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Preparation of magnetic nanocomposite beads by green-oriented methods and their application in water remediation

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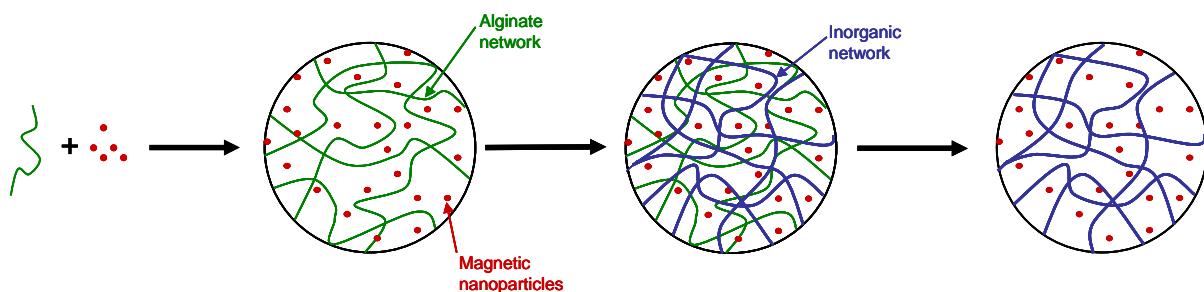
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The use of magnetic materials as adsorbents or heterogeneous catalysts in wastewater treatment is an innovative technology that is increasingly studied. [1] Indeed these materials may be easily recovered by the simple application of an external magnetic field given by a magnet or an electromagnet. This separation technique may be more interesting than conventional recovery methods such as filtration or decantation, particularly when the effluents contain particles in suspension.

Here we describe the preparation of magnetic nanocomposite beads for water remediation using green-oriented methods. We have thus prepared millimeter-sized magnetic silica beads using alginate as a green biopolymer template. Biopolymers produced from renewable resources are increasingly used in the synthesis of nanocomposite materials since they comply with the requirements of green chemistry and induce an original organization of the material, frequently at a multiscale level [2]. The beads were synthesized in three steps. First, magnetic nanoparticles were encapsulated in alginate beads. Secondly, an inorganic network was polymerised into the beads by a sol-gel method. Finally, the alginate template was eliminated by a mild method (see scheme). We have studied the porosity, morphology and magnetic properties of the beads using several characterisation methods. Finally, since these highly porous materials could be used as magnetic adsorbents in water remediation, we have tested their sorptive properties in aqueous solution.



We also present our first attempts to synthesize micrometer-sized magnetic silica beads by sol-gel method in water-in-oil emulsion. During this process, it is possible to use vegetable oil and natural surfactants. Since these materials may be modified by a TiO₂ shell they could be used as highly efficient magnetic photocatalysts for the removal of organic pollutants from water.

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Screening for pharmaceuticals and their metabolites in sewage water using Ultra-Performance Liquid Chromatography Quadrupole-Time-of-Flight Mass Spectrometry (UPLC/QTOF MS)

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Pharmaceutical residues are present in municipal sewage water both in their original form and as metabolites. This presentation describes a methodology to screen for pharmaceuticals and their metabolites in sewage water using Ultra-Performance Liquid Chromatography in combination with Quadrupole-Time-of-Flight Mass Spectrometry (UPLC/QTOF-MS). Reference mass spectra of metabolites were obtained from the analysis of urine samples originating from consumers of the pharmaceuticals in question. Municipal sewage waters treated by different technologies e.g. activated sludge, a membrane bio-reactor, biofiltration, activated carbon, ozonization, and UV-light in combination with hydrogen peroxide, were investigated. Metabolites of common pharmaceuticals such as ibuprofen, carbamazepine, diclofenac, and metoprolol were among the most abundant.

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Multivariate characterisation of industrial chemicals and strategies to identify potential environmental pollutants

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In this study chemical descriptors were calculated for chemicals of the European inventory of existing commercial chemical substances (EINECS) and those categorized as low and high volume production chemicals. A multivariate characterization of the EINECS chemicals using principal component analysis (PCA) and 68 chemical descriptors resulted in five principal components, mainly reflecting size, lipophilicity, flexibility, number of halogens, and electronic properties. These five PCs form the basis of the map of organic, industrial chemicals. The similarities and diversity in chemical characteristics of the substances in relation to their persistence (P), bioaccumulation (B) and long-range transport potential were then examined, by superimposing five sets of entries obtained from other relevant databases onto the map. These sets displayed very similar diversity patterns in the map, although with a spread in all five PC vectors. However, substances listed by the United Nations Environment Program as persistent organic pollutants (UNEP POPs) were clearly grouped with respect to each of the five PCs. Furthermore, different means to cluster the data is presented to identify potential environmental pollutants using multivariate techniques combined with various statistical designs and cluster based techniques. These tools can be used to illustrate similarities and differences in chemical properties, and to be able to make predictions of, and investigate new chemicals. The results of this presentation demonstrate that non-testing methods such as read-across, based on molecular similarities, can reduce the requirements to test industrial chemicals, provided that they are applied carefully, in combination with sound chemical knowledge.

The aerosolized biosphere - Recent insights into the chemical nature of biogenic aerosols

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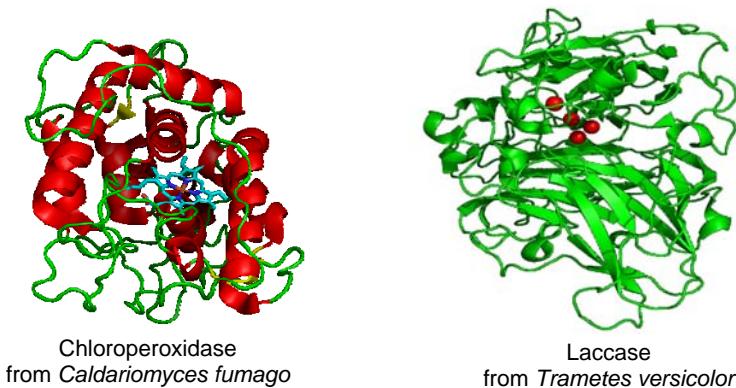
The biosphere is a major source of atmospheric aerosol particles. Figuratively speaking, there are different ways for parts of the biosphere to become airborne: 1) “deliberately”, 2) “accidentally”, and 3) “by force”. By “deliberately” I am referring to the fact that the biosphere releases gaseous aerosol precursors and primary biogenic aerosol particles (PBAP; e.g., spores) in an apparently controlled and purposeful manner. The production of secondary organic aerosol can in some ways also be thought of as the consequence of a “deliberate” release of terpenoids and other VOCs. Other types of PBAP are released more “accidentally”, when material such as leaf waxes, plant fragments and bacteria, are suspended from the ground or vegetation by atmospheric turbulence. Finally, a large part of the biosphere forcibly becomes airborne when vegetation is burned by humans action or wildfires. In my presentation, I will compare and contrast the optical, chemical and cloud nucleating properties of secondary organic, primary biogenic, and biomass-burning aerosols, emphasizing recent observations.

Enzymes as catalysts: Opportunities for green and selective oxidations

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Nature uses enzymes to catalyze a wealth of biotransformations. However in practice these transformations are carried out *in-vivo* under conditions which are far from suitable for large scale production of chemicals. It is our challenge to engineer or design enzymes in such a way that they can be employed *in-vitro* as catalysts. Especially for oxidations, the power of enzymes can circumvent the use of halogen-containing and environmentally demanding oxidants, by using oxygen or hydrogen peroxide as clean and selective oxidants [1]. In the lecture it will be discussed how different classes of enzymes can be employed as catalysts for biocatalytic oxidations. Both oxygen transfer - insertion of an oxygen inside the molecule - with peroxidases as well as oxidative dehydrogenation using laccases will be treated.



A peroxidase has all the characteristics of a promising biocatalyst: It is a cofactor-independent biocatalyst that uses hydrogen peroxide as the oxidant and that can introduce oxygen in the substrate. The chloroperoxidase from *Caldariomyces fumago* is such an enzyme that can perform a variety of selective oxidations, including epoxidations [2]. Our most recent studies involving stabilisation and immobilisation of chloroperoxidase will be presented here. In another approach, we have incorporated vanadate inside the protein phytase, thus generating a semi-synthetic peroxidase [3]. Other approaches which involve covalent anchoring of a redox-active metal ion inside the protein will be presented as well. In the field of oxidases we have studied the enzyme laccase which, in a cascade with the chemocatalyst TEMPO, is a highly active and selective biocatalyst for the aerobic oxidation of alcohols [4]. In addition we have applied ferritin from the hyperthermophilic organism *Pyrococcus furiosus* [5] – an iron storage protein – to encase metal clusters. In this way a stable redox-active protein core was obtained, that can be denoted as a semi-synthetic oxidase.

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Screening organic chemical inventories for human exposure potential

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Globally, scientists and regulatory agencies are assessing chemical inventories to identify persistent, bioaccumulative and toxic (PBT) chemicals and persistent organic pollutants (POPs) that may pose risks to humans and the environment. Measured chemical property and monitoring data are limited compared to the large number of chemicals making it necessary to use in-silico tools to screen and identify chemicals that pose the greatest concern for more comprehensive evaluations in subsequent assessments. Categorization methods based on binary PBT “bright-line” cutoff criteria cannot effectively rank chemicals of greatest exposure and risk potential. The present study outlines the first stage of a tiered holistic screening system to identify chemicals that are predicted to reach high concentrations in humans. This stage of the method is described and applied to a large compilation of organic commercial chemicals. The in-silico screening method relies on a mechanistic regional scale mass balance model and Quantitative Structure-Activity Relationships (QSARs). The Risk Assessment IDentification And Ranking (RAIDAR) model combines chemical emissions, fate and transport, aquatic and terrestrial food web bioaccumulation and effect to estimate exposure and risk to representative ecological species and human receptors. The Level II and Level III fate and transport and bioaccumulation models employ mechanistically based algorithms to quantify processes resulting in chemical exposures and QSARs are used to estimate chemical partitioning properties and chemical degradation. In the absence of metabolic biotransformation information, negligible rates are often assumed resulting in overestimates of exposure for substances that are subject to metabolic biotransformation. The mechanistic nature of the bioaccumulation food web models is exploited by including a novel QSAR for estimating biotransformation rates in fish from chemical structure. The screening method is applied to a list of approximately 10,000 discrete organic chemicals. The list is comprised of substances with any reported production in major industrial nations. An initial screening step was to remove all of the substances from consideration for which discreet organic structures could not be obtained. Adult human total body burdens are shown to span over 20 orders of magnitude based on a unit emission rate. The linearity of the model is used to refine unit body burden estimates by including estimates of actual emission rates. The screening and priority setting results from the mass balance/QSAR method are compared with results from a QSAR screening tool used to identify chemicals with structural similarities of listed POPs. Merits and limitations of the methods and future work are described.

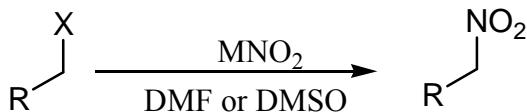
Ecofriendly synthesis of nitroalkanes

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Nitroalkanes are an important class of compounds both because (i) nitro group can be converted into a huge variety of other functionalities,¹⁻³ and (ii) are a valuable source of stabilized carbanions² since the high electron-withdrawing power of the nitro group provides an outstanding enhancement of the hydrogen acidity at the α -position (*cf.* pKa MeNO₂ = 10).⁴ Thus, the availability of nitroalkanes appears crucial and the development of ecofriendly procedures for their preparation remains an important goal.

The main source of this compounds is the conversion of alkyl halides into nitrocompounds, by using metal nitrite in *N,N*-dimethylformamide (DMF) or in dimethyl sulfoxide (DMSO), as reported in Scheme 1.³



Scheme 1

With the aim to increase the reaction efficiency and the ecosustainability of the conversion, other alternative solvents have been proposed for this transformation. Reaction conditions and results will be presented.

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Structure, Composition, Size, and Reactivity of Environmental Nano-Uraninite

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Nanoparticulate biogenic uraninite is formed from the bacterial reduction of uranium(VI) and is of great importance to planned bioremediation strategies at uranium-contaminated sites in the U.S. The primary barrier to uranium release from in the subsurface is the material itself. A thorough understanding the chemical and physical properties of the material is critical to predicting remediation performance and developing contaminant transport models. Biogenic uraninite is fascinating from the standpoint that particle size (typically 2 to 5 nm), molecular-scale structure, and unit cell composition all have been posited to strongly moderate its stability in the subsurface. In particular, there has been concern that the nano-size of this material induces strain that destabilizes the material, with potentially important implications for environmental remediation.

