, carbofuran adsorption is far more important than at the water-silica atmosphere, whereas ionic adsorption stays smaller despite its enhancement by coadsorption. A model based on Wagner-Onsager-Samaras' views of ionic interfaces positively accounts for the opposite behaviour of the systems according to the surface under concern. By adding pure water mimicking the effects of hard rain on the system, one observes a significative desorption of both pollutants from silica beads. They become able to adsorb at water surface and so, to favour the formation of polluted aerosols.

Conclusion: The concentration conditions were close to the environmental ones in this study. Thus, this one provides evidence that considering these facts is paramount to make a relevant assessment of environmental issues, like the impact of polluted sediments on the atmosphere purity.

P04.04

Distribution of Phosphorus in Postglacial Sediments of Lake Peipsi

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Background: Presently, the eutrophication is a major problem concerning water quality of freshwater as well as Lake Peipsi. The submeridionally elongated Lake Peipsi (3555 km² lake surface) belongs to the Baltic Sea catchment and is located south of the Gulf of Finland. Despite long-term and interdisciplinary investigations, very little is known about the sediments of Lake Peipsi and understanding phosphorus geochemistry in sediments is important because of the role of internal and external phosphorus loading on long timescales.

Aim: The main aim of the present study was to examine lake response to changes in nutrient loading during Holocene through understanding of the variability of sediment-associated P concentration.

Methods: Four lithological units were distinguished in the 8.5 m postglacial studied sediment sequence from the central part of Lake Peipsi. Three bulk gyttja samples were dated by the ¹⁴C method using accelerator-mass-spectrometry (AMS). The content of dry matter (DM) and organic matter as loss-of-ignition (LOI) was measured in sediments. Sediment samples were analysed following a sequential extraction method to quantify sedimentary phosphorus (P) pools: inorganic P (loosely sorbed or exchangeable P, ferric iron-bound P, and calcium carbonate associated P) and total P.

Results: Lithological units indicate large shifts in sedimentation processes in the past. The content of organic matter reaches its maximum value (ca 30%) at a depth of 3.9 m. A study showed that total P concentrations are relatively stable from 8.5 m to 0.6 m (0.7 mg g⁻¹ DM) with an increase in the depth interval from 4.0 to 3.0 m (up to 0.9 mg g⁻¹ DM).

Conclusion: The increase in the phosphorus content in the unconsolidated, high porosity (exceeds 89%) surface sediments (0.5 m) is connected with active diffusion and matter exchange between the water-sediment pools. The reasons for the relatively conservative behaviour of the phosphorus concentration through the whole studied sediment sequence remain to be elucidated.

P04.03

Spatial and Temporal Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in the Urban Surface Soil: A Case Study in Novi Sad, Serbia

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Soil is one of the main reservoir for PAHs in the environment, whereas soil PAH concentrations are usually considered as good indicators of the surrounding pollution and environmental risks. To date, there is only limited data on PAH concentrations in the Serbian urban soils. The extent of PAH-burden in the Novi Sad soil has been previously studied sporadically. Thus, there is no systematic long-term study and, consequently, there is no information about the extent of soil pollution in the city over years. The major objective of this study was to characterize the PAH concentrations in surface soils of Novi Sad and to compare these data with the previous findings in order to assess the temporal and spatial distribution trend. Samples were collected in the suburban settlement near the oil refinery, in the city center and in presumably unpolluted sites (control samples). PAHs determination from soil samples was based on US EPA Standard Methods 3550B, 3630C and 8100. Analysis of the prepared extracts was carried out using gas chromatograph (GC) equipped with flame ionization detector (FID). Sum of the identified PAHs components in the investigated samples ranged from 0.67 µg/g in control sample to 46.93 µg/g in school backyard near the oil refinery. All identified compounds were detected in the quantities higher than the target values regulated by the Dutch government for unpolluted soil. The determined total concentrations in soils collected in the vicinity of the refinery were higher than the intervention value for soil sanitation set by the Dutch government that is 4 µg PAH/g. Comparison with the previously data determined for Novi Sad soils revealed the increased PAH-burden. The estimated carcinogenic potencies of PAH mixtures found in the investigated soils were above the reference one estimated on the base of the Dutch target values for unpolluted soil.

P04.05

Influence of Grazing and Fertilisation on Nitrogen and Carbon Gas Fluxes from a Scottish Grassland

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"Background" Nitrogen supply influences the net greenhouse gas budgets of terrestrial ecosystems.

"Objective" It is therefore important to quantify N fluxes for the terrestrial biosphere and improve the understanding of C-N interactions.

"Methods" As part of the European project NitroEurope we measured the greenhouse gas fluxes N₂O, CH₄ and soil respiration since August 2006 from a fertilised and sheep grazed grassland site in the SE of Scotland. Inorganic fertilizer was applied at a rate of 500 kg N/ha/y, split into three applications. N₂O and CH₄ fluxes were measured weekly from closed static manual and daily from automatic chambers, and samples were analysed by gas chromatography. N₂O was also measured continuously by eddy covariance using a tuneable diode laser (TDL) during fertiliser events. Closed dynamic chambers were used for weekly soil respiration measurements, using infrared gas analysis.

"Results" First results show a high spatial variability of N₂O fluxes due to grazing. The release of N₂O after inorganic fertilizer applications resulted in short term losses of up to 950 ng N₂O-N /ha/day. Wet conditions further increased emissions. N₂O losses expressed as a percentage of fertiliser N added during the first 10 days after fertiliser application ranged between 0.33 and 1.52 %. N₂O fluxes measured with chamber methods agreed well with fluxes measured by TDL during fertiliser events (R² = 0.69). CH₄ fluxes were not influenced by fertiliser applications. Fluxes were always close to zero but occasionally increased to up to 340 µg CH₄-C/m²/h for short periods on various spots due to sheep dung. Carbon losses from soil respiration showed a high spatial variability with a maximum value of 21.7 µmol/m²/s in July and were increased after fertiliser applications.

"Discussion" Seasonal and temporal variations in GHG fluxes will be interpreted on hand of a range of measured soil and meteorological parameters and data will be compared with other sites across Europe.

Poster Presentations

P04.06

Isolation of Ice-Nucleation Active Microorganisms from Cloud Water

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The structure and function of microbial communities in clouds remain largely unknown. Atmospheric water represents, in some respects, an extreme aquatic environment characterized by low temperatures, relatively low pH and complex mixtures of organic and inorganic compounds. However, bacteria, fungi, yeast and protozoa not only survive in such media but some of them could also multiply and potentially modify the physical and chemical properties of clouds. This is due mainly to their hygroscopic and ice nucleation properties that could affect the initial process of droplet and crystal formation. Micro-organisms can also be considered as biocatalysts thereby transforming organic and inorganic compounds in cloud water (Amato et al. 2005).

In this study, the structure of the microbial population present in atmospheric water samples from clouds at the Puy de Dôme (altitude 1465 m, Massif Central, France) is described (Amato et al. 2007). The total microflora was quantified by epifluorescence microscopy and ATP concentration was measured by enzymatic assay. 90 bacterial strains and more than 40 fungi and yeasts were isolated and identified by 16S rDNA.

Twelve of these strains of fungi and bacteria, including *Pseudomonas*, *Pantoea*, *Verticillium*, *Botrytis* and *Fusarium* species, were tested for their ice nucleation activity by immersion freezing using the droplet freezing method. One bacterial strain of *Pseudomonas syringae* and one fungal strain of *Fusarium avenaceum* showed very high activities (ice-forming nuclei temperatures of -6°C and -3°C respectively).

In conclusion the presence of ice nucleation active microorganisms in cloud water suggests that microorganisms could play an active role in controlling the physical properties of atmospheric waters.

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P04.08

Analysis of the Environmental Sensitivity of A Karst Spring

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Background The Bükk Mountains, a typical karst area is located at Miskolc on north part of the country. There are several karst springs. Some of these have important role in the drinking water supply system in the region. Due to the special karst processes, sensitivity to environmental changes and special environmental effects, much research had focused on the karst systems.

Aim The present paper is a study of environmental effects to the karst spring water. This study is based on data obtained at monitoring of karst spring water.

Methods and Results Samples of groundwater from selected spring were collected. The samples were analysed for physicochemical parameters as pH, EC (Electrical Conductivity), TDS (Total Dissolved Solid), and chemical composition as Calcium, Magnesium, TH (Total Hardness), Chloride, Carbonate, Bicarbonate, alkalinity, Sodium, Potassium, Ammonium, Nitrite, Nitrate and Sulphate by using standard techniques. Surface water and precipitation (rain, snow) samples were collected in the studied area. Samples was analysed for the anions and for the cations in addition to pH and conductivity measurements. The anions from precipitation were determined by high-performance liquid chromatography.

We studied correlation among various parameters of water samples of karst spring. By comparing the water chemistry of spring and precipitation waters, an understanding may be gained of the interaction between surface water and ground water. The karstic ground water system is sensitive to the influence of point and non-point nitrate pollution. Within the region studied, the aquifers are dominated by carbonate rocks (limestone and dolomite). Dissolution of carbonate minerals largely determines the chemical composition of spring water.

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

P04.07

Distribution of Heavy Metals in the Soil of the Metropolitan Area of Belgrade (Serbia)

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Background: Belgrade is a capital city of Serbia with over 400,000 vehicles trafficking every day on its streets. Significant pollution produced by leaded gasoline and other fuel types left serious traces of heavy metals in the soil of Belgrade centre.

Objective: The goal of our work was to identify the main heavy metal pollutants, such as Zn, Cd, Pb, As, Hg, Co, Ni, Cu, Cr, Fe and Mn and to investigate their availability - mobilization potential under various environmental conditions.

Methods: The surface soil samples (0-5 cm) were collected at 12 locations nearby roadways and lanes and additional 4 samples from park areas. The sequential extraction procedure following a modified Tessier method (Tessier, 1979) was applied for speciation of the metal forms in the collected samples. Sequential extraction procedure, reagents and fraction description are given in table that follows.

Extraction step Reagents Treatment conditions Soil fraction affected

- I 1M CH₃COO(NH₄), pH 7 2 hour at room temperature (22°C) Exchangeable species
- II 0.6M HCl and 0.1M NH₂OH•HCl 12 hour at room temperature (22°C) Carbonates and Mn-oxide
- III 0.2M H₂C₂O₄ and 0.2M (NH₄)₂C₂O₄ 10 hour at room temperature (22°C) Fe-oxides
- IV 30% H₂O₂ adjusted to pH 2.0 with HNO₃ 2 hour at 85°C Organic fraction and sulphides
- V 6M HCl 9 hour at 85°C Residual fraction

The metal concentrations in extracts were determined by atomic absorption spectroscopy.

Results: Most of the heavy metals were dissolved/mobilized in the last two (IV&V) extraction phases except Mn that was already available in the II phase and Fe in the III phase. Among investigated heavy metals Fe and Mn are the most abundant and at some locations Pb and Zn. Higher concentrations of heavy metals were found in the very centre of Belgrade and along the roads with heavy traffic. The fate of these metals is influenced by several factors: local climate influences (rainy and dry season), winds and street maintenance.

Conclusion: Obtained results do not indicate that Belgrade is seriously polluted with heavy metals that can influence the health of the people living or working in these areas of Belgrade. In spite of that further investigations are directed to particulate mater (PM) and its relation to heavy metals found in soil.

P05.01

The Impact of Conifer Felling on Stream Water Quality in the Peatlands of Northern Scotland

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Background: The peatlands of Caithness and Sutherland represent the largest unbroken area (ca 400,000 ha) of blanket bogs in Britain, and possibly the world. This type of peatland is characterised by low pH, high rainfall and generally low summer temperatures. In northern Scotland, the main causes of blanket bog degradation are commercial forestry and gully erosion. They usually involve disruption of the water table and may lead to erosion and cracking of the peat. In an attempt to restore higher water table levels, the RSPB has been felling large tracts of forestry that were established on the Forsinard estate in the 1980s. There is evidence from other parts of the world that this practice may result in elevated concentrations of base cations, aluminium (Al) and nitrate in streams for up to 5 years after the felling.

Aim(s): The aim is to find if the deforestation programme at Forsinard, is affecting the cycling in the soil of the Flow Country. This research focus on the seasonal variations in the chemistry of the Sleach Water, a stream running alongside an area that was intensively planted with conifers at the beginning of the monitoring period (December 2006) but was felled in the following months.

Methods: Weekly measurements of conductivity, turbidity, pH, dissolved oxygen and uncomplexed Al were made at five adjacent forest sites and eight stream sites.

Results: The highest [Al₃₊] levels (400-700 µg/L) were found at some of the forest sites throughout February corresponding with the lowest recorded pH values (3.5-4.1). An inverse relationship between [Al₃₊] and pH was found at these sites. By contrast, pH was not a good predictor of [Al₃₊] in the stream water, where it reached a minimum in August (3.8-4.4) coinciding with the lowest stream O₂ saturation values (50-85%).