We have used EXAFS, *in-situ* synchrotron powder diffraction, TEM, XPS, and continuous-flow dissolution measurements to assess the impacts of size, structure, and composition on the stability of biogenic uraninite. In the absence of cation dopants, biogenic uraninite was found to be unstrained and structurally homologous to stoichiometric UO₂, and this similarity persists in the solubility and kinetics of this material. These results suggest that size does not intrinsically impact reactivity. In contrast, unit cell composition, and in particular the presence of structural impurity cations, was found to have a pronounced impact on stability (as predicted from sedimentary uraninites), as well as on structure and particle size. These findings indicate that ground water solute chemistry is an important moderator of biogenic uraninite stability and raise intriguing questions about the role of size in the reactivity of nanoparticles in aquatic environments.

Constructed wetlands. Can they remove emerging pollutants?

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Constructed wetlands (CWs) constitute wastewater treatment alternative to small communities due to their low operational cost, reduced energy consumption, and almost no sewage sludge production. Although much information is available about conventional water quality parameters (e.g. BOD₅ and TSS) in constructed wetlands, few data regarding pharmaceuticals and personal care products (PPCPs) are currently available. The objective of this work was to evaluate the elimination of selected PPCPs in CWs of different configurations. In this regard whereas in the horizontal flow (HF) CWs the organic matter removal is mostly by anaerobic pathways (i.e. denitrification, sulphate reduction and methanogenesis), in vertical flow (VF) CWs and surface flow (SF) CWs the aerobic environment prevails. These different environments, according to the CW configuration, are of primary interest in order to eliminate the emerging pollutants from wastewater because of their high oxygen dependence. The removal efficiency of PPCPs in constructed wetlands used as secondary or tertiary treatment is similar to or better than those obtained in conventional activated sludge WWTPs. Hence, whereas VFCW with unsaturated flow seems to be feasible as secondary treatment to attenuate the PPCP pollution from domestic wastewater of small communities, and the SFCW is as tertiary treatment and landscape restoration.

Table 1. Removal efficiency (%) of selected PPCPs in vertical flow (VF), horizontal flow (HF) as well as surface flow (SF) and their comparison with conventional WWTPs.

	CWs			WWTPs
	HF ^a	VF ^a	SF ^b	activated sludge
Ibuprofen	71	99	96	60-70
Clofibric acid	n.r.	n.d.	36	n.r.
Ketoprofen	n.r.	n.d.	99	48-69
Naproxen	85	89	92	40-55
Diclofenac	15	73	96	9-75
Carbamazepine	16	26	47	7/8
Caffeine	97	98	n.d.	99
Methyl dihydrojasmonate	99	99	n.d.	98

^a Secondary treatment; ^b Tertiary treatment.

n.d.: not detected, n.r.: not removed.

Is technical hexabromocyclododecane a persistent organic pollutant?

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1,2,5,6,9,10-Hexabromocyclododecanes (HBCD) are additive brominated flame retardants mainly applied in polystyrene foams, in textiles and to a minor extent in electrical equipment housings. HBCD comprises theoretically 16 stereoisomers of which three enantiomeric pairs of diastereomers ($\pm\alpha$, $\pm\beta$ and $\pm\gamma$) are the major constituents of technical mixtures. Several reviews have documented the widespread occurrence of HBCD in various environmental compartments. During the ongoing EU risk assessments of HBCD, an impressive amount of information has become accessible on the persistence, as well as the bioaccumulative and toxic properties of HBCD. On the basis of the intrinsic PBT-properties, HBCD has been proposed for inclusion in the Stockholm Convention on POPs as well the POP Protocol of UNECE Convention on Long-Range Transboundary Atmospheric Pollution (LRTAP). While there is no doubt that HBCD fulfils the inclusion criteria for bioaccumulation and for eco- and mammalian toxicity, as well as for potential for long-range transport, it is debated whether HBCD meets the "P" criterion. The criteria for persistence within the Stockholm Convention and the LRTAP are that the half-life in water is greater than 2 months, or that its half-life is greater than 6 months in soil, or in sediments. Alternatively, must be evidence that the substance is otherwise sufficiently persistent to be of concern within the scope of the conventions.

Biodegradation simulation tests according to OECD standards under aerobic and anaerobic conditions have been performed on the three major HBCD diastereomers by Davis et al. in two studies using a nominal concentration range of 0.034 to 0.09 µg/kg dry wt. (2003) and 3 to 4.7 mg/kg dry wt. (2004). The first study has several limitations and is therefore regarded less sound compared to the second one, though concentrations here are about 100 times higher than those reported for European environments. The EU risk assessment estimated the primary degradation half-lives of total HBCD under aerobic and anaerobic conditions at 20°C to 101 and 66 days, respectively, and extrapolated these values to 191 and 125 days for more environmentally relevant temperature of 12°C. With that, HBCD would fulfil the criteria for persistence in sediments under aerobic conditions. In aerobic soil at concentrations of 3.0 mg/kg dry wt., no degradation was observed over the 112 days of the test.

Further evidence of the persistence of HBCD is from investigations on temporal trends in environmental levels of HBCD which point to increasing levels during the last two decades. These are studies on sediments, on marine mammals and piscivorous birds as well as on human populations. In most studies, α -HBCD is found to be the predominant stereoisomer in biota which may be explained by a higher resistance to degradation of this stereoisomer compared to the γ -isomer which is the predominant isomer in the technical mixture. These results indicate that at least α -HBCD is stable enough to be transferred in food chains leading to accumulation in top predators. It may therefore be concluded that there is evidence that HBCD is sufficiently persistent to be considered as POP under the Stockholm and UNECE LRTAP Conventions.

Heat treatment effect and exchange kinetic study of strontium and cesium ions on NaX & NaY zeolites

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Zeolites have attracted considerable attention due to their potential applications in many fields, such as gas storage, catalysis and ion-exchange [1,2]. Among the zeolite family, types X and Y zeolites, a members of the faujasite family, are highly desired for many uses that range from crystal structure analysis, adsorption and diffusion studies to zeolite functional materials because of their unique crystal structure, their microporous characteristics, their high chemical as well as thermal stabilities, and their high cations content [3,4].

The potential applications of zeolites and other selective ion exchangers such as mineral clays have been well documented by Dyer [5]. These materials possess a high exchange capacity, element selectivity and specificity, and a good resistance to radiation and heat [6].

Ion-exchange in the aqueous phase has a strong influence on the structure and/or texture of zeolites. Variations in the structural and/or textural characteristics of zeolites including the degree of crystallinity, the size of crystals, the inner and outer surface areas, significantly influence their physicochemical properties [7].

The aim of the present work is to examine the efficiency as a cation exchanger of the X and Y synthetic zeolites for the removal of strontium and cesium ions from waste solutions. The effect of various parameters such as intial metal concentration, temperature, pH, and heat treatment are examined. The kinetics of an exchange reaction is also evaluated using current known models (Lagergren pseudo second order and Helfferich models) and the relevant parameters are determined.

On the basis of the results obtained from the examination of the ion exchange kinetics, the amount of Sr^{2+} and Cs^+ bound has been calculated for selected solid/liquid contact times. The ion exchange for both ions is rapid at initial times for all initial concentrations with prolonged slower uptake until equilibrium. The amounts of sorbed cesium and strontium ions increase with temperature, indicating the endo-thermic nature of the process.

The analysis of the initial rate data in accordance with the two kinetic models reveals that intraparticle diffusion is the rate limiting step for the sorption of both strontium and cesium. In addition, the obtained kinetic data provides valuable information about the exchange mechanisms.

The zeolites heat-treated at 800°C present a morphological change from the original cubic form to a bead-like shape induced by an amorphization process. Consequently, the exchanged ion is trapped in the zeolite framework.

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Mass transfer of artificial radionuclides and heavy metals in the water flow of the Yenisei River

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The type and mineral composition of water sources as well as physicochemical properties of radionuclides and heavy metals determine their speciation in the water flow. The main forms of artificial radionuclides and heavy metals involved in mass transfer in the surface waters are dissolved salts and/or complex compounds, colloids and/or pseudocolloids, and particulates of various sizes and origins. The composition, structure, and size of the aggregates and other physicochemical parameters of radionuclide and heavy metal compounds are not stable. With time, concentrations of radionuclides and metals in the water flow are significantly decreased due to dilution, co-precipitation with other, poorly soluble, compounds, and sedimentation of particulates (such as Fe and ⁵⁹Fe, Pu isotopes, etc.). However, speciation of certain radionuclides and metals (such as ²³⁹Np(V), U(VI), etc.) causes these substances to remain in dissolved form; hence, they are transported over considerable distances with the water flow. The ecosystem of the Yenisei River floodplain is contaminated by artificial radionuclides, which have been released into the environment by the Mining-and-Chemical Combine (MCC) of Rosatom – a facility producing weapons-grade plutonium – for more than fifty years. Artificial radionuclides are found at considerable distances downstream of the MCC discharge site, as far as the Kara Sea.

The purpose of this study was to describe the mass transfer of radionuclides and heavy metals in the water flow of the Yenisei River in the vicinity of the MCC discharge site, based on the data obtained by different physicochemical methods.

During summer and autumn seasons of 2006-08, water samples were collected in the vicinity of the MCC and investigated in the laboratory. They were found to contain a wide range of artificial gamma-emitting radionuclides (⁵¹Cr, ⁶⁵Zn, ⁶⁰Co, ²³⁹Np, etc.) and tritium, whose concentration was higher than its background value. Concentrations of heavy metals (Mn, Fe, Pb, U, etc.) and major anions (Cl⁻, SO₄²⁻) were determined and compared with the background values characteristic of the Yenisei water. Radionuclide concentrations decreased within the 5-km stretch of the river, downstream of the MCC. The concentration of ²³⁹Np decreased 19 times, ³H – 16, U – 8.5, Fe – 2.5, Mn – 3.2, etc. Concentrations of the major anions decreased, too, reaching the levels determined in the water samples collected from the main watercourse of the Yenisei River: SO₄²⁻ concentration decreased 2.4 times and Cl⁻ – 7.5 times. The water samples were filtered and the filtered water was then sorbed on ion-exchange resins to determine the forms of artificial radionuclides in the water flow. The major portions (75% to 100%) of such radionuclides as ⁵¹Cr, ¹³⁷Cs, Ce isotopes, and ¹⁵²Eu were found on particles of sizes >0.2 µm. Such radionuclides and metals as ⁹⁹Mo, ²³⁹Np, U, Zn, and Mn mostly (up to 98%) remained in the filtrate, probably as soluble salts, complex compounds or particles of various origins, of sizes <0.2 µm. Elements found in the filtrate were present either as anions (¹⁰³Ru, ¹⁰⁶Ru, ²¹⁴Bi, Mo) or as cations (⁶⁵Zn, ⁶⁰Co, ²³⁹Np, U). Thus, the water of the Yenisei River was found to contain a wide range of artificial radionuclides and enhanced concentrations of heavy metals and major anions, SO₄²⁻ and Cl⁻ – higher than the background values characteristic of this water environment. The study showed that mass transfer of radionuclides and metals occurs due to both advection of particulates and soluble compounds.

Harmonised protocols for method validation for monitoring and biomonitoring of emerging pollutants - Developed by the NORMAN network

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Comparability and reliability of monitoring data are essential for any meaningful assessment and for the management of environmental risks. For emerging pollutants, there is concern regarding the comparability of data at the European level. Methods used for the monitoring of emerging pollutants have often not been properly validated either in-house or at the international level. Such methods are often not well established in the scientific community, and far from being harmonised or standardised. In addition, they may only be applicable to specific conditions (matrix, organism) which may further complicate data comparability.

Within the EU-funded coordination action “NORMAN - Network of Reference Laboratories for Monitoring and Bio-monitoring of Emerging Pollutants”, a common European approach to the validation of both chemical and biological methods for the respective monitoring and bio-monitoring of emerging pollutants (or their effects) in a broad range of matrices has been developed. This guidance document addresses three different validation approaches, in increasing order of complexity. These are

1. Within-laboratory validation (research level)
2. Basic external validation (transferability at expert level)
3. Inter-laboratory validation (routine level)

The concept of these three approaches is strictly hierarchical, i.e. a method must fulfil all criteria of the lower level before it can enter the validation protocol of a higher level.

In the case of a specific monitoring task, this protocol will guide the user through the following steps:

- I. Evaluation and classification of existing methods with respect to their potential, both in terms of validation, and the selection of an appropriate validation approach.
- II. Development of a method, in terms of extending its application.
- III. The validation procedures to be undertaken in order to effectively demonstrate the validation status of a selected method according to the three approaches adopted.

The scope of the harmonised protocol covers quantitative and qualitative biological and chemical test methods for the analysis of water, air, soil and biota.