Conclusion: Near-continuous measurements of the chemical parameters and water flow would be needed, in order to fully understand the nature of these relationships and exploit them to assess the effect of deforestation in the Sleach catchment.

Poster Presentations

P05.02

Chlorophyll Transformation Products Induced by Elevated Solar Irradiance: Characterisation by Liquid Chromatography-Mass Spectrometry.

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Light-harvesting pigments of photoautotrophs are well established as biomarkers in chemotaxonomic studies both in contemporary and palaeo-environments. Similarly, diagenetic products of such pigments have been used to great effect to provide insight into the degradative processes that have operated on organic matter in the past in a range of ecological settings. In particular, the susceptibility of the chlorophylls to a range of transformation mechanisms according to the conditions to which they are exposed makes these products especially valuable as biomarkers.

Here, this biomarker approach is used to investigate the stress mechanisms that are induced by the exposure of phototrophic primary producers to elevated light levels. Chlorophyll a-like compounds were recently reported to be generated in zooxanthellae resident in corals prior to and during bleaching events brought about by exposure to elevated levels of solar irradiation. Liquid chromatography-atmospheric pressure chemical ionisation multistage mass spectrometry (LC-APCI MSn) has been used to enable the rigorous structural identification of these compounds as oxidation products of chlorophyll a, including 132-hydroxychlorophyll. A similar suite of compounds was observed in bleached sections of the chlorophyte *Enteromorpha linza* collected from intertidal rockpools.

Knowledge of the structures of these various products obtained from the LC-MSn analyses permits their use as indicators of the oxidative pressures experienced by photoautotrophs subjected to stressful levels of solar irradiance.

P06.01

Scotland Environment Protection Agency's Ecotoxicity Testing of Industrial Effluents Released into the Marine Environment

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Background: The Scottish Environment Protection Agency (SEPA) conducts ecotoxicity tests on various industrial effluents released into the marine environment around Scotland. Effluents released into Scotland's marine environment include companies producing alginates and pharmaceuticals, oil terminals and distilleries, as well as sewage treatment plants. Certain effluents are monitored by SEPA to ensure companies are within determined release consent limits.

Aims/Objectives: A brief survey of the ecological relevance of each toxicity test as well as any differences in species sensitivities related to effluent type will be presented. The chemistry and toxicity data will be presented and compared for certain effluents monitored by SEPA.

Methods: Effluents were tested with an array of organisms and endpoints including the oyster embryo development test, marine copepod lethality test, and Microtox™ bacterial luminescence test.

Results: For the various monitored effluents, certain ecotoxicity tests appear to be more sensitive than others. Chemistry results were often required to help determine potential causes of toxicity.

Discussion: Ecotoxicological testing is an important tool for assessing biological effects of complex effluents. In certain instances, chemistry data alone may not accurately predict toxicological effects on biota. Similarly, for certain effluents toxicity may occur where chemistry data may predict no biological effects to occur. It is important to consider using toxicity testing in combination with environmental chemistry to better understand potential environmental effects of complex effluents.

P06.02

P06.03

Toxicity of Perfluorooctane Sulfonic Acid and Perfluorooctanoic Acid on Freshwater Macroinvertebrates and a Fish

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Concerns about perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are growing, because of their global distribution, and persistent and bioaccumulative nature in the environment. We determined the toxicity of PFOS and PFOA using freshwater organisms including two cladocerans, *Daphnia magna* and *Moina macrocopa*, and a teleost *Oryzias latipes*. In general, PFOS is about ten times more toxic than PFOA with these organisms. The median lethal concentration for *M. macrocopa* was found at 17.95 mg/L for PFOS while 199.51 mg/L was determined for PFOA. Among water fleas, *M. macrocopa* exhibited greater sensitivity toward both perfluorinated compounds in either acute or chronic exposures: In 48 h acute toxicity tests, *M. macrocopa* was about two times more sensitive than *D. magna*. In chronic toxicity tests, 7 d exposure of *M. macrocopa* showed significant reproductive changes at 0.31 mg/L of PFOS, which is about 7 times lower than the effect concentrations of the 21 d *D. magna* exposure. The two-generation fish toxicity tests showed that the parental exposure to both compounds affected performance of the offspring. Without being exposed, F1 fish exhibited excess mortalities and histopathological changes which correlated with the exposure levels of parent generation. Continuous exposure from F0 through F1 generations increased the extent of damage. Considering the persistent characteristic of both perfluorinated compounds, more research should be needed for potential consequences of long term exposure of these compounds in the aquatic ecosystem.

Withdrawn

Poster Presentations

P06.04

Utilizing Germination Bioassay to Study Phytotoxicity of Oil Shale Semicoke and its Components

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Background One of the major environmental problems in Estonia is related with hazardous solid waste - semicoke, which is formed during oil shale retorting for oil production and is deposited in large heaps. Taking into account the need to cover old semicoke dumping sites and the fact that covering semicoke heaps by plants enhances bioremediation, the question about the suitability of semicoke for seed germination is currently of high interest. The semicoke has been dumped together with other oil shale industry wastes and thus high concentrations of phenolic compounds, polycyclic aromatic hydrocarbons and oil products have been found in these solid wastes. Potentially dangerous to the environment are also the high pH of the aqueous extracts of fresh semicoke and high content of water-soluble sulphur containing compounds.

Aims The aim of the work was to study phytotoxicity of oil shale semicoke, its aqueous extracts and different compounds found in them by seed germination bioassay.

Methods The timothy (*Phleum pratense*) seeds were used in the germination bioassay. In some experiments also lettuce (*Lactuca sativa*) and perennial ryegrass (*Lolium perenne*) seeds were used. The percentage of relative seed germination, relative root growth and germination index were calculated.

Results Fresh semi-coke completely blocked the germination of seeds. The growth inhibition effect for grasses decreased considerably with semicoke aging. The study of phytotoxicity of phenolic compounds to timothy seeds showed 50% inhibition of germination index in the range of 75-520 mg/l, which is much higher concentration than measured in the aqueous extracts of semicoke.

Discussion The results showed that the inhibition of germination was caused mainly by a high content of soluble salts. We could also expect the negative effect of pH, especially on the radicle growth, which turned out to be more sensitive than germination rate.

P06.06

Exocellular Oxidases can be Sensitive and Selective Biomarkers of Fungal Exposure to Metals

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INRA, France

Background: Biological methods based on enzymatic activity measurements may offer promising perspectives for ecotoxicological risk assessment in soils contaminated by heavy metals. Because of their ecological pertinence, we retain filamentous fungi as models for the development of enzymatic methods.

Aims: The present study aims to assess both selectivity and sensitivity of the response of exocellular oxidases secreted by the basidiomycete *Trametes versicolor* exposed to metals.

Methods: We spiked with high amounts of metals pure cultures performed in liquid media to assess the selectivity of the enzymatic response. We used media exhibiting several levels of metal complexation to measure its sensitivity.

Results: Laccase and manganese-peroxidase activities were highly stimulated in the presence of copper, mercury and cadmium. By contrast, lead and zinc were without significant effects on these activities. Lignin-peroxidase activity was not measured in the control cultures, but it was strongly increased after fungal exposure to copper. Assays performed with mixtures of metals, reflecting soil multiple contaminations, provided contrasted results. Then, culture media exhibiting low complexing properties led to an increased bioavailability of metals. As a consequence, we were able to measure the enzymatic responses at environmental levels of contaminants.

Conclusion: Our results validate our hypothesis and allow us to develop studies in soils. We will now introduce *Trametes versicolor* in contaminated soils and measure the resulting enzymatic activities.

P06.05

Lead and Cadmium in Pine Needles from Zlatibor Mountain: Needles as a Bio-Monitor of Heavy Metals

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Heavy metals are important anthropogenic environmental pollutants with high toxicity and persistence in the environment. Concern over the potential ecotoxicological hazards posed by elevated levels of metals in the environment has prompted a search to find reliable, low cost methods of assessing the extent of metal contamination. Botanical materials such as fungi, lichens, tree bark, tree rings and leaves of higher plants, have been used to detect the deposition, accumulation and distribution of metals. Literature data indicate the use of Pine needles as a bio-monitor of heavy metals.

The aim of this study was to apply *Pinus* sp. tree as a bio-monitor for lead (Pb) and cadmium (Cd) pollution in Serbia.

The needles of *Pinus* sp. tree were collected from six area of Zlatibor mountain (Serbia). Needle samples were dried at room temperature and homogenized. Cadmium and lead concentrations were determined by atomic absorption spectrometry (AAS, GBC932AA, Australia) after wet digestion with nitric and perchloric acid.

The obtained results for Pb and Cd in Pine needles were low and varied from 3.00 - 4.31 mg/kg for Pb and 0.20 - 0.37 mg/kg for Cd. These findings could be attributed to not polluted areas of Zlatibor mountain.

Further investigations are necessary for assessment of heavy metals content in Pine needles industrial and urban areas in Serbia.

P06.07

Ecotoxicological Evaluation of Polyurethane Foams

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Production of bio-based plastics and composites is thought to be one of the most important issues in the research and development for the protection of global environment. Research studies on bio-based polyurethanes have great potential in contributing to such development. In general, polyurethanes have been applied in various products. The preparation of various types of polyurethane products has been extensively studied in recent years, especially containing biomass-originated raw materials.

Polyurethane foams (PUFs) are expanded polymers synthesized according to a usual addition polymerization of multi-functional alcohols (polyols) and difunctional isocyanates. The use of cellulose and starch derivatives or wheat protein as biodegradable fillers for synthesis of biodegradable PUFs is considered to improve biodegradability and to lower the ecotoxicity. Environmental legislation demands the evaluation of the ecotoxicity at all types of waste. For this reason water leachates of modified PUFs were tested.

This work sums up the results of ecotoxicity tests, which have been conducted on seventeen selected polyurethane foams modified by addition of biodegradable compounds. Foams whose toxicity was tested were modified by sodium salt of carboxymethyl cellulose, acetylated starch, cellulose acetate, 2-hydroxyethylcellulose and wheat protein-gluten as the bio-polyols. For the evaluation of ecotoxicity two alternative toxicity tests, *Thamnotoxkit* FTM on sense organisms *Thamnocephalus platyurus* and *Daphnotoxkit* FTM magna on sense organisms *Daphnia magna* were used. The ecotoxicity was evaluated also by two phytotests: *Sinapis alba* root growth inhibition toxicity test and *Allium cepa* L root growth inhibition toxicity test. The recommendation of the most suitable phytotoxicity test and alternative toxicity test for the evaluation of the polyurethane foam degradation products ecotoxicity was pointed out.

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Poster Presentations

P06.08

The Response of Extracellular Enzymes to Copper depends on the Developing Phase in The Fungus *Trametes Versicolor*

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Background: Human activities introduce organic and metallic contaminants in the cropped soils that can alter their functioning. Environmental risk assessment needs the development of tools to quantify the ecotoxicity of the contaminants. Among soil organisms, filamentous fungi produce enzymes involved in the biogeochemical cycles. These enzymes may be used as indicators of fungal exposure to contaminants in soils.

Aims: The present study aims to establish how the developing phases of the fungus *Trametes versicolor* modulate the expression of extracellular enzymes after exposure to copper. For that purpose, it is necessary to monitor the activities of selected enzymes during the fungal growing and the stationary phases without metal contamination, then in the presence of the metal.

Methods: Hydrolase activities (namely urease, arylsulfatase, acidic and alkaline phosphatases, β -D-glucosidase and N-acetyl- β -glucosaminidase) as well as oxidase activities (laccase, manganese and lignin-peroxidases) were measured during two weeks in liquid cultures of *Trametes versicolor*. Copper was added either during the growing or the stationary phases.

Results: The results show that urease, β -D-glucosidase, acidic phosphatase and N-acetyl- β -glucosaminidase are mainly expressed during the growing phase of the fungus without metal spiking. By contrast, activities of the oxidases and β -galactosidase are increased during the stationary phase. Copper modify the expression of the enzymes. As a general way, hydrolase activities are decreased whereas oxidase ones are strongly increased. The sensitivity of enzymatic responses to copper depends on the development of the fungus and the type of secreted enzyme.

Conclusion: The exposure of *Trametes versicolor* to copper modulate the expression of its extracellular enzymes, whatever its developing phase. It is now necessary to identify enzymatic profiles that could be used as tools for metal ecotoxicity assessment.

P07.01

GIS in Pollutant Chemistry: Aral Sea Area.