The protocols have been tested in three case studies, each one matching one of the three validation levels. Based on the feedback from the case studies, the protocols have been improved. Future validation studies (for methods to monitor emerging pollutants) by the NORMAN network will make use of the protocols, and it is intended to implement the protocols at the level of European Standardisation (e.g. as CEN guidance document).

The curious case of the dying crocodiles in the Kruger National Park, South Africa

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Since May 2008, a large number of mainly large crocodiles have died in the Olifants River gorge in the Kruger National Park (KNP), South Africa. Post mortem examinations revealed that carcasses had hardened, yellow-orange coloured fat in their tails, abdominal cavity and around organs – a condition known as pansteatitis. The reasons for the development of pansteatitis in the crocodiles are unknown and we investigated different hypotheses regarding causes. Several matrices were tested for the presence of organic pollutants and other elements known for their ability to cause lipid peroxidation. The water and sediment from selected rivers in the KNP, as well as fish- and crocodile tissues, were analysed for dioxin-like chemicals, chlorinated pesticides, PCBs, polycyclic aromatic hydrocarbons (PAHs), polybrominated flame-retardants (PBDEs), methylsulphone derivatives of PCBs and DDE, and heavy metals, since many of these substances, or a combination thereof, may cause lipid peroxidation. We report here only on the sediment and crocodile fat results.

Sediment from the Olifants Gorge and some other rivers in the KNP contained traces of dioxin-like substances, some pesticides (DDT and HCH), PAHs, and PBDEs, but in general, the levels were well below sediment quality guidelines. Normal levels of trace and heavy metals were found in sediment and crocodile fat, and it was therefore unlikely that crocodiles were dying due to metal poisoning. No methylsulphone derivatives of DDE or PCBs were found in fat. The primary cause of the problem is still unknown, but it is speculated that the deaths are triggered by a combination of factors – environmental and dietary. At present, the mortality rate has come down substantially, but it may pick up again with the onset of winter (during this conference) when there will be greater demand for stored fat, or if decreased water levels lead to a concentration of pollutants in the gorge.

Implementation of poly-parameter linear free energy relationships in a multimedia fate model

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I prefer an **oral** presentation in the “In-silico tools in chemical risk assessment” session.

Contemporary multimedia fate models commonly describe partitioning to organic matter with single parameter linear free energy relationships (SP-LFERS), most often by correlating partitioning to organic matter with partitioning to octanol. It has previously been proposed that the range of applicability of multimedia fate models could be expanded by replacing the SP-LFERS with poly-parameter linear free energy relationships (PP-LFERS) to quantify phase partitioning¹. The argument for this is that SP-LFERS have been shown to make poor predictions of phase partitioning when applied to chemicals outside of the datasets used in their parameterization, but PP-LFERS can be successfully applied to a much wider range of chemicals because they specifically account for the different kinds of interactions between solutes and solvents². Subsequent work has shown that this approach is viable for chemicals, such as pharmaceuticals, which may usually be considered to be outside the range of applicability of traditional SP-LFER based models³.

Three major factors limited the implementation of a PP-LFER based multimedia fate model when the idea was originally proposed; PP-LFER equations were missing for several environmentally relevant phases, there was no method for calculating the temperature dependence of phase partitioning, and the availability of solute descriptors for environmentally relevant chemicals was quite limited. Much work has been done lately to address all three of these shortcomings and the required data it is now available from the literature to implement a PP-LFER based multimedia fate model.

We outline here the implementation of PP-LFER equations into CoZMo-POP 2; a non-equilibrium, non-steady state, fugacity based multimedia fate model⁴. A non-steady state model is preferred because a non-steady state simulation on a relatively short time scale will give the most realistic assessment of the potential differences between an SP-LFER based model and a PP-LFER based model. We expect that as chemicals near equilibrium the differences in predicted environmental fate will be larger due to the differences in the description of environmental partitioning.

Observations of the differences in chemical fate predicted by SP-LFER and PP-LFER based models are presented and discussed. In general, primary chemical fate is predicted similarly by both models, but in many cases the concentrations in secondary phases vary widely, which has implications for environmental mobility. The PP-LFER based model also allows for a direct exploration of the relationship between the interactions a chemical experiences and its environmental fate, for example we elucidate the chemical properties that allow a chemical to become a multimedia chemical capable of moving easily between environmental phases.

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New approaches to evaluate consolidation treatments for waterlogged archaeological wood objects

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In favourable aqueous environments, characterised by low temperature and low oxygen concentration, archaeological waterlogged wooden artefacts, such as shipwrecks, can survive in relatively good conditions. Nevertheless, as a result of the action of water and of anaerobic bacteria, waterlogged wood is often deeply degraded and has undergone loss of polysaccharidic components (cellulose and hemicellulose) with increase, under ageing, of porosity and of water content (up to 1000% in weight).

Conservation treatments of archaeological waterlogged wood artefacts are very often expensive and technically difficult, as they involve the replacement of the water with consolidating materials, filling the cell walls and all cavities in order to prevent stresses during the drying. The effectiveness of the treatment strongly depends on the penetration depth and the distribution of the consolidating material, and on the degree of cavities-filling.

The penetration and distribution of different types of consolidating treatments, applied to archaeological wood samples (pine and elm), have been investigated by synchrotron radiation X-ray microtomography (SR- μ CT). This non destructive technique permits to visualise in 2D and in 3D the internal structure of wood samples, and to localise the consolidants in wood cavities at various distances from the surface. Tomography experiments have been performed at beamline ID 19 of ESRF (European Synchrotron Radiation Facility) in Grenoble (France).

The examined consolidated wood samples have been prepared in the frame of a project for the experimentation of products and methods for the conservation of degraded waterlogged wood artefacts, coordinated by the Archaeological Superintendence of Tuscany (Florence, Italy) and aimed to the conservation of wooden objects and shipwrecks recovered in the archaeological site of the Ancient Ships of San Rossore (Pisa)

Determination of ionic liquids in natural samples by separation techniques. Problems and solutions?

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Ionic liquids look like classical liquids and are molten salts. They are built of a bulky organic cation such as imidazolium or pyridinium, and an inorganic or organic anion such as tetrafluoroborate. These factors result in ionic liquids having reduced lattice energy and hence lower melting points. Ionic liquids form a class of new environment-friendly compounds exhibiting low volatility, but also chemical and physical stability and recyclability. The specific properties of ionic liquids make them very useful in organic synthesis and catalyzed reactions, in liquid-liquid extraction, embalming and tissue preservation, and biocatalytic enzymatic reactions. They were also advantageous as electrolytes for batteries, electrochemical devices, and germicide and fungicide applications. Due to their properties, ionic liquids have been used in a variety of separation methods, for example as stationary phase modifiers in gas chromatography, as carrier electrolytes in capillary electrophoresis or as additives to mobile phases in high performance liquid chromatography.

The wide applicability of ionic liquids will increase their production and utilization in industry. This will probably cause their appearance in water or soils. For that reason methods for their qualitative and quantitative determination must be developed. For this purpose an analytical tool can be used, namely reversed-phase high performance liquid chromatography (RP HPLC). Chromatographic analysis of ionic liquids on different types of packings gives interesting possibilities to determine main interactions between the stationary phase ligands and the analyzed compound. As a consequence, their retention mechanism can be defined. This could allow the prediction of principal interactions responsible e.g. for accumulation of ionic liquids cations in soils and biota. RP HPLC may be used in the determination of those salts in environmental samples such as extracts from soil. Obtained results are essential for the estimation of bioavailability.

Study of black Roman glass via SEM-EDX and LA-ICP-MS

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Jewels and tableware made of black-appearing glass were popular in the Roman era, especially in the area of the Northern Provinces, nowadays Belgium and the Netherlands (Van der Linden et al. 2009). The aim of this work is that of determining the compositional changes (i.e. modifies in glassmaking technology and raw materials) that happened in the period considered (2nd century BC-6th century AD). This has been done by analyzing a large number of samples originating from various archaeological excavations in Europe, Northern Africa and the Near East.

Over 250 samples of deeply coloured glass were embedded into acrylic resin, which was mechanically ground and polished in order to obtain flat surfaces of unaltered glass. The samples were then analyzed with SEM-EDX and the quantification was performed by using a standard-less ZAF software. The trace elements contained in a selection of glass samples were then quantified via LA-ICP-MS.

The composition of the major part of the samples is similar to that of the Syro-Levantine Roman glass, produced by mean of sand and natron in primary workshops in the Near East. The characteristic black-appearing coloration is given by the presence of relevant quantities (up to 10%) of iron oxide (the resulting hue is a deep green) or manganese oxide (deep purple) added as separate ingredients. Another way of obtaining black/green glass was that of using Fe-rich sand, together with vegetable ash in many cases, leading to a 1-3% of iron oxide. This composition is typical of the earlier samples (up to year 150 AD indicatively) and coincides with typical stylistic features.

Finally, the trace contents enhance the perception of the different glass types: for instance the antimony content is related to iron only in the samples with a high Fe-amount. A few local differences can also be discerned, such as the samples originating from Trier (Germany), that appear to be produced with a particularly impure sand and relevant contents of copper and lead.

Fig. 1-4. Black Roman glass objects
(unguentarium, bracelet, jar, jug)

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Van der Linden V, Cosyns P, Schalm O, Cagno S, Nys K, Janssens K, Nowak A, Wagner B, Bulska E, 2009, Deeply coloured and black glass in the Northern Provinces of the Roman Empire: differences and similarities in chemical composition before and after ad 150, *Archaeometry* (early view)



Predicted and estimated distributions of trace metals in the sediment particles and pore waters of three freshwater sediment cores

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Metallic and organic contaminants released by past and present anthropogenic activities tend to accumulate in river sediments. This study takes place in the framework of the European research project INTERREG III – STARDUST which aims at investigating the fate of organic and metallic contaminants in river sediments and in particular at assessing the role of the sediment as a potential sink or source for pollutants. It is thereby of a high concern to study the speciation of metallic contaminants in pore waters as it strongly influences their mobility and their biodisponibility towards aquatic organisms.

Three sediment cores were collected in the Spiere, the Lys and the Scheldt canals. These rivers, which are located at the border of France and Belgium, flow through one of the most populated and industrialized area in western Europe. The software Visual Minteq (version 2.40b), incorporating the NICA-Donnan model for organic matter-trace metals interactions, has been applied to examine the pore water speciation of cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc.

Input data were:

- the concentrations of trace metals (measured by ICP-AES and ICP-MS) in pore waters,
- the concentrations of anions, cations, dissolved sulphides and dissolved organic carbon,
- *in-situ* measurements of pH and redox potential.

Thermodynamic speciation calculations allow for the apportionment of free, inorganic (bound to carbonates, sulphides and other inorganic ligands) and organic (associated to fulvic and humic acids) species of trace metals in pore waters. Results indicate a strong affinity of cadmium, lead and especially copper towards humic and fulvic acids. At the opposite, manganese and cobalt were predominantly present as free species or associated to inorganic ligands. This predicted speciation was compared to the labile species concentrations measured *in-situ* by DGT (diffusive gradients in thin films, Chelex-100 resin).

Ion activity products (IAP) were also calculated for several carbonates, phosphates and sulphides minerals in order to evaluate their degree of saturation in pore waters and predict their potential presence as a pure phase.

Finally, sequential extractions, X-ray diffraction and scanning electron microscopy were applied on sediment samples in order to complete and partly justify the results predicted by the Visual Minteq calculations.

Development and validation of a novel and selective extraction technique: a combination of liquid membrane and molecularly imprinted polymers

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In this study a novel, simple and selective extraction technique based on combination of liquid membrane and molecularly imprinted polymers (MIP) was investigated and validated using certified reference standards. The selectivity of such a combination was tested in the extraction of simazine, atrazine and propazine in food samples, wastewater and river water. Aqueous samples were extracted through the hydrophobic porous membrane that was impregnated with toluene which also formed the acceptor phase. In the acceptor phase, the compounds were re-extracted onto MIP particles which were part of the organic phase. The extraction technique was optimized for the amount of MIP particles in the organic acceptor phase, extraction time, and type of organic acceptor solvent and desorption solvent. Determined concentration of certified reference standards spiked in river water and wastewaters at single $\mu\text{g L}^{-1}$ level did not differ from the actual concentration values. The combination of liquid membrane and molecularly imprinted polymers produced a synergism in selectivity compared to liquid membrane alone.

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Antioxidants studied by on-line hyphenation of liquid chromatography, electrochemistry, and mass spectrometry (LC-EC-MS/MS)

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High antioxidant activity was obtained in birch bark extracts when pressurized hot water or ethanol was used as solvents ¹. In order to determine the antioxidant activity of the extracts, a radical scavenging assay based on DPPH (2,2-diphenyl-1-picrylhydrazyl) was used. The antioxidant activity measured was highest at the highest tested extraction temperature (180°C, 50 bar). The high antioxidant activity obtained was likely due to high extraction efficiency or chemical reactions, or a combination of both. However, the DPPH assay cannot give information on antioxidant activity of molecular species, and in addition, the DPPH assay is both time consuming and laborious. For that reason, an online hyphenation method of Liquid Chromatography, Electrochemistry, and Mass Spectrometry (LC-EC-MS/MS) ² was recently developed to analyze pre-treated birch bark extracts. This analyzing method is fast and sensitive. LC-EC-MS/MS is able to separate, oxidize and elucidate the oxidation products obtained on a molecular level. The differences in molecular composition between pre-treated extract at ambient temperature and 180°C, respectively, showed that it is a combination of improved extraction efficiency and degradation of extracted compounds that contributes to the increased antioxidant activity with increasing temperature in the pressurized hot water extraction process.

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Morphology and elemental composition of mineral dust particles from local, regional and long-range transport meteorological scenarios

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In Madrid, mineral dust is the second biggest contributor to PM₁₀ reaching up to 80% of the mass during certain North African transports (Artíñano et al., 2003). Three different types of phenomena have been found to be associated to the high particle concentration events in the city: local anthropogenic, regional recirculation and African dust transport episodes. The present study focuses on the characterisation of the individual mineral dust particles related to particle chemistry and morphology. To achieve this purpose, four different samples were selectively collected during 2004-2005 campaigns, covering each type of episode. Meteorological scenarios, air-mass back-trajectories, dust source identification, and impact on the PM concentrations were studied. Elemental composition and morphology of more than 30,000 mineral particles was analyzed by Computer-Controlled Scanning Electron Microscopy. Particles were grouped into chemical clusters and the Aspect Ratio (AR) of each category was compared for each type of episode (Coz et al., 2009).

Three chemical clusters were found to be the most abundant after classifying the particles based on their elemental composition, independent of the episode studied: silicates, carbonates and sulphates. The main difference has been found when comparing the samples associated with long-range transport and those with local and regional recirculation, with much larger concentrations of silicates associated with synoptic scale transport scenarios. The opposite trend occurred with the carbonate cluster. These differences between silicate and carbonate contents were directly related to the composition of the parent topsoil by studying the Ca/Si ratios of similar episodes around the Iberian Peninsula. Larger average AR values were found for studies characterising dust from long-range transport and smaller average AR values for studies from local and regional resuspended dust. The increasing average AR value has been linked to the silicate cluster and a reduction within the carbonate cluster, since the AR values for all the samples and size ranges generally follow the order found for North African transport episodes: AR_{sulphates}>AR_{silicates}>AR_{carbonates}. This finding is especially interesting, as consequently the differences in morphology of the mineral particles have been associated with each of the chemical clusters, independently of the type of meteorological scenario.

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Acknowledgements

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Diminishing European eel stocks: Survival of the fattest?

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Since the 1980s, the European eel (*Anguilla anguilla*) stock is in steep decline. Two large and independent data sets from Belgium and The Netherlands show an average one-third decrease in fat contents of yellow eels over the past 15 years: from 20 to 12% in the period 1994-2006 in Flanders, and from 21 to 13% in the period 1985-2004 in The Netherlands. Lipid reserves are essential to cover energetic requirements of silver eel migration to the Sargasso Sea and enable reproduction. Assuming fat levels in yellow eel are indicative of those in silver eels, only large individuals, females as well as males, with high lipid contents seem to be able to contribute to the spawning stock.

Eel is an ideal biomonitor for environmental contaminants: It has a high fat content, it does not spawn during its entire life-span, and does not migrate more than a few hundred meters. Therefore, eel was used to monitor polychlorobiphenyl (PCB), polybromodiphenylether (PBDE) and organochlorine pesticide concentrations in The Netherlands since 1977. From 1994 onwards such a program was also installed in Flanders (Belgium). The evaluation of these two programmes showed decreasing PCB concentrations at most locations from the rivers Rhine and Scheldt, in addition to the decrease in fat contents. There may be several explanations for the decreasing fat contents: 1) Hydroxy metabolites of PCBs, PBDEs and pesticides which showed very high concentrations in the 1980s in The Netherlands and somewhat later in Belgium could have caused this decrease in fat content. These metabolites mimic the well-known slimming tool 2,4-dinitrophenol. This could have caused a slimming process that cannot be stopped after a while; 2) Endocrine disruptors such as perfluorinated compounds, brominated diphenyl ethers, and also hormones such as estradiol and ethinylestradiol from the anti-conception pill have been found in increasing concentrations in the aquatic environment. They could stimulate female sex formation of the glass eels, after they enter The Netherlands and Belgium. Female eels have a significantly lower fat content than male eels; 3) Low eel density sites are characterized by a higher proportion of female eels. That would suggest that the lower fat contents would only be an effect of the decreasing stock. Although more research is needed to find the true relationship, the decrease in fat contents of yellow eels and the high levels of endocrine disrupting compounds in this densely populated part of Europe seem to be key elements in the explanation of the stock decline and raises serious concerns about the chances of the stock to recover.

Pharmacokinetics and bioavailability of perfluoroalkyl phosphonic acids (PFPAAs)

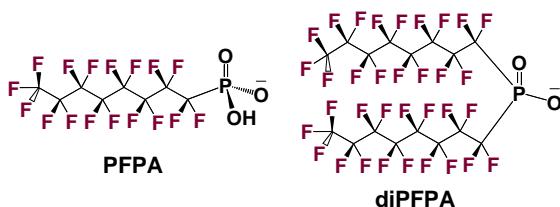
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Perfluoroalkyl phosphonic acids (PFPAAs) are a new class of perfluorinated acids that have recently been detected in Canadian surface waters and wastewater treatment plant effluent (1). PFPAAs are high production volume chemicals, with 4.5-230k kg produced annually between 1998 and 2002 (2). One specific applications of these chemicals has been defoaming additives to pesticide formulations applied to human food-use crops (3). As of 2008 the United States Environmental Protection Agency longer permitted PFPAAs to be used in this capacity (4). However, the potential for human exposure prior to this legislation is high, and further human exposure may occur via other sources.

To better understand the implications of human PFPA exposure we used a rat model to determine the fate of PFPAAs upon ingestion. Excretion kinetics and the partitioning were determined by dosing 4 female and 4 male Sprague-Dawley rats with the PFPAAs and diPFPAAs (shown below) by intraperitoneal injection at 25 ug/kg. Urine and feces were collected from the animals for 48h post-dosing, and blood was sampled biweekly for one half-life. At the end of the experiment the animals were sacrificed and necropsied to determine the concentration of PFPAAs and diPFPAAs in various tissues. The bioavailability of PFPAAs and diPFPAAs was determined by dosing 4 male Sprague-Dawley rats with both the PFPAAs and diPFPAAs by oral gavage at 20 mg/kg, followed by daily blood collection.

Results of this study will be presented in the context of human exposure and comparison with the pharmacokinetics of the perfluorinated carboxylic and sulfonic acids.



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Ozonation of quinolone antibiotics: analysis of degradation products

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The occurrence and fate of pharmaceuticals in the environment is of concern since pharmaceuticals can exert toxic effects against aquatic organisms. Hormone disrupting agents can interfere with natural hormones and antibiotics can induce bacterial resistance. Therefore, physical-chemical removal technologies, such as advanced oxidation processes (AOP), are necessary for their efficient removal from wastewater. Mineralization of parent molecules by AOP is hardly possible. Therefore, detection of reaction products is essential since degradation products might be toxic or still possess hormone disrupting or antibacterial features. A large diversity in degradation product detection methodologies can be found in literature, and a systematic approach how to deal with these methods is recently proposed (De Witte et al., 2009a).

In recent own research work, ozonation and advanced oxidation by the peroxone process of the quinolone antibiotics ciprofloxacin and levofloxacin were studied in a bubble column. Focus was on both the identification of degradation products and on the change of degradation product concentrations in function of reaction time and process conditions (De Witte et al., 2008; De Witte et al., 2009b). Samples were concentrated by solid phase extraction followed by degradation product identification based on liquid chromatography (LC) – UV and LC – high resolution mass spectrometry. Comparing UV and mass spectra of degradation products with those of the parent quinolone and with those of related chemicals were essential for elucidation of ozonation reaction pathways. Here, a strong pH dependency (pH 3, 7 and 10) was observed. For both ciprofloxacin and levofloxacin, degradation at the piperazinyl substituent was strongest at pH 10, i.e. when the amine group is unprotonated. Reaction products with degraded quinolone moiety, reported to be essential for antibacterial activity, were especially found at pH 7.

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Development and environmental application of TiO₂ photoassisted processes for water purification: Degradation of cyanobacterial toxins

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The enormous diversity of toxic and organic pollutants of different chemical composition eliminates the possibility of using a universal treatment method for water decontamination and has led to the development of efficient treatment methods. Nanostructured crystalline TiO₂-based nanomaterials have gained significant recognition in environmental remediation such as water and air purification [1]. This environmentally friendly technology is capable of treating non-selectively contaminants, even at very low concentrations, which are difficult or expensive to treat using other conventional methods. In this study, self-assembling surfactant strategies using novel sol-gel approaches were employed to synthesize and enhance the structural properties and photocatalytic activity of TiO₂ under UV and visible light for the degradation of the hepatotoxin microcystin-LR (MC-LR) [2-4]. MC-LR is an isoform of microcystins; a group of cyanotoxins produced and released from harmful strains of cyanobacterial algal blooms into drinking water sources. This represents a severe threat to public health due to its high stability and toxicity in water. The degradation pathways and mechanistic aspects of MC-LR degradation using immobilized TiO₂ films under UV light were unveiled [2, 3]. Moreover, to overcome UV-restricted photoactivation of conventional TiO₂ which account only 4% of the total solar spectrum, we also explored the synthesis, characterization and application of nitrogen and fluorine co-doped TiO₂ nanoparticles and films for the photoassisted degradation of MC-LR under visible light irradiation [4]. The synergistic effect induced by the co-doping of TiO₂ has significant photocatalytic improvement on the degradation of MC-LR under acidic conditions. The effects of several inorganic and organic compounds that may affect the effectiveness of this modified catalyst in natural waters are also addressed. These preliminary findings suggest the possibility of employing solar-driven water treatment technologies as a sustainable approach for water contaminated with cyanotoxins and other environmental contaminants of concern.

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Characterization of water chemistry in Lake Tranebärssjön - a former uranium open pit mine

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Mining activities have influenced the geochemical cycling of elements in several ways, e.g. production of tailings from the processing of ore, and by increasing mineral surfaces exposure to oxygen. This may result in environmental threats such as release of acids, bases, toxic elements as well as dust and suspended solids. The aim of this study is to characterize water chemistry, at different water depth in an artificial lake, a former open pit mine.

The closed uranium mine in Ranstad, Sweden left besides processed ore also an artificial lake - Lake Tranebärssjön, the former open-pit mine. The lake is dimictic but stratified most of the year with anoxic bottom water, probably caused by groundwater inflow to the deeper parts of the lake. Oxygenation during spring and autumn turnover causes precipitations of iron hydroxides with associated trace metals to be deposited also in the shallower, littoral areas of the lake. This considerably limits the use the lake for recreational purposes, which were the original plan after the restoration of the mining area.

The lake was sampled at stratified conditions in late summer at the deepest part of the lake at three depths of the water column; surface water, thermocline and bottom water. Samples were analysed for general water chemistry, dissolved organic carbon (DOC) and trace metals.

The oxygenated surface and thermocline water show pH 7.8 compared to 7.0 in the oxygen depleted bottom water. Conductivity, alkalinity and sulfate as well as several metals including Ca, Mg, Na, Fe, Ni, U, Mn, Mo, As, Zn, Cd and Co show higher levels in the oxygen depleted bottom water compared to the oxygenated surface water. However the levels of DOC and Cu are slightly lower in the bottom water compared to surface and thermocline water. The concentration of nitrate in the surface and thermocline water is higher compared to the bottom water, opposite to the distribution of ammonia.

The depletion of oxygen seems to be the strongest influencing factor for metals like Fe, Mn, Mo and U, favouring high concentrations in the bottom water. However, pH is also lower in the bottom water which may also contribute to the higher concentrations for the pH dependent metals like Cd, Zn and Ni. The only metal showing strong correlation to DOC is Cu, which is to be expected as the occurrence of Cu in the water column is largely controlled by the relatively strong binding to dissolved and colloidal organic material.

The concentration levels for U, Ni, As and Cd in the bottom water of Lake Tranebärssjön is 20-100 times higher than background levels for Swedish lakes. The levels in the surface water are lower but still more than 5 times higher for Ni, U and Cd.