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The problem of providing the population with safe potable water is being complicated due to growing deficit of water resources and difficulties in regular monitoring the quality content of water resources. To find out the regularities in formation of quality of water of water-bodies, all basic sources of their pollution with industrial, household, cattle-breeding waste water, pesticides and collector-drainage water have been investigated. The database and digital cartographic strata have been created in the geographic information system MAPINFO to characterize the risk of intestinal water-borne infections in the regions involved in the Project. The information on the main sanitary and bacteriologic indicators of water quality for 1996-2006 was summarized. The data on morbidity rates of somatic and endocrine diseases (oncological diseases, those of blood and hemopoietic organs, cardiovascular pathologies, those of the alimentary and urine excreting systems, endemic goiter), infections (enteric fever, bacterial dysentery, acute diarrheal diseases, viral hepatitis A) among the population of this three regions were also analyzed. The appropriate cartographic materials were created to reveal the most unfavorable areas by the water quality and morbidity rates among the population. The cause-effect relations typical for these areas were studied on the basis of analysis of environmental and epidemiological data and the administrative units of the territory. The GIS-technology used for these purposes allows forming a comprehensive conception of the risk of water-borne disease occurrence in some regions. The GIS-technologies are necessary both for monitoring, analysis, prognosis of the water-bodies' condition and for evaluation of the impact of water on population health, it facilitates making correct decisions by the sanitary and epidemiologic surveillance bodies and nature-protecting agencies.

P06.09

Novel Metabolomic Fingerprinting of Normal and Intersex Crustacea

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The application of metabolomic approaches to environmental biology offers exciting opportunities for the discovery on metabolic biomarkers of system change. The aim of this study was to ascertain whether two different methodologies (GCMS and LCMS) could highlight and differentiate sexual phenotypes in the amphipod, *Echinogammarus marinus*, and thus potentially yield new and novel biomarkers. *E. marinus* were collected from Thurso Bay (N.Scotland, UK). Ten pre-copular paired males and females were separated, snap frozen in liquid nitrogen, ground by pestle & mortar, and freeze dried. Samples were then extracted in acetone and analysed by GCMS following derivitisation with BSTFA, and by reverse phase LC-Electrospray MS. Data from each were normalised to total ion counts and subsequently auto-scaled, moderating peaks between 0 and 1. GCMS data was further transformed using a genetic algorithm and analysed using discriminate analysis. LCMS data were analysed by using Principal Component Analysis (PCA). A preliminary investigation was also undertaken into the feasibility of near-infrared microscopy in the "Chemical imaging" of major classes of metabolites using in both normal and intersex specimens. A number of key metabolic biomarkers were identified as being gender specific by statistical modelling approaches. The use of these novel methods, coupled with the expanding genomic, cellular, histological, physiological, behavioural and ecological data provide important data in interpreting the effects of contaminants between different levels of biological organisation.

P07.02

Mercury Bioaccumulation in Biota of the Flix Reservoir in the Ebro River Basin (Spain)

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In 2003, a large amount of mercury (Hg) was discovered in the Flix reservoir of the Ebro river, in front of a chlor-alkali plant at Flix (Catalonia, Spain). Later on, it was also discovered that during several decades, about 10 to 20 tons of Hg has been continuously dumped to the Flix dam's bed sediments. One of the main concerns is that Hg may be transported away from this site to downstream receptors. In fact, periods of high flow and/or storms may be able to transport such Hg downstream to their final receptor, the Ebro Delta Natural Park, the second most important wetland in the Iberian Peninsula. On the other hand, we have also concerned about the living biota in the proximities of these polluted sediments that should be highly affected. In order to know the levels of mercury in the biota of the Flix dam, several campaigns were carried out. Then, bioaccumulation and biomagnification were checked out for some aquatic species such as fish, mussel and crayfish by determining total Hg (THg) and methylmercury (MeHg) in biota tissue. Several fish species such as *Silurus glanis* (SGL), *Rutilus rutilus* (RRU), *Scardinius erythrophthalmus* (SER) and *Cyprinus Carpio* (CCA) were caught in waters of Flix's reservoir. On the other hand, zebra mussel, *Dreissena polymorpha*, and swamp crayfish, *Procambarus clarkii* *Procambrus clarki*, were collected in several stations according its size and its proximity to the chloralkali plant. Control samples were collected upstream. Concentrations of THg in fish tissues follow the order SGL >> CCA > SER > RRU, in accordance with its position in the aquatic food chain. Zebra mussel accumulates more Hg concentration in small sizes specimens and levels are eight times higher and significantly different ($p < 0.05$) in samples close to the chlor-alkali plant than others than there are not. American crayfish THg levels are also higher for samples trapped close to the plant. Other several interesting relationships have been assessed in the aquatic food chain of the Flix reservoir.

Poster Presentations

P07.03

Oxidative Degradation of Phenol Derivatives by Hydrogen Peroxide: Effect of Inorganic Salts

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Background: Oxidative degradation of persistent ecopollutants is considered as an alternative for biodegradation. Environmentally benign oxidizing agents are of interest, hydrogen peroxide being one of the preferential agents. Certain substances, e.g. ferrous and ferric cations, are known to generate highly reactive radicals from hydrogen peroxide and to increase redox potential of the system. Such systems were demonstrated to perform effective degradation of nitrophenols and ethoxylates of alkylphenols.

Objective: An objective of the present study was to estimate an influence of different inorganic ions on the process of oxidation.

Methods: Degradation of 2,4- and 2,6-dinitrophenols and three ethoxylates of isononylphenol with different ethoxylate chain length were carried out in the presence of several inorganic salts. Following anions were investigated: nitrate, chloride, sulfate; several cations were explored: sodium, cesium, ammonium. Concentration of salt added was varied in a wide range.

Results: Only chloride additive was found to affect significantly oxidation of all pollutants under study. Any chloride with concentration of 1 mole/l is able to suppress oxidation of dinitrophenols. It can be ascribed to a participation of chloride in concurrent redox processes. For alkylphenol ethoxylates slight influence of sulfate was also detected, presumably it was due to colloid effects in the surfactant solutions.

Conclusion: Thus oxidative degradation of ecopollutants used in water clean-up process can be negatively affected by chloride presence in waste water.

P07.04

Comparison between Various Leaching Procedures Used to Evaluate the Mobility of Metallic Elements from Industrial Slags

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Since the past century, slags are currently used as building materials. Valorisation depends on the evaluation of the potential mobility of metallic elements (ME) which can be released in the environment. Miscellaneous protocols are available, considering either the operational conditions used or the origin and the characteristics of the waste material. The main parameter considered is pH but other parameters as the redox potential (E) remain few studied. Moreover, solid characterization is seldom associated to the leaching procedures whereas it can explain release mechanisms and the potential risk according to slag reuses.

This study compares the results obtained from usual standard procedures (i.e. EN 14429; EN 12457-1 & 2; EA NEN 7371) carried out on a Mn-rich slag sampled from a metallurgical plant. To underline the importance of the operational conditions, the parameters considered in the usual procedures (particle size, contact time, pH, liquid/solid ratio) were studied. A supplementary leaching test was carried out in controlled oxydoreducing conditions (sodium ascorbate solutions) to underline the importance of the parameter E. Mineralogy was determined before and after all these leaching experiments (XRD and SEM-EDS).

The mobilisation of ME depends on operational conditions in the selected procedure. Usual protocols such as EN 12457-1 & 2 (leaching solution: high purity water, contact time: 24h) lead to a low ME release, which increases with the liquid/solid ratio, the contact time and with an acidic pH. In reducing conditions, for example after 24h of leaching (particle size < 1 mm) at - 200 mV (vs. Ag/AgCl/KCl 3 M), the amount of Mn released was about 40 times higher than according to the standard EN 12457-2 (the reference for regulation).

From these results, the use of redox potential is highlighted to evaluate the potential ME mobility, as well as the re-evaluation of contact time used in standard protocols.

P07.05

Polybrominated Diphenyl Ethers In Birds From System Of Ponds In The Czech Republic

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In this paper reports the group of polybrominated diphenyl ethers (PBDEs), which are used as flame retardant additives in variety of products such as electrical appliances, furniture, building materials, textiles and vehicles, and they more likely leach out and transfer into the environment and biota. The presence of PBDE was proved in all the components of the environment such as air, sediment and sewage sludge as well as biological samples including biota, human blood, adipose tissues and breast milk. This paper presents results of measuring concentration of ten PBDE congeners (BDE-3, 15, 28, 47, 99, 100, 118, 153, 154 and 183) in terrestrial birds (buzzard) and freshwater birds (cormorants, herons) by using gas chromatography with electron captured detector (GC-ECD). These samples were collected from specific system of ponds named Záhlinice, which are situated in a central Bohemia resort. S PBDE concentrations in the liver, kidney, pectoral and heart of cormorant ranged from 38.2 and 65.4 ng/g w.w., buzzard from 17.8 and 192 ng/g w.w., and heron from 23.9 and 126 ng/g w.w. BDE-3, BDE-47 and BDE-154 were the most abundant congeners followed by BDE-15, BDE-99, BDE-100, BDE-153 and BDE-183 in birds collected from Záhlinice. Keywords: flame retardant, congener, GC-ECD

P07.06

Laboratory Study on the Ability and Efficiency of Microbial Consortium in Degradation of Oil Pollutants

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Background

Laboratory biodegradation assessments can provide information on the ability of microorganisms to degrade chemical substances of concern under controlled conditions. These results can also be valuable in predicting biodegradation efficiency of investigated microorganisms in environmental conditions.

Objectives

The objectives of this study were to evaluate the ability of naturally-occurring microorganisms to degrade petroleum hydrocarbons in soils and to compare their efficiency in biodegradation of selected target compounds in two different oil pollutants.

Methods

The microbial consortium was isolated from the soil contaminated with effluents from a petrochemical plant (Novi Sad, Serbia). Microbial biodegradation ability and efficiency were investigated in the same contaminated soil the microbial consortium was isolated from, and in a soil with high content of lubricating oil. All experiments were conducted in shake flasks with biostimulation during a period of 12 weeks. The extent of biodegradation was monitored analyzing the residual oil by gas chromatography. Gas chromatography-mass spectrometry was used to determine biodegradability and degradation rates of n-alkanes, isoprenoids, steranes, diasteranes and terpanes.

Results

The biodegradation pattern was very similar in both investigated soils. During a period of 12 weeks n-alkanes and isoprenoids were completely degraded. Order of steranes degradation: C27>C28>C29, was observed. Diasteranes were seriously depleted. Terpanes were the most abundant compounds in both residual oils at the end of the indicated period. Tricyclic terpanes and homohopanes in the C35>C34>C33 sequence were biodegraded but all other terpanes remained intact.

Conclusions

Considering the fact that very similar biodegradation pattern was observed in two different soils containing different oil pollutants in different amount, this biodegradation pattern can be considered as a characteristic of investigated microbial consortium.

Poster Presentations

P07.07

Tree Rings and Peat Bog as a Geochemical Archives in the Vicinity of a Lead Smelter

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The content of Pb, Cd, Mn, K, Ca, Mg and $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios in spruce tree rings (*Picea abies*) and peat cores from the Brdy Hills area (10 km E of the Pb smelter) were compared with those in spruce tree rings in the vicinity of the Pb smelter. Maximum Pb content in tree rings (up to 60 mg/kg Pb) corresponds to a peak of metallurgical production in the mid 1970s and highest smelter emissions in the early 1970s. The Pb concentration curves obtained from peat deposit profiles closely correlate with the Pb concentrations in tree rings at both sampling sites. The small differences between the individual tree cores, with the identical general trend, may be attributed to the difference in distance from the smelter and the altitude of each sampling site. Similar behaviour to Pb can be observed for Cd and Ca. Lead isotope composition in tree rings ($^{206}\text{Pb}/^{207}\text{Pb}$ ~1.143 – 1.174) is controlled mainly by the smelter emissions ($^{206}\text{Pb}/^{207}\text{Pb}$ ~1.16 – 1.17), with the exception of the youngest segments from the more distant locality from the smelter, which yield isotopic signatures corresponding to car-emission Pb ($^{206}\text{Pb}/^{207}\text{Pb}$ ~1.143 – 1.150). Higher content of Mn, Mg and Ca in tree rings corresponding to the 1970s and 1980s may be related to soil chemistry changes caused by acid deposition. In addition, an increase in K, Mg (and in some cases also Mn) in the youngest part of wood cores corresponds to the physiological processes in sapwood, and may be influenced by a decrease in Pb in organic soil horizons, which limited the cycling of basic inorganic nutrients.