This study shows that the high stratification of LakeTranebärssjön, the former open pit mine, with anoxic bottom water, results in solubilisation of redox dependent metals, redistributed to littoral zones and further downstream at the spring and autumn turnover.

The lithium-ion battery - is it as "green" as we need?

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Rechargeable Li-ion batteries are today dominating the market for portable devices such as: laptops, mobile phones and camcorders, etc. Primary Li-batteries have their use in medical devices or for powering cameras or the flash of the camera. The next technological step is either to up-scale the battery to be used in hybrid-electrical-vehicles (HEV) or in plug-in HEV or to down-scale the battery, with the use of nano-technology, to power sensors or MEMS.

This rich portfolio of applications implies the need for tuning the chemistry in-side the battery to precisely fit to the requested energy- or power density of the different systems. Li-ion batteries consist, therefore, of a family of different chemistries.

The basic construction of a Li-ion battery consists of a positive electrode that can be a lithium-containing metal-oxide or phosphate, a carbonaceous material as the negative electrode and an electrolyte based on a lithium-salt in an organic solvent. In a commercial battery of today LiCoO_2 is a typical cathode material. Cobalt is too expensive for an up-scaling of the battery for HEV and this metal must therefore be replaced with a cheaper, abundant and environmentally benign redox-metal. The systems of interest for the future battery are based on iron, titanium or manganese.

In this presentation, the different alternative materials to LiCoO_2 will be discussed with respect to their environmental impact but also with respect to their electrochemical performance.

For high power applications, the graphite anode also needs to be replaced with a material that can host large amounts of lithium-ions. How will this influence the safety of the battery? This is also be addressed in this presentation.

Remediation of soil/sediment with activated carbon amendment: results from two Norwegian field studies

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For the first time in Europe, a novel and innovative remediation technique is used in a field pilot study. This technique is amendment of the soil with activated carbon (AC). The idea is that the added AC binds organic contaminants so strongly that they cannot be taken up in living organisms or transported to other environmental compartments. Laboratory studies with 2% (wt%) AC amendment to an urban soil reduced the freely dissolved pore water concentrations of polycyclic aromatic hydrocarbons (PAH) by 17% to 99% (Brändli et al. 2008).

Two separate field trials will be presented: Drammen (soil, 2007-2009) and Trondheim Harbor (sediment, 2007-2009). In Drammen, 2% AC was mixed into the soil which thereafter was placed in a test plot (5m×5m and 2m deep) with concrete walls. Rain and melt water passing through the soil is drained into a drainage pipe where sub-samples can be collected. PAH, dissolved organic carbon (DOC) and nutrients were analyzed in the drainage water. The freely dissolved PAH concentrations were reduced with 82-96% between untreated soil and soil with pulverized AC. The DOC and NH₄ were reduced with 50-70%. Further, there were no measured effects for K, NO₂ and NO₃ in the drainage water.

For the Trondheim Harbor sediment, a thin film of AC was spread out onto the sediment surface as a thin film acting as an active barrier which absorbs organic pollutants passing from sediment to the overlying water. In the test fields, the PAH flux from sediment to overlying water have been measured in a first round. However, the results have so far been inconclusive. This may come from: i) sedimentation of contaminated material on top of the AC layer which in turn decrease the effect of the active AC barrier, ii) the AC layer not working as effective in the field as shown in lab experiments, and iii) the flux chamber used for the PAH flux determinations not working properly. On the other hand, a laboratory test showed that the AC being out in the field between 6 months (Trondheim) and 1 year (Drammen) still had a strong sorption capacity for newly added PAHs that was as good as "fresh" AC within a factor of two. The application of AC did not result in adverse effects on biodiversity or numbers of individuals in the sediment.

Amendment of soil/sediment with AC remediates the soil/sediment from organic contaminants when these pollutants are sorbed to the AC surface. This is an easy technique that can be performed to a relatively low cost. However, the AC particle may also sorb other constituents of the effluent water such as DOC and nutrients which in turn may lead to reduced plant growth rate. Therefore, the long-term effects of this amendment technique have to be studied carefully. Further, the mass transfer of PAH to the AC particle under field-like conditions has to be investigated more closely.

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Non-incineration treatment of persistent organic pollutants (POP) with iron oxide nano-particles

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Persistent organic pollutants (POP) have been recognized as a global problem (Stockholm Convention, 2001) because of their wide-spread use, persistence, and transport. Polychlorinated biphenyls (PCB), polychlorinated dibenzodioxins and furans (PCDD/PCDF), and chlorinated pesticides such as lindane, DDT, dieldrin, endrin, and related compounds remain as residues in soils and sludge or as high-concentration product in many countries around the globe. Many innovative alternatives to the common treatment method for POP, incineration, have been tested but have been applied at a large-scale only rarely.

Iron nano-particles dechlorinate PCB and other chlorinated pollutants (P. Varanasi, A. Fullana, S. Sidhu, *Chemosphere* 66 (2007), 1031-1038; W. Zhang, *Journal of Nanoparticle Research* 5 (2003), 323-332). This presentation describes the catalytic dechlorination by iron oxide nano-particles of γ -lindane (hexachlorocyclohexane, HCH) and of PCDD/PCDF produced during the reaction.

The experimental system consisted of two columns in series, each containing 7-cm ceramic plugs of 3.4 cm diameter consisting of 3-7 % nano-iron oxide particles on a ceramic foam. And operating at 300°. A special feed system was designed and built to volatilize synthetic γ -lindane at 250 ° and feed lindane at a rate of about 12 g/hour and air/oxygen. The vapor stream was sampled after the first and second column by adsorbing organics on XAD resin and analysis by extraction/gc-ms in accord with USEPA analytical method SW8081A/8082. PCDD/PCDF congeners were analyzed according to USEPA Method 1613.

Over 100 analyses of lindane on XAD showed that the first column lost efficiency after about 0.2 g of lindane per cm³ of catalyst had been introduced. Chlorobenzenes (0.03-0.3 %) were observed at the outlet of the first column but were reduced by a factor of 10 in the second column. Similarly, chlorinated dibenzodioxins present in the gas stream after the first column (19,750 ng I-TEQ/m³) were reduced to 195 ng I-TEQ/m³ in the second column. Other reaction products included hydrogen chloride, carbon dioxide, and carbon monoxide. Lindane reductions ranged from 90-100 % in column 1, 95-100 % in the second column. In total, about 212 g of synthetic lindane were treated at 90-99 % efficiency over 10 experiments.

The long-term effectiveness of this process depends on the lifetime and regenerability of the catalyst with waste material. HCH waste consisting of an 80 % mixture of α -, β -, δ -, and γ -lindane in soil was obtained from a closed industrial landfill. A system consisting of dual columns about 1 m long with an inside diameter of 15.2 cm containing a packed bed of catalyst is being operated at a feed rate of about 1 kg of HCH/hour.

Prediction and analysis of biotransformation product formation during sewage treatment

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Many chemicals entering the aquatic environment through sewer systems, such as pharmaceuticals and biocides, are partially removed in sewage treatment plants (STPs) through degradation by the bacterial community. However, degradation often falls short of complete mineralization and instead leads to the formation of transformation products (TPs). Existing risk assessment guidelines for pharmaceuticals require assessment of the exposure to and the risk of such environmental TPs, but provide little guidance on how to do so. To work towards developing such guidance, in this study we:

- (i) tested the suitability of small, laboratory-based batch reactors in combination with high-resolution mass spectrometry (HR-MS) to identify the main TPs of selected compounds formed in STPs, and;
- (ii) developed and tested a model that uses the results from the batch reactors to predict the formation and fate of TPs in a real-world STP.

For this purpose, we simultaneously collected activated sludge for batch experiments along with influent and effluent samples of two different STPs in Switzerland at two different dates in the winter 08/09. The batch reactors were spiked with 10 pharmaceuticals that are mostly widely used in Switzerland, that are known to be partially degraded during activated sludge treatment, and for which sorption was not expected to play a major role in their removal. Batch reactors were repeatedly sampled over a period of 6 days and screened for possible TP structures based on a list compiled from the literature and a biodegradation pathway prediction system (UM-PPS, <http://umbbd.msi.umn.edu/predict/>). Screening was carried out based on the extraction of the exact mass from the HR-MS chromatogram and the HR-MSMS spectra of all possible products [1]. In the case of positive identification of a TP, parent compound and TP concentrations were semi-quantitatively or, if analytical standards were available, quantitatively analyzed over the entire time series. At the same time, parent compound and TP levels in the influent and effluent samples were determined using mixed-cartridge solid-phase extraction and liquid chromatography followed by HR-MS.

For 7 out of the 10 spiked compounds, the formation of one or several biotransformation products was clearly demonstrated in the batch reactors and they were identified based on their HR-MSMS. Three of the TPs identified had not been previously reported, and thus could not be quantified with analytical standards. However, standards were available for five TPs whose rates of formation and subsequent degradation could consequently be quantified. All TPs found in the batch experiments could also be identified in the STP effluents, with the exception of AMDOPH, whose parent compound aminopyrine is no longer sold in Switzerland. Finally, using a cascade-reactor model to represent compound degradation within the investigated STPs, quantitative agreement between modelled and measured effluent concentrations of each TP could be demonstrated.

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Catalytic oxidation of cyclohexanol with supports from biosorption of hexavalent chromium

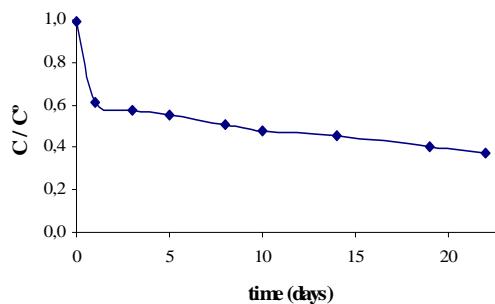
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Current research in the pollution control field has led to the development of several technologies for prevention and remediation. However, due to several constraints as cost, efficiency and availability of mineral resources, recovery-reuse processes are commonly suggested as the most appropriate practices [1]. Metal contamination of aqueous streams or sources is a known environmental concern, which originates mainly from the discharge of contaminated industrial effluents into the environment. Chromium is a heavy metal commonly found in effluents from tanneries, electroplating facilities and textile finishing. Unlike most heavy metals found in waste streams, Cr is commonly found in anionic form, as chromate or dichromate ions. This fact renders the treatment of Cr contaminated effluents difficult, and chemical precipitation is the most widely used process [1]. A system combining a biosorbent and an inorganic matrix, zeolite, has been proposed as a recovery-reuse process for the treatment and reutilization of chromium [2]. The biotreatment of Cr^{VI} is performed by the *Arthrobacter viscosus* bacterium, which reduces this ion to the lower Cr^{III} oxidation state. The latter exists as a cationic species that can be ion-exchanged by the zeolitic support, which is only able to exchange cations. The reutilization of the Cr containing zeolite (the exhausted supports from biosorption process) is performed in catalytic processes.

This work reports the usage of a NaY zeolite as support for the *A. viscosus* bacterium for the treatment of a Cr^{VI} solution (100 mgCr/L) and the recovery and reuse of the Cr loaded NaY as catalyst for the oxidation of cyclohexanol into cyclohexanone. The concentration of biomass has a role in the performance of the system. The higher biomass concentration (4 g/L) favoured the reduction of Cr^{VI} into Cr^{III}. The figure to the right presents the Cr^{VI} concentration over initial concentration during experimental time. After 24 hrs the initial concentration decreased 40%, with a slower decrease afterwards.



Cr loaded NaY (CrNaY) was able to improve oxidation of cyclohexanol into cyclohexanone using *tert*-butyl-hydroperoxide as oxidant. The parent NaY zeolite shows no catalytic activity for the reaction (4.5 % conversion compared to 4.0 % for the blank reaction). However, after loading with the biotreated Cr, CrNaY catalyst increased conversion to 38 %.