P07.09

Effect of Extraction Method on Composition and Metal Binding Ability of Extracellular Polymeric Substances (EPS) from Anaerobic Granular Sludge

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Extracellular polymeric substances (EPS) represent an important part of the biomass in bacterial aggregates (biofilm, activated sludge, granular sludge). Those biopolymers are composed of proteins, polysaccharides, humic like substances, and in smaller quantities uronic acids, lipids and nucleic acids. They play structural and protector roles within aggregates. For example, their biosorption ability allows them to fix metals to protect microorganisms. An extraction step is needed to study EPS. There is few data about EPS extraction in anaerobic granular sludge and there is no standard extraction method. Five physical extractions (centrifugation, sonication, heating, cation exchange resin (CER) and CER associated with sonication) and four chemical protocols (ethanol, EDTA, formaldehyde coupled either with NaOH or with heating) were compared on two different granular sludges. The composition of EPS solution was then determined by assaying the different organic molecules and an infrared analysis of the EPS samples was done. A polarographic method was used to estimate the influence of extraction technique on EPS metal binding ability. The complexation study was performed with lead and cadmium. The assays of EPS have shown differences of composition. EPS quantities extracted were greater with chemical techniques. Infrared analysis and total organic carbon measurement brought to the fore the contamination of EPS samples extracted by chemical method. This pollution by the extractants could disturb the chemical properties of EPS. Physical extraction, like heating, could also denature molecules and alter their metal binding ability. Those results have shown that it would be necessary to take the samples contamination into account to evaluate the effectiveness of the extraction. The first results of polarographic study have shown a greater affinity of EPS for lead than for cadmium and confirmed the differences of complexation ability according to the extraction method.

P07.08

Levels of POPs in Soil and Sediments of Kosova

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Polychlorinated biphenyls (PCBs) and Organochlorine Pesticides (OCPs) are organic compounds and one of the most stable organic pollutants. Because they persist in environment for a long period of time, they are often named as Persistent Organic Pollutants (POPs). The majority of well-known persistent organic pollutants based on their chemical structure and environmental behavior belong to the category of halogenated aromatic hydrocarbons. The latest investigations of their harmful influence on biological systems indicate, how the PCBs are one of the most dangerous organic pollutants in environment generally, and especially in water ecosystems. Investigation of the contamination of river sediments and soil samples with PCBs in the areas of Kosova have been carried out in the sampling locations where exist indications for the spilling of these very dangerous and stable organic pollutants into the environment. The most probable origin of these contaminations is vicinity to the spots where the oil leaking from damaged capacitors has been observed, vicinity of coal mines, industrial areas and places of waste water spilling over, and also damaged military relays. Levels of PCBs were determined by capillary gas chromatography with the electron capture detector. Concentrations of PCBs are expressed in $\mu\text{g}/\text{kg}$ (ppb) of dry sample weight. Results show that the average values from soil samples are from 7.06 $\mu\text{g}/\text{kg}$ up to 45.4 $\mu\text{g}/\text{kg}$, while these results for OCPs are from 0.32 $\mu\text{g}/\text{kg}$ till 52.13 $\mu\text{g}/\text{kg}$. Results for PCBs in river sediments are from 18 ng/g until 205 ng/g, and the values for OCPs are 0.4 ng/g until 2.8 ng/g. Based on the overall level of PCBs and OCPs, it can be concluded that the environment in Kosova is not polluted in high level.

P07.10

First Results of Outdoor and Indoor VOCs Measurements Using PTR-MS in Belgrade, Serbia

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The first results of volatile organic compounds (VOCs) measurements using Proton Transfer Reaction Mass Spectrometer (PTR-MS) in Belgrade are presented in this paper. Many of VOCs are known to be harmful to human health. Benzene, acetaldehyde, formaldehyde and acetonitrile in high concentrations are carcinogen; styrene and toluene are irritable for eyes and respiratory system, and methanol makes damage of nervous system. PTR-MS allows on-line measurements, has high sensitivity, low detection limit of 30 ppt and a fast time response of 1s. This study analyses different types of ambient air. Outdoor measurements took place at two, urban and semi-urban, locations in Belgrade. Higher oxidant concentration tends to appear in semi-urban rather than in the city center. Indoor air is often more polluted than the outdoor air; most of detected VOCs are associated with building materials, furniture, chemicals in everyday use, instruments, etc. Daily variations of concentrations and weekly cycles were identified on both locations for all measured VOCs. Decreasing of concentrations during rainy days has been observed. Pearson's correlations between VOCs were calculated. The highest correlation coefficients were observed for the compounds originated from motor vehicle exhaust emission (benzene, toluene, xylene and styrene). The obtained results are in agreement with the results from other studies in some European cities; benzene average measured values in the city center was 0.48 ppb.

Poster Presentations

P07.11

Non Target Screening of Organic Contaminants in Sediments from the Industrial Coastal Area of Kavala City (NE Greece)

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Lipophilic anthropogenic contaminants derive from different kind of activities (direct or indirect) and corresponding emission sources. These contaminants enter the aquatic environment by different pathways like surface runoff, erosion or leaching of soils, aerial deposition or direct discharge of wastes and accumulate frequently in specific zones, in particular coastal areas, forming natural reservoirs of pollutants.

Sediment and soil samples from a coastal industrial area in Northern Greece have been analyzed in order to have a detailed view of the pollution state within this area. Based on extended application of GC/MS non-target screening approach interesting well known or rarely reported contaminants have been identified and quantified e.g. plasticizers, halogenated carbazoles, N- and S- compounds, etc. The numerous compounds identified in the area have been classified dominantly according to their molecular structure. Furthermore, they are discussed with respect to: (a) their quantitative data (b) their potential sources specificity and (c) their usage and/or applications if such data are available. However, the most important value of non-target screening analyses is to provide suggestions for including so far unnoticed or new contaminants in optimized monitoring programs.

In general, the application of a non-target screening approach have provided the opportunity to expand the knowledge on low molecular weight organic pollutants in this restricted region and have revealed a first deeper insight into the state of pollution.

P07.13

Biodegradation of Mesotrione in a Whole Soil

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Background: Mesotrione [2-(4-methylsulfonyl-2-nitrobenzoyl)-1,3-cyclohexanedione] is a pre-emergence and post-emergence selective herbicide for control of broadleaf and some grass weeds in maize. It belongs to a novel class of herbicides targeting the inhibition of the 4-hydroxyphenyl pyruvate dioxygenase, enzyme involved in the carotenoid biosynthesis pathway of plants. To date, few data only are available concerning the fate of mesotrione in the environment. In the few studies published, mesotrione was found as a nonpersistent herbicide and two compounds have been described as metabolites: 4-methylsulfonyl-2-nitrobenzoic acid (MNBA) and 2-amino-4-methylsulfonyl benzoic acid (AMBA). Nevertheless, the mesotrione biodegradative pathway is poorly known so far.

Objectives: The aims of this work were first to explore the potential of pure strains to degrade mesotrione and to identify the metabolites formed by combining different analytical techniques such as ¹H NMR (performed directly on the incubation medium without any previous step of purification), LC-NMR and LC/ESI-MS. In a second part, the modulation of the biodegradation was monitored in the presence of a bulk soil.

Results: One bacterium of the 65 microbial strains tested was found to transform mesotrione. It was isolated from cloud water and identified as *Bacillus* sp. Kinetics of mesotrione degradation were monitored by HPLC and ¹H NMR. Complementary studies by NMR and LC/ESI-MS in positive and negative mode allowed us to identify several metabolites and to propose a biodegradative pathway for mesotrione. First results indicated that no sorption of mesotrione on the soil tested occurred for a 1/200 solid/liquid ratio (against 30% for a 1/10 solid/liquid ratio). The presence of soil did not affect the biodegradation rate of mesotrione whereas kinetics of metabolites were quantitatively affected.

Conclusion: The metabolite behaviour in the environment has to be taken into account to estimate the complete fate of a pesticide.

P07.12

Characterization of Gas/Particle Partitioning of Polychlorinated Biphenyls in a Pilot Area of Voivodina

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Polychlorinated biphenyls are a well-known class of ubiquitous, persistent and semi volatile organic compounds found in all environmental compartments. Even though PCBs are present in the atmosphere primarily in the vapor phase, they can distribute between the gas and particulate phase depended mainly on ambient temperature and vapor pressures. Gas/particle partitioning of polychlorinated biphenyls in the atmosphere controls removal processes as wet / dry deposition and atmospheric degradation and influences their long-range transport and environmental fate. During the June and July 2004 air sampling campaign was conducted in the region of Voivodina, Serbia, and concentration levels of seven PCB congeners was determined. Applying high volume samplers, equipped with a glass fiber filter for collecting particle phase and polyurethane foam filters for gaseous compounds, the phenomena of gas/particle partitioning were studied. Gas/particle partitioning of PCB congeners was analyzed and the obtained values of fraction adsorbed to particles was tested according to Junge-Pankow approach. The measured particle-bound compound concentrations for lower MW PCBs (PCB 28 and 52) were higher than those predicted by the model, while the opposite was observed for higher MW PCBs (PCB 101, 118, 153, 138 and 180).

P08.01

Liquid Chromatographic-Tandem Mass Spectrometric Analysis of Pharmaceuticals in Surface Water Improved by Ultra-Performance Liquid Chromatography

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Background: By consumption or improper disposal, pharmaceuticals end up in waste water, where they are not fully degraded. These chemical substances which are made to interact in living beings, have the properties to induce acute or chronic effects.

Objectives: A liquid chromatographic-tandem mass spectrometric (LC-MS/MS) method was already developed [1,2], consisting of a sample preparation with phenyl-SPE and a sample clean-up using NH₂-SPE. Matrix effects are a huge problem related to competition of analytes during ionisation. Due to the fact that matrix effects could not be sufficiently eliminated, and that they are different for different surface water samples, the standard addition method was necessary for quantification [1,2]. The aim of this study was to simplify this method by an ultra-performance liquid chromatographic-tandem mass spectrometric (UPLC-MS/MS) method. This method should provide more resolution and more speed. Matrix effects could be lower or eliminated with UPLC, so the standard addition method for quantification could maybe be omitted in favour of internal standardization.

Results: An UPLC-MS/MS method was optimized and compared with the existing HPLC-MS/MS method. The same solvents and sample preparation was used. The UPLC-method, using an Acquity UPLC HSS T3 column (1.8 μm, 2.1 x 100 mm), is faster: 9.6 instead of 24 minutes. When the UPLC-method is used, matrix effects are diminished and in most cases even eliminated. When using 3 internal standards (structural analogues), matrix effects are almost eliminated for all compounds (matrix effects ranging from 85 to 130%), and are more similar for different surface water samples. This means that the standard addition method can be omitted, and that calibration can be done with internal standardization. In this way a less time-consuming and more simplified method is achieved.

[1] J.C. Van De Steene and W.E. Lambert. *J. Chromatogr. A*, submitted.

[2] J.C. Van De Steene, K.A. Mortier and W.E. Lambert, *J. Chromatogr. A* 1123 (2006)71.

Poster Presentations

P08.02

Environmental Impact of Parabens

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Parabens are a group of the alkyl esters of p-hydroxybenzoic acid. Parabens (or their salts) are widely used as preservatives in cosmetics, toiletries, and pharmaceuticals. Studies indicated that parabens, used as anti-microbial agents in food, cosmetics, and pharmaceuticals.

Parabens are added to the list of household chemicals whose environmental levels are maintained under surveillance. Indeed, testing of parabens has revealed to varying degrees that individual paraben compounds have weakly estrogenic activity in some in vitro screening tests (Edwin, Golden). Reported in vivo effects include increased uterine weight, male reproductive tract effects and had been found in human breast cancer tissues. Moreover, laboratory studies have confirmed the presence of parabens and other species with relatively weak estrogenic potencies.

In previous work we evaluated the environmental toxicity of parabens using Microtox and Protokit. Moreover we confirmed that the Yeast Estrogen Screen was a sensitive method for the determination of six parabens: methylparaben, ethylparaben, propylparaben, butylparaben, isobutylparaben, and benzylparaben in water samples.

The aim of this study is analyse the environmental impact of parabens through the oestrogenic activity measurement using the Yeast Estrogen Screen. We will examine whether there were synergistic or additive effect in combinations of binary mixture of parabens and four other chemicals (17 beta-estradiol, estriol, bisphenol A, 17 alpha-Ethinylestradiol).

Analysis of different treated sewage waters will be compared with a conventional SPME/LC-MS-MS analysis. Thus the impact of estrogenic compounds on estrogenic activity of a water sample can be estimated

P08.05

Assessment of Adsorption on Powdered Activated Carbon and UV Photo-Oxidation as Tertiary Treatments to Eliminate Pharmaceutical Products.

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The presence of pharmaceutical products (PPs) in the environment is a current matter of interest because some of them are persistent to conventional treatment (physico-chemical and biological processes) and are rejected through effluents of sewage treatment plants (STPs). In the frame of preserving the quality of water resources and to prevent pollution from PPs, it would be judicious to consider tertiary treatments of STPs effluents in the future.

In this study, adsorption on powdered activated carbon and UV photo-oxidation were tested as tertiary treatments. The target compounds are constituted of a set of 10 PPs considering the different therapeutic classes (antibiotics, tranquilizers, α -blockers, non steroidal anti-inflammatory drugs, hormones, ...), their occurrence in the environment and their potential impact.