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Chemicals in food - additives, adulteration, environmental contaminants - analytical challenges and response

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The presence of chemicals in food can generally be due to

- natural occurrence
- intentional (legal) addition as additives (e.g. flavours, colours, antioxidants, sweeteners)
- formation during processing (e.g. acrylamid, furan)
- fraudulent adulteration of food commodities (e.g. diethylene glycole, melamine)
- residues from application of pesticides on crops or pharmacological active substances in food producing animals
- environmental contamination (e.g. dioxins, PCBs, brominated flame retardants)

While the intentional adding of food additives does normally pose no health problem as these substances have to be evaluated and registered before use and are EU wide regulated, the fraudulent adulteration of food is of long-standing concern ever since food is produced commercially and no longer for own consumption only. Earlier examples were the dilation of precious spices with stone dust or the illegal addition of lead acetate and diethylene glycol to wine. The latest case concerns the addition of melamine to baby food and other food commodities causing numerous considerable health problems including some deaths of babies in China. Knowing that the determination of the protein content in food is normally performed via the amount of nitrogen, the nitrogen rich compound melamine was mixed into food in order to pretend a high protein content. This case demonstrates the need for official food control to apply modern and sophisticated analytical methods. Especially in the past two decades a number of highly sensitive and selective analytical techniques found their way into the laboratories which considerably improved the capabilities of control authorities. In this context, high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS) as well as high performance liquid chromatography coupled to mass spectrometry in MS/MS mode (LC-MS/MS) or to time of flight mass spectrometers (LC-TOF/MS) have to be mentioned. Modern LC-MS systems using the Orbitrap technology allow resolutions up to 100,000 and thus make the simultaneous identification and/or determination of compounds with only little mass differences possible. Because of the high selectivity and sensitivity of the above systems, the clean-up of extracts and thus the analysis time can often substantially be decreased and thus the number of samples to be analysed considerably increased. The huge technological progress regarding sensitivity nowadays permits the detection of compounds that are present in the environment and food since decades but could for a long time not be analysed because of lack of sensitivity. This is especially true for dioxins and PCBs. Their findings in food and human specimens entailed the issue of EU wide Regulations including the request for the Member States to perform comprehensive monitoring programmes. As a result, these programmes discovered numerous incidents, such as the adulteration of guar gum with pentachlorophenol, including dioxins as a contaminant or the latest dioxin case concerning pork from Ireland.

Microextraction approaches for the determination of organophosphate esters in water samples

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Organophosphate esters (OPs) are used extensively as flame retardants and plasticizers in many products such as hydraulic fluids, polyurethane foams, textiles, electronic equipment, etc. They are usually utilized as additives, not chemically bonded to the materials they are intended to protect, and thus they are easily leached into the environment. Consequently, several OPs have been detected in different environmental matrices, e.g., air, water, wastewater, sediments and particulate matter from indoor and outdoor areas [1].

In general, the information about the toxicological impact of OPs is still scarce; however, deleterious effects for some of them have been already reported. In terms of toxicity, persistence and mobility, triphenyl phosphate (TPP), tris(2-chloroethyl) phosphate (TCEP), tris(chloropropyl) phosphate (TCPP) and tris(dichloropropyl) phosphate (TDCP) are the most concerning OPs. Specifically, the chlorinated ones might be considered as persistent pollutants since they are not effectively removed in conventional urban wastewater treatment plants. This behaviour joined to their growing usage, in part due to the latest years bans on brominated diphenyl ethers (BDEs) utilization, have promoted the interest of the authorities and some of them have been included in European lists of aquatic priority substances [2,3].

The development of simple, affordable, solvent-free (or with low solvent consumption) and miniaturized sample preparation techniques is a challenge for chemists. In this way, the performance of different microextraction approaches for OPs analysis in environmental samples has been evaluated until now [4,5].

The aim of this work is to present three microextraction techniques which have been applied to the analysis of OPs in water samples, namely: dispersive liquid-liquid microextraction (DLLME), microporous membrane liquid-liquid extraction (MMLLE) and solid phase microextraction (SPME). Several parameters affecting the performance of these methods were evaluated in detail. Furthermore, a comparison in terms of cost, solvent consumption, suitability, easiness and limits of quantitation is also presented.

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Quantification of weathering factors for medieval like model-glass

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Under general exposure conditions, ancient stained glass windows undergo different kinds of degradation processes that modify their optical properties, chemistry and structure. The different forms of deterioration observed on stained glass windows are leaching and corrosion, particle deposition and formation of salts (neocrystallizations) potentially growing into a crust. Previous researches show that, in the unsheltered areas of the bays, the water runoff is the main factor inducing leaching, while in the areas sheltered from the rain, the alteration processes are less pronounced and consist mostly in crust formation. The main goal of this study is to quantify the role of intrinsic (glass chemical composition) and extrinsic (environmental parameters) factors on atmospheric glass weathering.

K-Ca low durability model-glass samples were manufactured in order to simulate the composition of medieval stained glass windows. Those samples, along with other samples of Na-Ca modern durable glass, were exposed to an urban atmosphere sheltered or unsheltered from the water runoff (ISO 8565:1992). The unsheltered samples were used to quantify the effect of wet deposition on the glass weathering, while the sheltered samples were used to assess the effect of dry (gas and particle) deposition. After withdrawal at different exposure-time intervals, samples were analysed by: Ion Chromatography, SEM-EDS and ICP-AES, in order to identify the neocrystallizations present at the surface of the sheltered glasses, gravimetric measurements, to quantify the mass variations, and EMPA and FTIR spectroscopy, to quantify the structural modifications of the glass surface. A parallel *in situ* monitoring of atmospheric gas and particle concentrations and meteorological parameters was carried out.

During the first two years of exposure, the total particle deposition on the surface of the sheltered medieval glasses was 2.8 times as important as on the durable glasses. The soluble deposits represented 62% of the total deposited mass for the medieval glass, against 25% for the durable one, with a total deposited mass 41% higher on the medieval type glass. SEM observations confirmed the presence of crystallized K and Ca salts on the surface of the medieval glasses. The chemical analysis of the soluble fraction of the deposits, found on the medieval type glass, showed that SO_4^{2-} was the major anion (74%), followed by NO_3^- (19%) and Cl^- (7%). The concentrations of SO_4^{2-} and NO_3^- on the glasses surface were well correlated to the atmospheric concentrations of SO_2 ($R^2=0.92$) and HNO_3 ($R^2=0.87$). The flux of gas on the medieval glass was calculated from those concentrations ($0.48 \mu\text{mol.cm}^{-2}.\text{s}^{-1}$ for SO_2 and $0.20 \mu\text{mol.cm}^{-2}.\text{s}^{-1}$ for HNO_3). The comparison between the different glasses and types of exposure led to the quantification of the following contributions to the weathering. The wet deposition contributes to 82% of the weathering, while particle and gas depositions contribute respectively to 7 and 11% of the different processes. Finally, the comparison between durable and low durability glasses showed that the weathering of these last ones was always higher than that of the first ones (for instance, the hydration is 3 times higher in sheltered condition and 11 times in unsheltered condition).

Copper-based alloys in outdoor applications - aspects on patina growth, composition and dissolution at different urban and marine sites in Europe

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Outdoor monuments and structures of copper alloys spontaneously develop a patina of corrosion products as a result of atmospheric corrosion. Such patina is normally considered to have significant historical and aesthetical value, and its appearance may be dark, greenish or reddish depending on age and environmental exposure conditions. Patina thickness and composition depend on parameters such as alloy composition, time of exposure, prevailing climate, pollution and exposure conditions in terms of surface orientation, inclination and degree of sheltering. The formation of a patina is mainly an electrochemical process where the metal alloy surface is oxidized as a result of the environmental interaction. Patina dissolution on the other hand is primarily a chemical process where a fraction of the patina dissolves and can, by the interaction with precipitation, be transported from the surface. This metal transport is commonly referred to as metal runoff or metal release, an important aspect of atmospheric corrosion that has been disregarded for many years. Patina dissolution and corrosion (oxidation) are two distinct phenomena and should not be mixed up.

To improve the understanding of patina growth and dissolution it is essential to evaluate the relation between these processes and their correlation with prevailing environmental and pollution conditions. Such information is of paramount importance for the preservation of our cultural heritage in order to facilitate the selection of the most suitable conservative procedures.

Pure copper, bronze (6%wt Sn) and brass (20%wt Zn) have been exposed at unsheltered conditions for two years in five European environments of significantly different climatic and pollutant conditions: three urban sites (Stockholm-Sweden, Milan-Italy and Madrid-Spain) and two marine sites (Brest-France, Cadiz-Spain).

Generated data are interpreted with respect to parallel multi-analytical studies of changes in patina characteristics, patina dissolution, and corrosion rates as consequence of the different prevailing environmental conditions. The occurrence of selective corrosion induced by chloride and sulphate ions, for example dezincification of brass (Cu-Zn-alloys) is also investigated and highlighted.

Tracking diene toxicology

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Many elderly persons are deficient in vitamin B₁₂ and this may predispose to cancer and degenerative illnesses such as Alzheimer's disease.^{1,2} Methionine synthase utilises the reduced form of vitamin B₁₂, cob(I)alamin, to remove the methyl group from N⁵-methyltetrahydrofolate giving methylcobalamin, which reacts with homocysteine to afford methionine. Deficient methylation, as a consequence of B₁₂ deprivation, causes accumulation of homocysteine, which is a risk factor for heart disease.³ Inadequate levels of vitamin B₁₂ may be caused by dietary lack, inefficient absorption/transport or possibly scavenging by xenobiotics.

Many environmental and occupational carcinogens form metabolites, e.g. epoxides, that give DNA adducts, which may initiate cancer if not repaired. Because of the exceptional reactivity of the cob(I)alamin form of vitamin B₁₂ towards electrophiles, these reactive metabolites and direct acting genotoxic carcinogens could have a significant effect on cellular levels of vitamin B₁₂. A critical issue is whether vitamin B₁₂, as cob(I)alamin or cob(II)alamin, is an effective scavenger of electrophilic xenobiotics, and therefore protects against their deleterious effects, or does the depletion of B₁₂ by such xenobiotics have downstream effects relevant to human disease? Concerning the possible role of vitamin B₁₂ in human toxicology we found, using a liver microsome system *in vitro*, that vitamin B₁₂ can significantly influence the profile of xenobiotic metabolism.⁴ Most significantly, the cob(I)alamin and cob(II)alamin forms of vitamin B₁₂ were shown to react with epoxide metabolites derived from important industrial dienes, for which occupational and environmental exposures occur. It was also found that vitamin B₁₂ could be protected by glutathione against depletion by epoxide metabolites.

The effective scavenging of diene epoxides by reduced cobalamins enables the important dienes buta-1,3-diene and 2-methylbuta-1,3-diene (isoprene) to be measured in biological milieu. We will describe applications of cob(I)alamin as an analytical tool in tracking dienes. In view of the possible role of vitamin B₁₂ in protecting against cancer caused by electrophilic xenobiotics we have carried out model studies *in vitro* to explore the vitamin's effects on DNA adduct formation by genotoxic carcinogens. We will report the results of studies concerning the effect of vitamin B₁₂ (as hydroxocobalamin) on DNA adduct formation *in vitro* by e.g. styrene, a precursor carcinogen, which requires metabolism to exert its carcinogenic effect.

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Source apportionment of atmospheric black carbon, *n*-alkanes and PAHs using natural abundance radiocarbon analysis

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Combustion-derived carbonaceous aerosols have large effects on both climate and human respiratory health. Unfortunately, substantial uncertainties still exist regarding the relative importance of various fossil versus biomass combustion sources. This presentation aims to illustrate how recent development in natural abundance radiocarbon analysis offers a novel approach to constrain the sources of key constituents of atmospheric aerosols (1,2,3).

For the Asian Atmospheric Brown Cloud, emission inventory models suggest that biofuel/biomass burning accounts for 60-90% of the sources of these aerosol components whereas measurements of the elemental composition of ambient aerosols compared with source signatures point to combustion of fossil fuel as the primary culprit. However, both approaches acknowledge large uncertainties in source apportionment of the elusively-defined black carbon. Our study approached the sourcing challenge by applying microscale radiocarbon measurements to aerosol particles collected during the winter monsoon both over the Indian Ocean and in central India (4). The radiocarbon approach is ideally suited to this task as fossil sources are void of ¹⁴C whereas biomass combustion products hold a contemporary ¹⁴C signal. High-volume air samples of total carbonaceous aerosols revealed ¹⁴C signals that were similar for N. Indian source and Indian Ocean receptor regions with a 60-70% contribution from biomass combustion and biogenic sources. Isolates of elemental or soot carbon fractions varied between 40-70%, depending on isolation method.

Compound-specific radiocarbon analysis (CSRA) studies of semi-volatile n-alkanes and polycyclic aromatic hydrocarbons (PAHs) in air collected at various locations throughout Europe combine to reveal both inter-compound (5), inter-regional (6,7) and inter-seasonal variations in sources. For instance, modern biogenic sources contribute a significant portion (frequently up to 50%) of the atmospheric load of priority pollutant PAHs and long-chained n-alkanes, suggesting that such sources should be scrutinized for effective reduction.

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Quantitative structure-photodegradation relationships of polybrominated diphenyl ethers, phenoxyphenols and selected organochlorines

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The consequences of the extensive use of chemicals in modern society can be detected in the environment worldwide, i.e. in wildlife and humans. To facilitate screening, models such as qualitative structure-activity relationships, quantitative structure-activity relationships and multimedia fate models may be used. Applying computational modelling for prediction of properties and fate of chemicals can minimize both laboratory work and animal testing. In this study we examine how structural characteristics can quantitatively describe laboratory determined photolytic half-lives of halogenated compounds of different classes, such as polybrominated diphenyl ethers (PBDEs), hydroxylated brominated diphenyl ethers (OH-PBDEs), and some neutral organohalogens. A total of 30 chemicals with experimentally measured half-lives are used. Results revealed that the most important descriptors for describing the half-lives of the brominated compounds excluding HBB were the energy gap between HOMO-1 and LUMO (GAP-1), the lowest partial charge on a halogen atom (Qhal-), topological polar surface area (TPSA), the atom with highest radical superdelocalizability (Rad-super+) and LUMO density (LUMO+). For the whole dataset, without HCB, three compound class separation descriptors were present in addition to the atomic descriptors Qhal- and LUMO+.

Factors influencing the preferred biodegradation pathways of xenobiotics with amide functionality

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Transformation products (TPs) of many xenobiotics released to the environment may have greater persistence and/or eco-toxicological effects than their parent compounds (PCs). Biodegradation pathway prediction tools could be used to inform studies aimed at screening for persistent TPs. However, these tools employ structure-biodegradability relationships built from databases of biodegradation data derived from pure culture experiments and may not be suitable for environmental applications. Further, these tools often predict several possible transformations at individual compound moieties, resulting in low selectivity. Prediction selectivity can be greatly enhanced by identifying preferred pathways when multiple transformations are predicted at a given structural fragment. Amide groups are common structural fragments whose preferred biodegradation pathway remains ambiguous; studies have reported both hydrolyses and oxidative de-alkylation at the amide bond. Understanding how environmental conditions or chemical properties influence the preferred biodegradation of amides could significantly improve the selectivity of TP prediction, but experimental data is needed. The primary goals of this work were to generate a large set of biotransformation data for a diverse group of amidic xenobiotics in an environmentally relevant test system and to identify how transformations are influenced by environmental factors and/or the stereo- or electrochemical properties of each compound.

To meet these goals, a biodegradation test system (BTS) was designed and optimized to simulate the microbial-mediated transformations that may occur in sewage treatment plants, the major biodegradation compartment for many xenobiotics. The BTS was optimized as a low volume system to generate a large set of biodegradation and biotransformation data for a large number of compounds spiked at low concentrations (ng/L to µg/L range) and without the need for analytical standards. The compounds selected consisted of a diverse set of basic amides (which contained no other functional groups) along with several environmentally relevant amides (e.g., pharmaceuticals, pesticides). Degradation of the PCs and formation of the TPs was measured using liquid chromatography coupled to high resolution mass spectrometry. Positive identification of TPs was achieved by using the exact masses of a list of predicted TPs and their MS/MS fragmentation patterns.

Some of the tested compounds have had their biodegradation pathways previously studied in pure culture and reported in the literature. For these compounds (e.g., propachlor, DEET), the TPs formed in the BTS were different than those reportedly formed in pure culture, but consistent with those reportedly found in surface waters. This may be attributed to how the microbial populations respond to the compound in each system, as a carbon source or a co-metabolic substrate. Further, it was shown that competition for enzymes that catalyze reactions at amide groups can result in either partial or complete inhibition of reactivity at the amide group or enhancement of reactivity at other compound functional groups. On-going work aims to study the observed biodegradation pathways of the amides and compare the stereo- and electrochemical properties that result in the preferred biodegradation pathways.

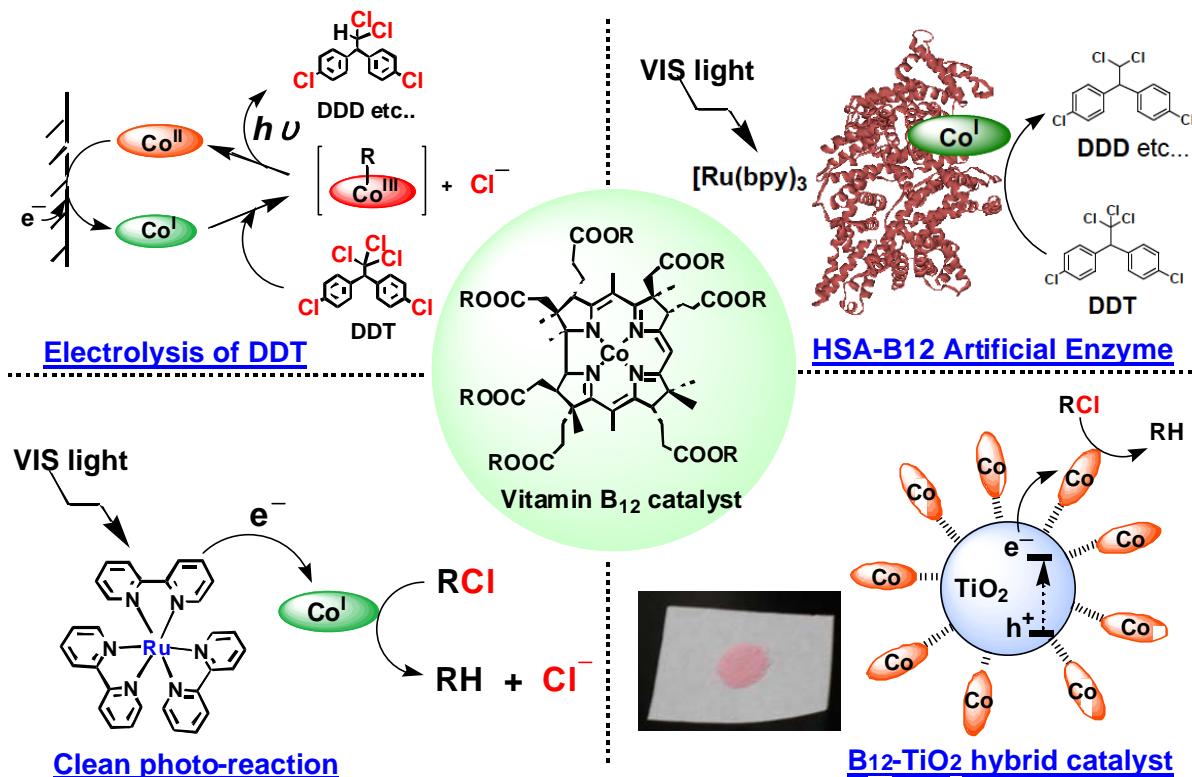
Bio-inspired Catalysts with vitamin B₁₂ functions for degradation of organic halides pollutants

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We have been interested in vitamin B₁₂-dependent enzymes, involving the cobalt species as a catalytic center, and dealing with a hydrophobic vitamin B₁₂, heptamethyl cobyrinate perchlorate, which has ester groups in place of the peripheral amide moieties of the naturally occurring vitamin B₁₂. In order to construct a good catalytic system, we prepared various nanomaterials with vitamin B₁₂ activities such as a vitamin B₁₂-titanium dioxide hybrid catalyst. In this talk, we will focus on degradation of DDT.¹⁻⁴ These bioinspired materials can apply to the catalytic reactions for not only the degradation of organic halides but also various organic syntheses. These bio-inspired catalysts are very interesting from the viewpoint of green sustainable chemistry.

Vitamin B₁₂ as Green Catalyst



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Sources and exposures of airborne PCB congeners in a contaminated waterway of Lake Michigan USA

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The Indiana Harbor and Ship Canal is a PCB-contaminated waterway that lies in the community of East Chicago, Indiana, USA. This waterway is a significant source of PCBs to Lake Michigan and we have hypothesized that it is also a source of airborne PCBs to the surrounding community. We have been examining the fate of PCBs in the waterway and the potential for a relationship between the emissions of PCBs from the waterway and the accumulation of PCBs in the blood of the residents. Using a conservative approach that ignored resuspension and turbulence due to storms and barge traffic, we determined that approximately 6 kg of PCBs are released each year from the sediments of the IHSC and that approximately 12 kg of PCBs are volatilized each year from the waters of IHSC. The congener profile distribution of the air and the sediment is strongly supportive of our prediction: the congener distributions in the air and water are very similar to Aroclor 1248, the PCB commercial mixture that contaminates IHSC ($R^2 = 0.69$ and $s = 0.0061$). To quantify the uncertainty in the flux predictions, we used a Monte Carlo simulation model to examine the importance of each of the independent variables (e.g., equilibrium coefficients, mass transfer coefficients, wind speed and water temperature). In this paper, we report our methods for measuring PCBs in the sediment, water, air, and our preliminary results regarding the relationships between the environmental compartments.

Novel analytical tools for the comprehensive profiling of environmental samples

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Analysis of environmental samples is a challenging task owing to the diversity of sample matrices and the large amount of different organic species of compounds, which often are even present at trace levels. Many laboratories still use conventional methodologies which are often extremely time- and labor consuming, poorly suitable for analysis of large number of samples and often the sensitivity, selectivity and reliability is not satisfactory. Recent developments in analytical methodologies include miniaturised and (nearly) solvent free extraction techniques, faster separation methods and more efficient separation by comprehensive two-dimensional techniques. From liquid samples, SPME, SBSE, miniaturised SPE and LPME systems have several advantages over more traditional methodologies. For solid and semisolid samples, PLE is replacing conventional Soxhlet extraction methods, as the extraction is much faster and automated systems can be utilised. However, especially the extracts from solid and semisolid samples require further purification and currently this part of the analytical procedure is becoming the bottleneck of the analytical scheme. Increasing the speed of analysis is essential, when large amount of samples have to be analysed, or when comprehensive profiling of chemical composition of a single sample is required with 1-dimensional chromatographic methods. Thus, development of both fast GC and fast LC method is essential. For very complex samples the separation efficiency of one-dimensional chromatographic techniques is often not satisfactory. GCxGC and LCxLC increase the separation efficiency substantially. An example of the advantages of GCxGC with TOFMS over the conventional GC-MS methods is demonstrated in Figure below. The example shows that in the case of complex samples, the sensitivity and selectivity of conventional GC-MS was not sufficient for identification of compounds present in trace level. By using GCxGC-TOFMS, both the sensitivity and selectivity are clearly higher, and identification is easier and more reliable.

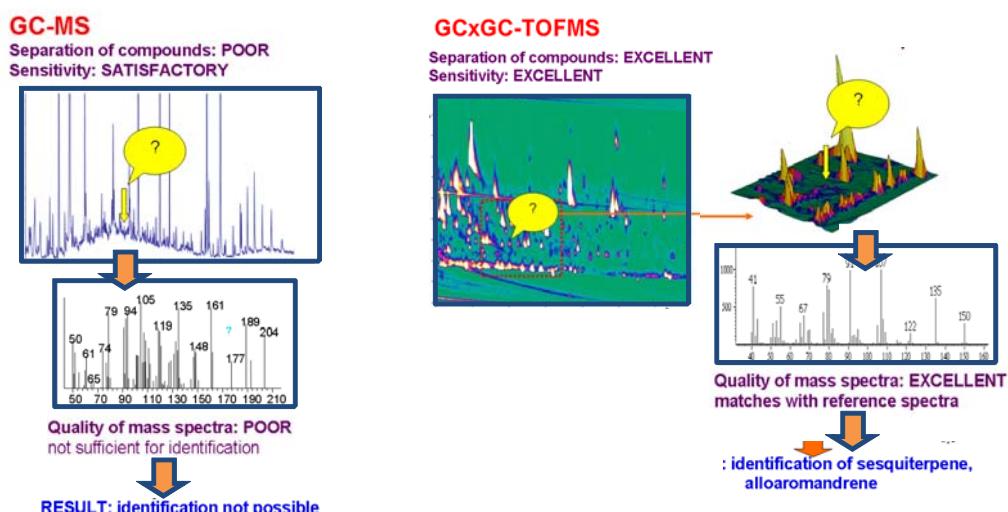


Figure. Identification of compounds in aerosol particles by GC-MS and GCxGC-TOFMS.