The efficiency of both methods has been assessed with the use of direct LC-MS/MS analysis. In a first part, synthetic aqueous solutions at concentrations of about 100 $\mu\text{g/L}$ of PPs have been tested. Secondly, the obtained results were compared to those acquired within environmental matrices (STP effluents) in order to evaluate the potential influence of the matrix on the treatments efficiency. It is important to notify that the global organic load of the matrix could be at least 100 times higher than the concentration of PPs. Indeed, results, obtained in conditions nearby the conditions of STP effluents, could be more easily transposable to future applications.

The results show that the selected PPs present different behaviour for both techniques. In general, the addition of 50 g/L of powdered activated carbon proved to be efficient to eliminate at least 80 % of all PPs within 10 minutes, except amoxicillin. On the other hand, a 20 seconds exposure to UV is enough to eliminate about 90 % of all PPs except carbamazepine.

P08.04

Analysis and Monitoring of Phthalate Compounds in Scottish Waters.

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Diethylhexyl phthalate (DEHP) has a range of uses including as an additive in plastics, an antifoaming agent in paper production, an emulsifier for cosmetics, in perfumes and pesticides, and printing inks. The Water Framework Directive designates it as a Priority Substance. A method for analysing DEHP and some other phthalates by GC-MS has been developed and accredited for analysis of rivers, groundwaters, effluents and marine waters. As normal laboratory equipment contains sources of DEHP this involved ensuring that contamination does not occur as well as overcoming challenges in the extraction, analysis and sampling. A monitoring programme covering Scottish rivers, groundwater, and effluents has been in place since late 2006 and is ongoing. Results to date have indicated that DEHP is the most commonly detected phthalate and was present in many of the samples analysed. The environmental significance of these results is not yet clear as a new EQS for DEHP is still being developed. Results from this monitoring will be used to assess the environmental risk posed by phthalates and to target future monitoring.

P08.06

Kinetics of Few Emerging Pollutants Phototransformation in Dilute Aqueous Solution: Application to Environmental and UV Disinfection Processes

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Background: Emerging contaminants i.e. pharmaceuticals are regularly detected in environmental samples. Most of them are continuously introduced in surface water that can be used to produce drinking water. Solar light and/or UV light (used for disinfection) may produce degradation products with different kinetics.

Aim: The photodecomposition in aqueous solution of emerging organic pollutants (4 hormones : estradiol, ethynylestradiol, progesterone testosterone; and 2 nonsteroidal anti-inflammatory drugs : diclofenac and naproxen) has been investigated. The half-lives (environment) and removal (UV disinfection) of the pollutants have been evaluated according to the photochemical efficiency. Methods: The photolysis experiments were carried out under monochromatic irradiation (250, 253.7, 265 and 280 nm) and under polychromatic irradiation ($\lambda > 275$ nm).

Results: The results indicated weak quantum yields of photodecomposition under monochromatic and polychromatic yields (between 0.02 and 0.08 mol/Einstein) except for diclofenac whose values were about 0.30 mol/Einstein. The influence of the wavelength and the concentration of oxygen were examined. In addition, the removal yields of these compounds under conditions used for UV-disinfection of drinking water at 253.7 nm and the half-lives of these products under solar irradiation were calculated from our data.

Conclusions: For environmental processes, half-lives ranging from several years to few hours have been calculated. In the case of a disinfection process, removal percentages ranging from few percents to almost 50% have been evaluated.

Poster Presentations

P08.07

Detection of Human Pharmaceuticals in effluents and a Scottish River

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The use of human pharmaceuticals in contemporary society is both extensive and expanding. However, it has been demonstrated that wastewater treatment results in the incomplete removal of these biologically active compounds and that they may be returned to natural water systems impacting upon non-target organisms. Investigations in countries including Switzerland, Norway, Spain and Germany have already revealed the presence of human pharmaceuticals in natural waters at ng/l-ug/l concentrations. However, no data are currently available for Scotland. The aim of this research was to investigate the presence of eleven selected pharmaceuticals in effluents discharged by a wastewater treatment plant and in a Scottish river which is the river where the effluents are discharged. Two monitoring studies were conducted during five consecutive days of different sampling periods. River samples were collected in three points located after the discharge pipe along the river. In the laboratory, pharmaceuticals were extracted by solid phase extraction (SPE) and analysed by high performance liquid chromatography in conjunction with tandem mass spectrometry (HPLC-MS/MS). Four pharmaceuticals were detected in the river (paracetamol, diclofenac, mefenamic acid and ibuprofen) and two of them were the most dispensed pharmaceuticals in Scotland during 2006. Results also indicated that pharmaceuticals detected in the river samples were the most frequently detected pharmaceuticals in the effluent.

P09.01

A Critical Evaluation of the 0.05 M EDTA Extraction of Pb from Forest Soils

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Among many single-step extraction procedures proposed, the 0.05 M EDTA (ethylenediaminetetraacetic acid) extraction is widely used. Despite it has been often criticised, this protocol remains an effective and simple approach for a fast determination of the potential availability of several metals (e.g., Pb, Cd, Cu, Zn etc.). However, other metallic elements present in soils at high concentrations (Fe, Ca) can possibly influence the results. This is even more emphasised in the case of Fe as EDTA partly dissolves Fe(hydroxides). Furthermore, sequential and Pb isotope analyses (206/207Pb) were used in order to obtain more detailed information. The results of this study showed that especially the concentration and crystallinity of Fe play a very important role during the extraction and this fact should be taken into account during result interpretation.

Keywords

single extraction; EDTA; soil; lead; Pb-isotope ratio; contamination

Acknowledgements

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P09.03

Calibration Methods in Determination of Volatile Organic Compounds in the Air Using Thermal Desorption - Gas Chromatograph System

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Background: Thermal desorption is a process using heat and a flow of inert gas to extract (semi)volatile organics from a sorbent and to introduce analytes in vapor phase into an analytical system. The instrument calibration is a critical step in analyses of volatile organic compounds (VOC) and requires loading and analysis of the standards as similarly as possible to that of the samples.

Objectives: The objective of this study was to evaluate two procedures commonly used to introduce calibration standards into sorbent tubes: 1) In vapour phase using the calibration solution loading rig and 2) Directly as liquids.

Methods: Liquid calibration standards of benzene, toluene and xylenes were introduced into sorbent tubes (using Tenax as a sorbent) at a mass of each component in the 20 to 500 ng/tube range. Calibration standards were analyzed by Markes thermodesorption unit connected with Agilent 7890A gas chromatograph with flame ionization detector. Separate calibration curves were constructed for each analyte and for both methods. The accuracy of the analyses was verified analyzing Certified Reference Standards (CRS).

Results: System calibration using the first method resulted in good calibration characteristic in the whole investigated mass range of selected analytes. CRS tube analysis using these calibration curves showed results within 15 % of the true value, which is considered as high accuracy according to international standard methods relating to calibration in VOC analyses.

The second method resulted in significantly poorer calibration characteristic, all of them indicating analyte losses.

Conclusions: The evaluation of two procedures commonly used to introduce calibration standards into sorbent tubes for analyses of VOC in the air using thermal desorption showed that instrument calibration is the most important step in these analyses and confirmed that high accuracy can be achieved only if loading and analysis of the standards are as closely as possible that of the samples.

P09.04

Interest and Validity of Integrative Passive Sampling Techniques for the In Situ Measurement of PAHs and Trace Metals in Wastewaters.

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Wastewaters convey important amounts of trace metals and organic contaminants into the environment. Still, the monitoring of dissolved micro-pollutants in wastewaters remains a major issue of environmental chemistry because of their high temporal variability and of the complexity of the organic matrix. Hence, measuring labile contaminants in wastewaters constitutes an interesting application of the various passive samplers that appeared in the mid 90's.

The Diffusion Gradient in Thin Films (DGT) technique was proposed as a robust way to quantitatively measure free and labile metal species in aquatic environments. Because the technique provides in situ preconcentration of metals, it allows avoiding most contamination problems. Moreover, because the measurement is performed in the acidic eluate of the binding resin, DGT considerably reduces the analytical difficulties linked to complex chemical matrices. Similarly, Semi-Permeable Membrane Devices (SPMD) have been developed in order to sample truly dissolved hydrophobic organic contaminants in water. As DGTs, SPMDs concentrate the contaminants and simplify detection limit and analytical interferences problems. In addition, DGTs and SPMDs are believed to sample bioavailable contaminants, and could eventually give an insight on the potential toxicity of the effluents.

In this study, the use of DGTs and SPMDs in wastewaters was investigated. Passive samplers were deployed directly into wastewater at different stages of the treatment for 6 days. In SPMDs, the systematic use of Performance Reference Compounds allowed to calculate proper sampling rates for individual SPMD that would have otherwise be underestimated. Accumulated metals and Polycyclic Aromatic Hydrocarbons were related to a time-weighted average labile concentration in wastewater. This experimental procedure allows estimating labile concentrations coherent with total dissolved concentrations.

Poster Presentations

P09.05

Determination of Non-Ortho Chlorobiphenyls in Three Deep Water Fish Species Caught West of Scotland

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Background: Chlorobiphenyls (CBs) are included on the Oslo/Paris Commission (OSPAR) list of chemicals for priority action due to their persistence, toxicity and potential to bioaccumulate. CBs 77, 81, 126, 169 are non-ortho CBs and are classed as 'dioxin-like' CBs. These compounds are more toxic than CBs with more than one chlorine in the ortho position.

A variety of extraction and clean up methods have been used for non-ortho CB determinations, including Soxhlet extraction and gel permeation chromatography, with high performance liquid chromatography (HPLC) being used to separate the ortho and non ortho CBs. With the advent of new extraction techniques such as accelerated solvent extraction (ASE) with fat retainers, extraction and lipid removal can be combined in a single step. The increased sensitivity of modern mass-spectrometers (MS) means high resolution- MS is no longer a prerequisite of non-ortho CB analysis.

Deep water fish species tend to live longer and feed at a higher trophic level than shallow water fish species and therefore, may have a greater potential to accumulate contaminants. FRS has CB data from deep water fish species to the west of Scotland, however, this is restricted to one species for ortho -CBs only.

Aims: The aim of this study was to develop a GC-MS method for the determination of non- ortho CBs (CB77, CB81, CB126 and CB169) in biota and analyse deep sea fish.

Method: Extraction of CBs was by accelerated solvent extraction (ASE), with fat retainers, followed by silica column chromatography. CBs are separated on the basis of structural polarity by high performance liquid chromatography (HPLC) on a Cosmosil 5-PYE column.

Results: A method was developed for the determination of non-ortho CBs in biota using ASE with fat retainers and low resolution GC-MS. This method was applied to deep sea fish (Round Nosed Grenadier, Black Scabbard and Black Dogfish) caught from the Atlantic shelf edge at depths of between 1000-1500m. Preliminary data will be presented at the meeting.

P09.07

Development and Validation of Flow-Injection ICPMS Methodology to Determine the Elemental Composition of Dissolved Otolith Samples

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The ear stones of fish (otoliths) consist of approximately 96% calcium carbonate (as aragonite), 3% protein and 1% of other inorganic components. Otoliths are metabolically inert and are not subject to resorption, therefore their composition does not change after deposition. Elements incorporated into otoliths at the time of deposition reflect the physical and chemical environment of the fish's habitat and so determining the composition of otoliths can reveal information on environmental conditions and has the potential to elucidate fish migrations, population structure, and natal habitats. The purpose of this study was to develop analytical methodology for the determination of Ca, Na, Mg, Mn, Sr, and Ba in otoliths using Inductively Coupled Plasma Mass Spectrometry (ICPMS). Sample preparation was optimised so that otoliths were digested using 50% v/v nitric acid and subsequently diluted to obtain a final sample solution consisting of 0.2% total dissolved solid in 2% v/v nitric acid. Matrix-matched external calibration standards were used. Flow-Injection Analysis System (FIAS) and instrument operating conditions were optimised to consist of triplicate 200 µl sample injections, 1.52 mm ID pump tubing, and 20 rpm FIAS pump speed. The ICPMS was run with a hot plasma (1500 W) in order to reduce polyatomic interferences. The performance of the method was assessed through the use of a certified reference material (FEBS-1) and a small inter-laboratory comparison exercise. The performance of the optimised method was good for Na, Mg, Mn, Sr, Ba and Ca in comparison to the certified values in FEBS-1 (93-99% recovery; 2.1-9.6% RSD; n=5). It also produced results comparable to those of two other laboratories. The validated method was used to examine the variability of cod otolith composition between sampling areas for the purpose of determining the degree of isolation among 0-group Atlantic cod. In common with previous studies Mg, Mn and Ba were found to give the greatest discriminatory power for this purpose.

P09.06

Geochemistry and Electron Probe Microanalyzer (Epma) Characterization of Primary Gold from the Bukit Koman Area (Raub), Pahang, Malaysia

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Keywords: EPMA, primary gold, roundness, sphericity, fineness values

As gold is precious and usually occurs in very small quantities as primary gold in mineralized quartz veins and secondary gold in alluvial deposits, the EPMA turn out to be the perfect tool for characterizing the primary and secondary gold by utilizing the BSE and SE images, EDS and WDS scans, X-ray maps and geochemical datas. The Bukit Koman area is one of the most important gold mining areas in Peninsular Malaysia. This area lies in the western side of the Second Gold Belt of Peninsular Malaysia and is bounded approximately by latitudes from 3 48' N to 3 51' N and longitudes from 101 51' E to 101 53' E. Rock types in this area occur in a complex of lithology of sedimentary and metasedimentary rocks which are part of the Raub Group and Lipis Group. Normally gold occur associated with quartz veins in fractures, faults and joints hosted in strongly deformed graphitic shale. Generally, four types of faults controls gold mineralization in this area namely compression, tension, minor oblique and major oblique faults. As primary gold, they show angular to sub angular roundness and discoidal to sub discoidal sphericity. Gold grains from the vicinity of quartz veins range from 20 µm to 80 µm in size. Gold (as electrum) in quartz veins are mainly associated with pyrite (FeS₂), arsenopyrite (FeAsS), chalcocopyrite (CuFeS₂), scheelite (CaWO₄), rutile (TiO₂) and iron oxides. Gold (Au) composition together with variable quantities of Ag, Te, Cu, Al, Fe and Si shows some variation in this area. The Bukit Koman gold (Au) composition ranges slightly from 89.48 wt% to 95.28 wt%. EPMA data of these samples show that there are four distinctive fineness values for primary gold in this area, namely, 957.97, 926.94, 898.88 and 880.77. These distinctive average fineness values suggest at least four different episodes of gold mineralization in the Bukit Koman Area.

P09.08

Development of a Analytical Method for Methylmercury Determination in Marine Sediment

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Background: Methylmercury is of particular concern due to its extreme toxicity and its ability to bioaccumulate in fish tissues; this compound is routinely determined in fish samples to control the contamination levels. Recently MeHg contents in sediment played an important role in the mercury cycling. However, the determination of MeHg in sediment is not easy: the very low concentrations of MeHg in marine sediment account for <1% of total Hg and the presence of interfering substance represents the main analytical complications. In this study a analytical method for MeHg determination in marine sediment has been developed. The singularity of this method is the use of Direct Mercury Analyser (EPA 7473). The analytical performance of this method was evaluated by analysis of reference certified sediment: CRM-580.

Methods: Analysis of MeHg in sediment samples was made by separation of organic mercury forms from the sample matrix, then MeHg extraction with organic solvent and finally reading of Hg contents. The analytical performance was checked taking in account various parameters: repeatability, reproducibility, recovery, absolute detection limit (LOD) and limit of quantification (LOQ).

Results: Repeatability, as variation coefficient, relating to measurement made under repeatable conditions (same method, same operator, narrow time) was 3,5%; reproducibility, relating to measurement made under reproducible conditions (same method, different operator, long time period) resulted equal to 4,8%. The results obtained showed a good agreement with the certified values. LOD and LOQ were respectively 0.1 ng MeHg and 0.2 ng MeHg which corresponded respectively to 0.9 ngg⁻¹ and 1.5 ngg⁻¹ in the analysis of dry samples.

Conclusion: Low LOD and LOQ values, repeatability and reproducibility less than 5%, high founded recovery, corroborate a good method performance. The methodology proposed is relatively simple, then this method can be considered a good alternative over the existing methodologies for routine analysis of MeHg in marine sediment.

Poster Presentations

P09.09

Withdrawn

P09.10

Towards Fungal Descriptors as a New Tool for the Assessment of the Quality of Agricultural Soils

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Typically, ecotoxicological studies concerning the soil ecosystem are performed using a combination of two approaches. The first one deals with the dynamics of toxic compounds in the soil, the second one concerns the effects of these compounds on selected non-target species. In addition, ecotoxicological risk assessment needs probabilistic or modelling features.

Nevertheless the interpretation of the results obtained using these approaches is often difficult in the case of soil micro-organisms (the main actors of soil functioning) and can be in many cases non-conclusive. It is especially true regarding cultivated soil ecosystems because of numerous pedoclimatic and environmental situations, agricultural practices, parameters and protocols to measure their levels... Thus, for all these reasons, a biological state of reference is difficult to precise in cultivated soils.

We develop an approach intended to combine physico-chemical and biological descriptors of the soil (bacterial/fungal biomass and activity) in order to (i) define characteristics of the biological status of the soil, (ii) assess/rank the effects of soil pollutants (copper) on that state, in excluding the natural variations of the microbial communities in response to pedoclimatic and agricultural conditions.

Here, our work is centred on three main topics: -the development of analytical tools to characterize fungal biomass for natural (meadow) or cultivated (crop) soils, -the study of the variation of this microbial community in response to environmental (pollutions) or agronomic (practices) in microcosms, -the validation of these descriptors (ergosterol, PLFAs, 18S DNA) as indication the soil quality. The experimental data will be used for mathematic modelling in order to explain/predict the variation of the fungal biomass compare to the other compartments (bacterial communities and the activities).

P09.11

Characterization of Organic Micropollutants in River Sediment by Ion Profiles Obtained using GC/MS System

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Keywords: river sediments, pollutant profiles, aquatic environment, GC/MS

Background The specific human activities lead to contamination of the aquatic environment with a wide variety of natural and synthetic compounds not found prior to modern times. Due to an incomplete elimination in wastewater treatment plant (WWTP) residue of contaminants are found both in waste and surface waters. Many of these compounds provide a means of identification sources of inputs and pathways of movement of chemicals through ecosystem.

Objective The present paper purpose is the Mass Spectrometric (MS) characterization of organic pollutants to evaluate the degree of contamination of the surface waters sediment in high populated catchments from Romania. The samples were collected from few places along of the Somes river (North west of Romania) near Cluj-Napoca (400 000 inhabitants).

Methods Sediment sample were prepared by Ultrasonic Solvent Extraction (USE). An aliquot (PMF: 2g) of freeze-dried sediment was extracted successively with 10 ml CH₂Cl₂+methanol (2:1) 3 times for 15 min. every. The extract was fractioned on Al₂O₃ with following organic phases: n-hexane, n-hexane+CH₂Cl₂ (1:2), CH₂Cl₂+methanol (1:1) and methanol respectively. The final extracted was dried to 1ml in n-hexane The GC/MS analyses were performed using a mass spectrometer operated in EI mode to 70 eV.

Results and Discussion The families of pollutants are visualised by chromatograms on diagnostic ions obtained: 1) n-Alkanes which show compounds with the number of carbon atom ranging from 12 to 30. 2) Acyclic isoprenoids compounds with a large number of methyl branching points in their structure, including pristane and phytane often used as an indicator of depositional environments. 3) Pentacyclic triterpanes (Hopanes) is a class of compounds that has a great impact on petroleum geochemistry, as source indicators. 4) An important group of pollutants found in the sediment samples is the Lineal Alkylbenzens (LABs). They comprise isomers of LABs with number of carbon from 10 to 13. 5) An abundant class of compounds is Polycyclic Aromatic Hydrocarbons (PAHs) of environmental concern due to their carcinogenic proprieties. 8) Sulphonated Polycyclic Aromatic Hydrocarbons (SPAHS) is other important group of pollutants used very often as biomarkers by the source information.

Conclusions The obtained profiles of pollutants are a function of their sources and reflect the industrial and domestic activities at regional level.

P09.12

Fourier-Transform Infrared Spectroscopy (FT-IR) as High-Throughput Techniques for Environmental Chemistry

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Background: In assessing the interactions of biota with environmental parameters a battery of single assay techniques have been optimised for parameters such C%, N% N-NH₄, C:N ratios etc and are important indicators for waste management. The application of these in large field scale experiments usually requires significant investment in sample preparation, time and expense. FT-IR is a rapid optical technique requiring minimal sample for the direct analysis of solid and gaseous samples, as well as liquids after evaporative preparation. It delivers chemical "signatures" from virtually all organic molecules with high levels of quantification and sensitivity.

Objectives: The study compared FT-IR to traditional assays commonly applied to the study of soils and also composts. Specifically the study sought to identify signatures of "maturation" within composts containing a variety of recyclable wastes.

Methods: Samples were obtained from an experimental site at intervals up to an 86-day maturation point. Minimal sample preparation was then applied consisting of drying and rapid milling to a fine powder. FT-IR analysis used a Bruker Optics Equinox 55 equipped with a attenuated total reflectance (ATR) accessory. Data analysis was undertaken using OPUS (Bruker Optics) and MatLab.

Results: The results showed that FT-IR could identify chemical signatures that could be directly correlated with decomposition time, waste type and a basic mechanistic understanding of the microbiological activity. In contrast the results from a battery of single assays, for pH, electrical conductivity, OlsensP, C% N%, N-NH₄ and N-No₃ etc, showed little in the way of significant or interpretable differences.

Conclusions: FT-IR was shown to be a rapid and sensitive technique for biochemical analysis offering significant advantages of the traditional chemical assays. The application of multivariate statistical modelling for such data sets as well as the wider applications of FT-IR in environmental chemistry will be discussed

Poster Presentations

P10.02

Synthesis of Cements from Rice Hull Ash Using Microwave Oven

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There is a continuous interest in the utilization of agricultural by-products and residues in productive processes, in order to provide renewable and environmental-friendly technologies and materials. For instance, rice hull is an abundant by-product of agricultural activities around the world. It contains about 10-30% of silica as inorganic material which is responsible for its rigidity and intrinsic mechanical resistance.

In previous works, our research group has developed a method to prepare $\beta\text{Ca}_2\text{SiO}_4$ using rice hull ash as starting material. $\beta\text{Ca}_2\text{SiO}_4$ is an important component of Portland cement and presents excellent properties as construction material. Commercial Portland cement is produced at temperatures around 1500°C. The utilization of rice hull ash allows the synthesis to be completed at 800°C.

This work describes the utilization of a domestic microwave oven in order to prepare $\beta\text{Ca}_2\text{SiO}_4$, using rice hull ash as starting material. Under these circumstances, a solid susceptor has to be used to provide high temperatures (above 800°C). The susceptor is a solid capable of absorbing microwave radiation causing a fast temperature rising. As a consequence, this material helps to transfer thermal energy to other solids present around the susceptor and promoting chemical reactions. We develop a copper-based susceptor.

An aqueous suspension of the solids (silica, calcium oxide and barium chloride, in stoichiometric proportion) was prepared and treated in an ultrasonic bath for 60 minutes. After drying, solids were grounded, sieved and heated in the microwave oven using the copper-based support. This method allowed the synthesis of $\beta\text{Ca}_2\text{SiO}_4$ in commercial microwave oven after 10 minutes of radiation.

P10.04

Production of Struvite by Ion Exchange Isothermal Supersaturation Technique using a Microporous Carboxylic Resin

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This work considers a new productive process which permits phosphate and ammonium sustainable recuperation producing a high quality and slow release commercial fertilizer - struvite MgNH_4PO_4

6 H₂O - from natural and waste waters. In this way the quality of the aquatic ecosystems will be improved and in the same way the non renewable natural sources such as phosphates will not be exploited, which is one of the most important tasks of the modern environmental chemistry. The Ion Exchange Isothermal Supersaturation (IXISS) process allows the recovery of phosphates and ammonium from wastewaters producing - besides magnesium from seawater- the struvite. This technique allows obtaining the target substance (struvite) beyond its solubility level. The supersaturated solution remains stable for a long period and after leaving the column it crystallizes spontaneously. Previous studies have been determined that the ion exchanger required to that process must be a carboxylic and microporous resin. Nowadays it is difficult find a commercial resin with those characteristics, so it has been necessary a wide search of them. Finally, it has been chosen the Amberlite IRC86 resin. This paper describes the characterization of this resin by the determination of its ion exchange capacity and its humidity. Moreover some assays have been carried out with this resin in fixed bed and they have been determined the suitable feed concentration and flow rate to run in column. The stripping of magnesium has been determined along the time and the purity of the obtained product has been analyzed by X ray diffraction. On the other hand, it has been studied the possibility of use the resin Amberlite IRC86 to the selective recuperation of magnesium from seawater. This fact reduces the price of the process. The main problem of this process is the selection of a resin that permits a selective recuperation of magnesium respect of calcium. It has been observed that this resin procures a selective recuperation of magnesium.

P10.03

Membrane Conditioning Influence on Diffusion for PEMFC Application

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Polymer electrolyte membrane fuel cells (PEMFC) are a promising technology for the generation of environmentally clean energy. The core of a PEMFC is the membrane electrode assembly (MEA) that is made up of a cation exchange membrane placed between two porous electrodes physically bonded to the membrane and two gas diffusion layers. These cationic membranes based on perfluorosulfonated polymers act like a physical barrier between the anode and the cathode avoiding direct contact between reactants, but allowing the transport of protons at a rate enough to fulfil reaction rate requirements. Membrane has to be conditioned before use. This conditioning step can change membrane counter-ion and modify its physical characteristics which affect to the diffusion coefficient.

The objective of the present work was to analyse the effect of conditioning methods on physical characteristics, swelling pressure, hydration number and thickness of the membrane. These properties affect on proton diffusion, calculated by diffusion coefficients. In order to analyse and quantify the effect of conditioning techniques on membrane performance, several experiments with Nafion 117 cation exchange membrane were carried out. Membrane was conditioned following different conditioning methods. The reactives used were ultrapure water, nitric acid, hydrochloric acid, hydrogen peroxide, sodium chloride, potassium chloride and ethylene glycol all of them carried out at room temperature. Some conditioning methods were carried out using heated solvents at 100 °C.

Results related with effect of conditioning on physical characteristics of the membrane show a clear anisotropic behaviour being the swelling clearly different on the three spatial directions. Moreover, we can see an increase of hydration number while swelling pressure and thickness of the membrane rise. About diffusion coefficients, they were modelled using Nernst-Planck equations. Calculated coefficients were in the range 10⁻⁸-10⁻⁹ m²/s. Diffusion coefficient depends on used conditioning method.

P11.01

Withdrawn

Poster Presentations

P11.02

Withdrawn

P11.03

Interaction Between Microorganisms and Materials : Choice of Growth Media for Experimental Studies

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Unravelling the effects of microorganisms on materials in the natural environment is complicated by the fact that comparable observations under similar but sterile conditions are not available. Another difficulty is the choice of reliable tracers to evaluate the alteration rate of materials in laboratory experiments. Elements useful for experimental study should be good tracers of alteration rates, implying that they should not be complexed with other constituents in the medium (sodium, boron, caesium or lithium).

Our objective is to evaluate the influence of microorganisms on the alteration rate of materials, by measuring the flux of elements from the solid to the liquid phase. Towards this goal, new bacterium-specific growth media have to be designed, which take the major constraints inherent to such studies into account. Indeed, a suitable medium should fulfill the criteria of allowing both bacterial growth and detailed chemical analysis. Many of the growth media described in the literature so far, have been designed by microbiologists primarily for optimal biomass production. In a majority of cases, such media are not compatible with the chemical analyses needed for the investigation of materials alteration. In this work, two main types of modifications in medium design were performed. On the one hand, medium composition was simplified when the minerals whose alteration was under study themselves contained nutrient elements (e.g. iron, phosphorus, magnesium, sulphur or carbon), so that these were not required in the growth medium. On the other hand, the maximal total ion concentration of the medium was reduced to fit the requirements of analysis of trace elements by ICP-MS. These modifications allowed to define new specific media for *Pseudomonas aeruginosa* and for *Acidithiobacillus thiooxydans*, which allow both bacterial growth at 25°C in the presence of silicates, and the detailed chemical analysis of material alteration associated with the growth process.

P11.04

Application of pH-static System for the Determination of Metallic Contaminant Leaching from Pb Smelter Fly Ash

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Background: Mineral wastes from the base metal metallurgy are hazardous materials significantly affecting the environmental systems. Fly ashes from Pb smelters are highly reactive waste products that can be partly emitted by smelter stacks. As a result, these materials are responsible for a significant pollution of soils in the vicinity of the smelters.

Aim: The aim of this work was to study the release of metallic contaminants from a Pb smelter fly ash using the pH-stat leaching tests.

Methods: The pH values between 3 and 9 were imposed to this material during the leaching. The physico-chemical parameters (pH, Eh, conductivity) and concentrations of major elements and metals (Pb, Zn, Cd, Cu, Ni) were measured in leachates (Schott multimeters and atomic absorption spectrometer). The chemical analysis was coupled with the speciation-solubility modelling using the PHREEQC-2 geochemical code and the mineralogical investigation of solid products by X-ray diffraction analysis (XRD).

Results: Generally, highest amounts of metals were released under acid conditions. Cadmium and zinc were significantly leached from the fly ash at pH values of 3 and 4 (up to 3322 mg/kg and 3286 mg/kg, respectively). The concentrations strongly decreased under neutral-to-alkaline conditions (pH 7-9). Significantly lower amounts of Pb were leached in the pH range of 3-7 (mean: 1300 mg/kg) with a sharply decreasing trend towards the alkaline region. The leaching behaviour of Ni and Cu showed a minimum at pH 6; their concentrations were 3 orders of magnitude lower in comparison with other metals (units mg/kg). Discussion: Cadmium represents the most important contaminant in this system being probably released into the solution through the dissolution of primary caracolite ($\text{Na}_3(\text{Pb,Cd})_2(\text{SO}_4)_3\text{Cl}$). Lead concentrations in leachate are likely controlled by the precipitation of newly formed products, mainly $\text{PbSO}_3/\text{PbSO}_4$ and phosgenite ($\text{PbCl}_2 \cdot \text{PbCO}_3$).

P11.05

Heavy Metals Immobilization by Phosphates in Polluted Soils from an Industrial Site

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"Background:" Phosphates minerals have the potential to immobilize heavy metals such as: Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in contaminated soils so that heavy metal phosphates are more stable under ambient environmental conditions than the analogous oxides, hydroxides, carbonates and sulphates.

"Aims:" In this study synthetic hydroxyapatite (HA), fluoroapatite from Florida (USA) (FAP) and from Morocco (MAP1 and MAP2) were used to investigate the effectiveness of phosphates to attenuate heavy metal mobility for a future field use on a vast scale.

"Methods:" Soils were from an industrial site, part from "Nuova Rayon S.p.A." and part from "Immobiliare SNIA S.r.l." (Rieti, Central Italy), where wastes from the production of synthetic textile fibres (e.g. H_2SO_4 , ZnSO_4 and TiO_2) were spilled on the soil. The fraction < 2mm were used for the analyses. Soils chemical and mineralogical compositions were determined by ICP-AES and XRD analysis. Leaching tests on the polluted soils were carried out using solutions with pH: 4, 5, 6, and 7, for 24h (interaction time) at room temperature (25 ± 2 °C). Metal immobilization tests were carried out in batch at room temperature with suspensions prepared with 5 g of the soil and phosphates (from 0.2 g to 5 g) in 100 ml of pure water. All the solutions were analysed by ICP-AES and the solid materials were analysed by SEM-EDS.

"Results and Discussion:" ICP-AES and mainly XRD analyses show that phosphates can immobilize heavy metals. Generally, the effectiveness of natural apatites were higher than HA, suggesting that phosphates could be used as a cost-effective option in remediating metal-contaminated soils, wastes and water.

Poster Presentations

P11.06

Vanadium Recovery From V-Na-K-S2O7-SiO2 Catalysts Used in SO2 Industrial Conversion.

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

Aim: The aim of this work is to recover the vanadium, without the use of any amine and organic solvent.

Methods: The kinetics of the dissolution of the catalytic phase in acido-basic aqueous (H₂O, H₂SO₄, NH₃, NaOH) solutions was studied. Vanadium recovery by precipitation from the leaching solutions was then studied in terms of concentration, pH and H₂O₂ treatment. Electrochemical way was studied in terms of pH and voltage.

Results: Whatever the leaching solution, the catalytic phase (Na, K, V) was dissolved within two hours. In the best precipitation conditions, a large amount of the vanadium forms a red precipitate within 6 hours. Electrochemical way, as function of pH and voltage, leads to the precipitation of a vanadic yellow phase, but at lesser extent.

Conclusions: This work i.) confirms the danger for groundwater to leave the catalyst in open dump ii.) shows the possibility of leaching the catalytic phase before throwing the catalyst out, iii.) shows the possibility of recovering the vanadium from the leaching solution.

P11.07

Wastewater Treatment Plant Faced to Detergents and Pharmaceutical Substances What processes to decrease their release to aquatic system?

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A general awakening about the impact of the human activities on the environment has emerged and is nowadays a common project for political authorities, scientists or citizens. Today, more than 100 000 chemical products are registered by European Union, 30 000 are currently used in amounts greater than 1 ton. With the implementation of the European Water Framework Directive and its objectives to ensure achievement of the good status of water systems by 2015, a need to improve knowledge on the fate and behaviour of a wide range of organic pollutants in wastewater treatment plant has emerged. Wastewater treatment plants are considered as the main entrance into aquatic systems for many emerging contaminants like alkylphenol-polyethoxylates (APEO) and pharmaceutical substances. It is now well known that many aquatic media (surface water, marine water, groundwater) are chronically contaminated by both classes of compounds. Regarding their ubiquity and their potential toxicity, some of these compounds require a specific attention.

The work focuses on the occurrence of APEO and their metabolites and pharmaceutical substances for human uses from a wide range of therapeutic classes (antidepressants, non steroidian anti-inflammatory drugs, anti spasmodic, etc...) in different wastewater treatment plant purification processes. Each plant (representative of the French purification process network) has been studied regarding dissolved phase, suspended matter and sludge at different levels of the purification process (influent, effluent, specific key point).

The results highlight the presence of the 2 classes of compound in each studied phases in concentrations ranging between ppt and ppb. APEO, especially their metabolites, are present in higher concentrations than pharmaceuticals (whatever the matrix). Some trends in term of quantification and distribution during treatment processes are also presented.

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P11.08

P11.09

Experimental Design for Determination of Optimal Conditions in Alkaline Baths for Aluminium Extrusion Dies Cleaning

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Background: The aluminium extrusion industry has a significant presence and economic importance in the Galician region (in NW Spain). The aluminium extrusion process leaves extrusion dies filled with aluminium, making disassembly and preparation for re-use difficult. To remove the aluminium, the industry has relied for years on a cleaning method where the dies are loaded into tanks filled with a hot solution of NaOH and water to soak. This dies cleaning process generates large volumes of alkaline spent baths and large amounts of aluminium hydroxide sludges.

Objectives: The aim of this work consists in optimize the parameters affecting this process in order to enhance the alkaline bath life and reduce the volume and frequency of spent baths treatment.

Methods: A full factorial designed experiment has been set for studying four factors a 2-levels, 24. It has been considered four factors or parameters that could affect the efficiency of hot alkaline dies cleaning process: NaOH initial concentration (% m/v), stirring rate (rpm), time of permanence of the die in the cleaning solution (min) and temperature (° C). Each process parameter is studied at 2-levels based on the ones found in the extrusion companies. The response of interest was dissolved aluminium concentration (g/L) in the alkaline bath. Each experimental condition has been replicated twice (involving 32 runs).

Results: This model allows the evaluation of the effects of each factor and also the interaction effects within factors. Data analysis is being performed using the statistical package MINITAB. Preliminary results show that temperature and permanence time are the most influent factors in aluminium dissolutions, followed in importance by initial NaOH concentration. Stirring rate can be considered as negligible.

Conclusion: Control of these parameters during dies cleaning according to the experimental design will offer a wide range of advantages for Galician aluminium extrusion companies: chemical savings, increase useful chemical life, reduction of hazardous waste removal costs and others.

Withdrawn

Poster Presentations

P12.01

Aqueous Photocatalytic Oxidation of Oxygenated Fuel Additives Using Sulphur-Doped Titania

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Objectives: In this work, aqueous photocatalytic oxidation (PCO) of 2-ethoxy ethanol (2-EE), methyl-tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) was studied using sulphur-doped titania with varying sulphur content under near-UV, artificial visible light and solar irradiation.

Background: 2-Ethoxy ethanol and MTBE can be found in natural aquifers as a result of accidental fuel spillage, whereas TBA is known to be a product of MTBE hydrolysis. These substances are resistant to biodegradation and other conventional treatment strategies, although previous studies demonstrated their effective PCO with UV-irradiated TiO₂. Commercial photocatalysts, however, due to wide band gap of TiO₂ are able to utilise only about 4% of solar radiation using UV part of solar spectrum reaching the Earth's surface. This makes photocatalysts sensitive to visible light a point of interest on the course of promotion of practical application of PCO.

Methods: Several sulphur-doped titania catalyst with different dopant concentration were synthesised. Their performance was tested on the oxygenated fuel additives under different spectra radiation following the dependence of the catalyst performance on the content of the dopant. The testing results were compared to those obtained with Degussa P25 titanium dioxide.

Results and discussion: Visible-light PCO with S-TiO₂ appeared to be ineffective against 2-EE. Nevertheless, MTBE and TBA readily yielded to PCO showing the efficiency exceeding those of UV-irradiated Degussa P25: PCO experiments with S-TiO₂ were conducted also under UV-irradiation to allow correct comparison. The acidic media showed the best performance followed in descending order by basic and neutral media. The adsorption on the surface of the catalysts appeared to be poor for 2-EE and MTBE, and reasonably fair for TBA. The experiments with MTBE and TBA under solar irradiation showed the PCO efficiency of the doped catalysts comparable to or even surpassing that of Degussa P25 photocatalys.

P12.02

Withdrawn

P12.03

Zeolitic Tuff for the Removal of Humic Substances from Water

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Background: Humic substances (HS) are produced by biological decomposition of organic matter from plants and other organisms and account for about 50–80% of the organic matter in water from terrestrial sources, lakes, and rivers. HS are natural polymers containing aromatic blocks, with a broad molecular weight distribution and high chemical heterogeneity. They have an acidic character due to carboxylic and phenolic groups. Depending on their solubility in water, HS are distinguished into fulvic acids, humic acids (HA) and humins. HA is the fraction soluble in water at pH > 2. In previous studies, we have shown that the zeolitic Neapolitan yellow tuff (NYT) was able to bind HA through the action of surface extraframework cations. The HA-binding properties were markedly enhanced when the zeolitic material was enriched with divalent cations, especially Ca²⁺, that probably act as micro-bridges between the negative charges of the HA carboxylic and phenolic groups and those on the tuff surface. Accordingly, we have proposed the use of Ca²⁺-enriched tuff as an effective and relatively cheap method to remove HA from water.

Aims: Here we report a study on the HA-adsorbing properties of new Ca- and Mg-NYT derivative forms obtained by thermal treatment at 170 °C of the raw material with concentrated salt solutions.

Methods: A solution of 3.5 M CaCl₂ or MgCl₂ was added to native NYT (1.0 mL : 1.0 g) and the mixture was kept at 170 °C in an open container for three days. The powder was then washed with small volumes of water until the conductivity did not change anymore. Sorption isotherms were obtained by batch method at 25 °C in Tris/HCl buffer, pH 7.2.

Results: Experimental data showed that the NYT derivatives enriched with divalent ions with the procedure above reported exhibited HA sorption ability markedly higher than the raw materials.

Conclusion: This investigation clearly show that NYT enriched with metal ions by thermal treatment could be used for HA removal in water plant.

P12.04

Exhausted Coffee Waste as Detoxification Agent for Aqueous Solution Containing Hexavalent Chromium

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Background: Recently, the study of Cr(VI) adsorption on exhausted coffee revealed that Cr(VI) is reduced to Cr(III) as a part of the sorption process[1].

Objective: The objective of the present work was to assess the effect of initial pH and sorbent mass on Cr(VI) reduction and removal using exhausted coffee waste.

Methods: Batch experiments were performed at four different initial metal concentrations, three pH values and different sorbent mass. Column experiments using a 10 cm length and 1cm internal diameter glass column were performed to study the effect of flow rate and bed depth on Cr(VI) reduction and adsorption. Experiments were carried out at pH 3.0, three different flow rates, three bed lengths and three metal initial concentrations.

Results and Discussion: Results showed that initial pH solution plays an important role in both adsorption-reduction processes. Although Cr(VI) reduction is favored at pH 2, initial pH 3 is the most appropriate for metal detoxification because both processes, adsorption and reduction, occur in similar extent and provide a major metal removal yield. In the experimental conditions, both reduction and adsorption processes are favored when increasing sorbent mass.

From the column results, the reduction process is favoured at low flow rates. During 24 hours of column operation, at flow rates lower than 15 mL/h and for an initial concentration of Cr(VI) 5.2 mg/L, the maximum outlet chromium concentration was 0.3 mg/L, for all bed depth studied. It must be remarked that chromium is released from the column as non-toxic Cr(III) ions, thus, the inlet effluent is detoxified and chromium concentration is under the limits fixed by the environmental directives.

Acknowledgements: Thanks are due to Frédérique Backaert for helping in the experimental work. This research was supported by Ministerio de Ciencia y Tecnología, Spain, CTM2005-07342-C02-01/TECNO. References: [1] Tanghe, B; Fiol, N; Villaescusa, I., 7th European Meeting on Environmental Chemistry (EMEC7), Brno, 2006.

Poster Presentations

P12.05

Cost Effective Solar Photocatalyst for Wastewater Treatment

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Background: Titanium dioxide (TiO₂) is non-toxic, chemically stable and relatively inexpensive. Its active only in the ultraviolet (UV) region because of its wide band gap (E_g = 3.2 eV). Several approaches for TiO₂ modification have been proposed. However, all these approaches either required a special apparatus for synthesis or required tight control of experimental conditions. Moreover, to prepare the TiO₂ nano particles, relatively expensive chemicals as a source of titanium are required. Many researchers showed the poor activity of the P25 under solar or visible light.

Aim: modifying the P25 (relatively cheap and available commercially) to improve its solar photoactivity is an interesting subject for wastewater treatment. P25 Degussa was doped with thiourea (TH) as a source of sulfur raw material.

Methods: S-doped TiO₂ powders was prepared as follows: 0.25, 1.5, and 3 g (TH) was dissolved in 75 ml of ethanol, then 1 g P25 Degussa was added slowly to the solution. The system was then left for stirring for 4 h at room temperature, and then dried at 85 °C for 8 h to evaporate ethanol. The obtained powder was grounded and calcinated for 4 h in air (100, 450, 550 and 700 °C). The photocatalyst was characterized by DRS, XRD, and SEM and the activity was examined by solar-decolorization of azo dye Orange II in waste water.

Results: The results obtained showed that decolorization rate increased 1.5 time as the calcinations temperature of the S-doped-TiO₂ increased, from 100 to 550 °C, which is attributed to gradual crystallization of the anatasa TiO₂ with temperature rising.

Discussion: Further increase in the calcinations temperature (700 °C) resulted in an obvious decrease in the activity due to the increase of the crystalline size. It was found from XRD results that increasing the TH reduced the crystalline size. S-doped-TiO₂ (at 550 °C) has an approximate crystalline size of 19 nm while that of the non doped was 20 nm. This means the TH can retard the grain growth of TiO₂ to some extend.

P12.08

pH Effect on Fenton's Reaction during the Phenol Removal in Wastewaters

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Area: Water treatment and reuse

The aim of this study is to investigate the effect of operating pH by applying Fenton reagent to phenol degradation of wastewaters. Although several studies have analyzed the reaction in dept, currently it is not yet established the causes that determine the optimal operating pH. Experimentally has been checked that pH is a control parameter of phenol removal. The data collected demonstrate the effectiveness of Fenton oxidation operating at acidic levels, around pH=3.0. It was noticed that acidic levels between pH=3.0-4.0 significantly increased the phenol oxidation rates for the same reagent dosages. To try to explain these effective system conditions this work has analyzed separately the performance of hydrogen peroxide, iron species and organic matter depends on pH.

Here is demonstrated the important contribution of oxidant species, because the chemical treatment requires the hydrogen peroxide activation to generate free radicals that react with the organic matter. The experimental results show that the oxidant decomposition takes place at acidic conditions higher than pH>3.0. Working at lower acidic values, lower than pH=2.0, hydrogen peroxide is a stable specie that no lead up to oxidation reactions.

The maximal degradation occurred between pH=3.0-4.0 can be explained on the basis of the dependences of ferrous ions and ferric ions on this parameter. The activity detected for pH=3.0 can be associated to the formation of Fe(OH)₂ that yield for OH• production along Fe(II) regeneration. At lower pH, Fe+3 is more concentrated, being the regeneration of Fe(II) and TOC degradation lower. For larger pH although Fe(OH)₂ dominates, the solution becomes unstable with Fe(OH)₃ precipitation.

On the other hand, during the first oxidation mechanism steps phenol is degraded to dihydroxylated rings (catechol, resorcinol and hydroquinone) that are oxidised to the respective quinones compounds. The analysis of these species indicates that once oxidant is activated, it takes place the generation of these reaction intermediates in the system. All compounds reach similar concentration levels into the range pH=3.0-4.0. However hydroquinone show a maximum concentration value at pH=3.0 during the first t=30 minutes of the oxidation. This effect may be related with the existence of a viable oxidation pathway that generates species with high formation rates.

Keywords: phenol, pH effect, Fenton reagent; hydrogen peroxide; iron species

P12.06

2-aminobenzothiazole Degradation by Free and Immobilized Rhodococcus Cells

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Benzothiazoles are organic compounds made of a benzene ring fused with a thiazole ring. Widely used in the industries of pneumatics, medicines, fungicides, herbicides and dyes, their presence in different compartments of the environment, particularly the aquatic one, can not be avoided. Their toxicities towards microorganisms, animals or humans led researcher teams to study their degradation.

Biodegradation of benzothiazoles is still few described in the literature. Among the studied benzothiazoles, some are rapidly degraded but others like 2-aminobenzothiazole called ABT remain persistent. To improve the efficiency of ABT degradation, a new approach combining bio- and photodegradation processes was investigated. Direct photolysis did not show any degradation on the molecule since the molecule does not absorb in the solar spectrum, but degradation was observed both in presence of bacteria *Rhodococcus Rhodochrous*, light and an iron complex acting as photoinducer. FeNTA complex - NTA for nitrilotriacetic acid - is used in the experiments as a good model of iron complexes present in organic natural mater. Degradation products were identified and the main pathways involved in ABT degradation processes were established.

To optimize the degradation process, immobilized microbial cell systems was developed. Compared with free suspended cells, immobilized cells exhibit tolerance to toxic substances, enhance fermentation productivity, present more biological and physical stability and are re-usable. Polysaccharide gel matrices, particularly Ca-alginate hydrogels are the most frequently used materials for harmless cells entrapment so the experiments were led using this immobilization technique.

The main objective of the work presented here is the qualitative and quantitative comparison of ABT degradation between free cells system and immobilized cells system combining bio- and photodegradation processes. The reusability of both systems is also an important aspect of the comparison.

P12.09

Electrocatalytic Materials for Cleaner Environment

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Electrooxidation, part of a domain of great interest electrocatalysis, is more and more intensely researched. The electrochemical methods of anodic oxidation for the treatment of waste waters containing organic polluting agents have drawn attention [1] mainly because of the easy control and high efficiency ensured by the use of new electrode materials [2]. Later, modified DSA type electrodes incorporation Sn, Sb and Ir have been used for the oxidation of some organics pollutants [3].

Three different oxide electrode SnO₂/Ti, Sb/SnO₂/Ti, SnO₂/IrO₂/Ti obtained by sol-gel procedure. Voltammetric experiments were performed in a classical three electrodes cell, where the WE was the mentioned anodes and for electrolysis the micro-flow cell (Electrocell) was used.

For the composition SnO₂/IrO₂/Ti the displacement for the more positive value in the presence of formaldehyde is higher.

During the electrolysis in galvanostatic conditions (I=20-60 mAcm⁻²) the decrease of formaldehyde concentration and the oxidation products (formic acid and carbon dioxide) have been followed. The oxidation is a function of anode nature, electrolysis time and conditions. After 4 hours of electrolysis the decrease of formaldehyde concentration was higher for the anode containing Ir (96-98%). The concentration of the initial formed formic acid is higher after 2-2.5 hours, when the CO₂ concentration (calculated from mass balance) is more important. That is experimental evidence for the formation of CO₂ from formic acid. The formaldehyde, a small pollutant molecule can be considered as model molecule. Further work is in progress to improve the electrocatalytic properties of SnO₂/IrO₂/Ti electrodes by changing the rapports Sn/Ir and the experimental parameters for their preparation. The electrodes will be tested concerning the electrocatalytic activity for the oxidation of other pollutants.

The copper nanostructures were obtained by deposition through an alumina membrane (AAO) that is later dissolved. The diameter of the copper nanorods deposited on Cu is about 200 nanometres, which is in good agreement with the AAO membrane pore size used in the electrolysis process. The nanorods were found to be vertically aligned and no collapsing was observed with the height deposited, which was around 2 μm.

Tin dioxide was obtained by using hydrothermal synthesis. The obtained average particles size, observed by TEM, was 3 nm. The X-ray diffraction pattern showed that pure phase, tetragonal tin dioxide was obtained. The chemical surface modification of SnO₂ nanoparticles was done starting from a solution of SnO₂ particles in ethanol - phosphate ester - polyvinyl butyral a dispersant.

Electrochemical characterisation of nanostructured Cu/SnO₂ electrodes was performed with a BAS100W computer aided potentiostat, equipped with a three- electrode system (WE- nanostructured Cu/SnO₂; CE-Pt wire and RE-standard calomel electrode).

On nanostructured Cu/SnO₂ electrodes, the oxygen reduction occurs at -(0.6-0.65) V with an increase in the reduction peak current and decrease in overpotential when compared with copper nanorods. This result suggests that these structures can be used for catalytic oxygen reduction.

Further work is in progress to study the electrode reaction kinetics and the electrocatalytic activity of these electrodes for the total oxidation of phenols.

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