Partitioning and photodegradation of alternate brominated flame retardants in aquatic surface microlayers

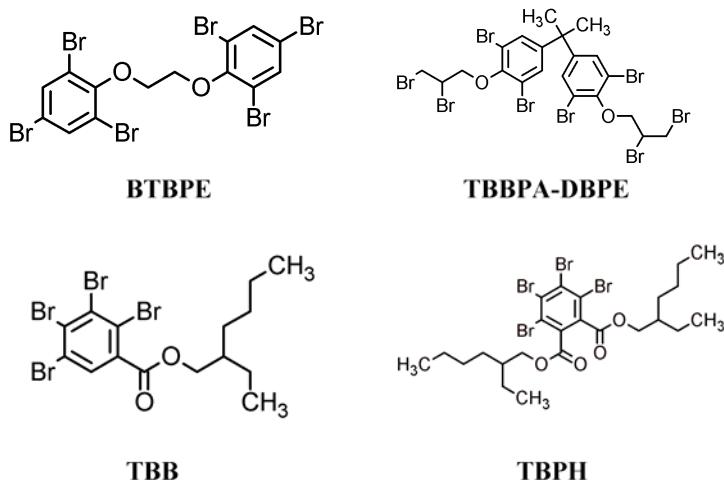
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The aquatic surface microlayer (SML) is a complex and stratified system which covers all natural water columns that are biologically active [1]. The topmost layer of SMLs are hydrophobic and can act as a reservoir for POPs and other organic pollutants. SMLs are exposed to high intensities of solar radiation, making photodegradation of compounds in SMLs a relevant yet currently unexplored process. It is the objective of this research to understand the role and relevance of SMLs on the environmental behaviour and degradation of organic pollutants using model systems and field experiments.

In this study, the partitioning behaviour of alternate brominated flame retardants (BFRs) spiked into experimental 12,000 L mesocosm ponds was investigated. SMLs were sampled using a silanized glass plate [2], extracted with dichloromethane followed by cleanup. Subsurface water was also sampled and extracted using C₁₈ SPE. Quantification was performed using GC-MS. One such BFR, bis(2,4,6-tribromophenoxyethane) (BTBPE, structure given below) was shown to have microlayer enrichments from 2.7x10⁵ to 1.4x10⁶ relative to the subsurface water. Enrichment measurements of other BFRs: TBBPA-DBPE, TBB and TBPH (structures given below), are ongoing.

Preliminary molecular characterization of lipids in SMLs without derivatization and minimal sample preparation using high temperature GC will also be discussed. Further experiments in this area include the preparation of a synthetic microlayer system which can be used for laboratory-based photolysis experiments using halogenated probe compounds.



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Fabrication of solid oxide fuel cell by thermal spray

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Solid Oxide fuel cells (SOFC) are interesting because of their high efficiencies and reduced emissions, over conventional power generation methods. With the development of SOFC one of the biggest challenges facing the industrial application of SOFCs is to reduce the manufacturing cost.

Solid oxide electrolyte is made from a ceramic such as Yttria-Stabilised Zirconia (YSZ) which acts as a conductor of oxide ions at temperatures from 600 to 1000°C[1]. Thermal Spray is very common in production of SOFC electrolyte and other layers because of its potential in obviation of sintering process, reducing costs and fast rate of ceramic layers fabrication [2]. Air plasma spray (between different types of thermal spray) can melt ceramic materials of SOFC. However existence of pores in electrolyte layer decreases output voltage[3]. In Fig1 this procedure is shown.

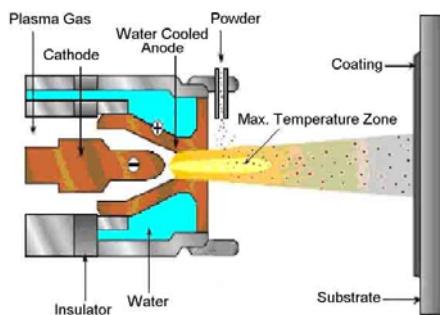


Fig1: air plasma spray procedure

Anode is made by flame spray of 50% Ni5Al+ 50% YSZ on aluminum substrate. Thick anode layer increases strength and because of low electrical resistance of Ni, the resistance of anode remains low. YSZ doesn't melt completely and increases open pores and Triple Phase Boundary (TPB).

Cathode materials are prepared by composition of 80%LSM+20%YSZ. Fine powder of cathode can be sintered in test temperature and Rough electrolyte surface increases stickiness and TPB in electrolyte and cathode interface. Maximum 13.2 mw/cm² power density are generated which is higher than other reported result that used plasma spray for electrolyte fabrication[4,5]. It may be because of anode pores with high TPB that increases current density.

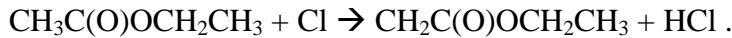
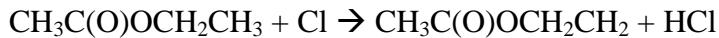
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Atmospheric impact of bio-diesel analogs. Kinetics of the gas phase reactions of a series of acetates with OH and Cl

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The production of bio-ethanol increased by 22% in 2006, and the production of biodiesel by 80%. It is essential to know the atmospheric impact of any potential biofuel. The principal biodiesel under consideration are fatty acid methyl esters (FAMEs). We will consider the atmospheric degradation of acetates $\text{CH}_3\text{C}(\text{O})\text{O}(\text{CH}_2)_x\text{CH}_3$ (where $x=0,1,2\dots$) which serves as model compounds for . The main atmospheric loss processes of the acetates are the reactions with OH radical and Cl atoms. When OH or Cl react with an acetate by hydrogen abstraction. For ethyl acetate reacting with Cl atom there are three reaction channels



Little is known about the branching ratio of the various reaction channels but the hydrogen abstraction on the $-\text{O}(\text{CH}_2)_x\text{CH}_3$ group dominates the reaction. For the reaction between Cl and $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$ more than 95% proceeded via H-abstraction at the $-\text{OCH}_3$ site¹. A detailed study of the reaction mechanisms for acetate reacting with OH radical and Cl atom is needed.

In this presentation we will study the hydrogen abstraction mechanism between acetates and OH radical or Cl atoms systematically using electronic structure calculations. The temperature dependent rate constant will be determined using standard transition state theory. We will obtain an estimate of the branching ratio of the the reaction channels. The rate constant will be compared to experimental values. It has been observed that the rate constants of methyl acetate show negative temperature dependences, while acetates with CH_2 groups have a positive temperature dependence^{2,3}.

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Measurements of mercury species in Deûle river ecosystem using diffusive gradients in thin films and other common techniques

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The Deûle River in Northern France has been polluted by important industrial metallurgical activities during all the XXth century. What has resulted in an historical pollution of river water and sediments by metallic pollutants. Because of natural high concentration of mercury present in the ores used by this factory and its waste-water management, the mercury has been progressively introduced in the whole aquatic ecosystem together with other metals.

In study presented, mercury species concentrations in surface water, sediment pore water and sediment were assessed at two different sites near the former Zn-Pb smelting factory – Metaleurop (near Douai). The first site was located directly in area of Metaleurop factory, where potentially higher mercury contamination was expected. The second one was situated outside the factory area and was supposed to be less contaminated.

Mercury pore water concentration was measured by two different approaches, in situ by the diffusive gradients in thin films technique (DGT) followed by analysis on advanced mercury analyser (AMA 254) and also using atomic fluorescence spectrometry, after centrifugation of sediment. Analysis of total mercury in dried sediments, were carried out using AMA 254 and analysis of methylmercury by headspace gas chromatography with atomic fluorescence detection following aqueous ethylation with sodium tetraethylborate. Moreover, subsequent analysis of other metals and sulfides in sediment and sediment pore water were performed. All obtained results were compared and discussed.

**Persistent organic pollutants (POPs) in the polar atmosphere:
First results from simultaneous year-around monitoring of POPs in Arctic and
Antarctic atmospheric samples in 2007**

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Atmospheric monitoring of POPs in atmospheric samples is already ongoing for more than 15 years at the Norwegian Atmospheric monitoring site “Zeppelin mountain” (Ny-Ålesund, Svalbard). Important scientific results on the fate and distribution properties of selected POP contaminants in the Arctic atmosphere have been derived from this unique data set. However, no comparable long-term monitoring information is available from Antarctica. Thus, as a part of the new scientific atmospheric program for the Norwegian Antarctic station “Troll” at Dronning Maud Land, the Norwegian Institute for Air Research (NILU) has established a long term atmospheric POP monitoring program based upon identical analytical methods, sampling strategies and selected target POP compounds as applied for the Arctic “Zeppelin mountain” atmospheric monitoring station in Ny-Ålesund. A set of 33 polychlorinated biphenyl (PCB) congeners and 14 organochlorine pesticides (HCHs, chlordanes, and DDT derivatives) have been quantified in high volume air samples from both stations. The first year-around atmospheric POP monitoring on the Antarctic continent (Troll station) has been completed for 2007. A first critical evaluation of the data and a comparison with the simultaneously collected POP contamination levels from high volume air samples from the “Zeppelin mountain” station revealed surprising concentration and pattern differences (table 1).

Table 1: Comparison of POP concentration ranges [min. – max. pg/m³] in air samples from Zeppelin (Arctic) and Troll (Antarctica) during the sampling period 2007.

Compounds	Zeppelin air	Troll air
SUM PCB (33 congeners)	7 - 70	0,2 - 3
SUM hexachlorocyclohexanes (HCH)	7 - 20	0,3 - 5
SUM chlordanes (<i>trans-/ cis</i> chlordane and nonachlor)	0,2 - 4	0,1 - 1
SUM dichloro- diphenyl- trichloro ethane derivatives (<i>p,p'</i> - and <i>o,p'</i> -DDT, DDD, DDE)	0,2 - 2	0,1 - 1
Hexachlorobenzene (HCB)	3 - 11	15-30

Distinct differences in POP pattern and level distributions have been identified. PCB levels seem higher in Arctic atmospheric samples as well as pesticides like HCH isomers and DDT derivatives (table 1). Cyclodiene pesticides (eg., chlordanes) are slightly lower concentrated in Antarctic samples, whereas HCB is found in higher levels for Antarctic ambient air. Compound and congener specific differences will be elucidated in the presentation in more detail. A combination of available emission and application inventories as well as meteorological back trajectory modeling will be applied in order to identify atmospheric transport properties, seasonal distribution patterns and potential source regions on the southern hemisphere.

Pharmacologically active compounds in the environment and their chirality

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Pharmacologically active compounds that include both legally used pharmaceuticals and illicit drugs are a group of emerging environmental contaminants that have been receiving steadily growing attention over the last decade. Surprisingly, there are limited data and minimal understanding of the environmental occurrence, transport, fate and exposure for many pharmaceuticals, despite their frequently high annual usage. Some of the most commonly used pharmaceuticals are sold in the UK in hundreds of tonnes per year. Illicit drugs, belonging to the same group of biologically active compounds, have however hardly been studied in the environment. Although several projects concerning the presence and fate of pharmaceuticals have been carried out across Europe and the USA in recent years they have usually concentrated on a limited number of pharmaceuticals. Additionally, only a very limited, if any, investigation into the presence of their metabolites has been undertaken despite the fact that the analysis of pharmaceuticals' transformation products is a crucial factor in understanding their fate and effects in the environment, especially because many metabolites of pharmaceuticals are biologically active. The one very important phenomenon that has been overlooked by environmental researchers studying the fate of pharmaceuticals and illicit drugs in the environment is their chirality.

Chirality plays an important role in the life of plants and animals but it is also a key factor in the agricultural, pharmaceutical and chemical industries. More than half of the drugs currently in use are chiral compounds and many of these ones are marketed as racemates consisting of an equimolar mixture of two enantiomers. Enantiomers of the same drug have similar physico-chemical properties but differ in their biological properties such as pharmacology, toxicology, pharmacokinetics, metabolism etc. Distribution, metabolism and excretion in the body usually favour one enantiomer over the other. This results from the fact that enantiomers stereoselectively react in biological systems for example with enzymes. Additionally, due to different pharmacological activity, chiral drugs can differ in toxicity. Furthermore, degradation of chiral drugs during wastewater treatment and in the environment can be stereospecific and the degradation of chiral drugs can lead to chiral products of varied toxicity. Distribution of different enantiomers of the same chiral drug in the aquatic environment and biota can also be stereospecific. Biological processes can lead to stereoselective enrichment or depletion of enantiomeric composition of chiral drugs. Therefore the very same drug might reveal different activity and toxicity and this will depend on its origin and exposure to several factors governing its fate in the environment.

This presentation will tackle the phenomenon of chirality in drugs as an important parameter determining their occurrence, fate and toxicity in the environment. Recent results of the monitoring programme carried out for a selected group of 40 chiral and achiral drugs in the UK will be discussed. Current trends in worldwide chiral drugs distribution and UK prescription patterns for chiral drugs will be discussed in the context of their possible toxicity and environmental fate.

Sensitive Methods for the Analysis of Decamethylcyclopentasiloxane (D5) in Air and Biota

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To date risk assessments of decamethylcyclopentasiloxane (D5) have been based on almost no environmental data due to the lack of analytical methods with sufficient sensitivity. Trace analysis of D5 has proven to be difficult, in particular due to method blank problems caused by the ubiquitous presence of D5 in high concentrations in indoor air. Here we present novel analytical methods for the determination of D5 in ambient air and fish. Both methods employ solid phase extraction using ENV+ cartridges. The air method involves pumping air through ENV+ cartridges at 250 L/h. The method is characterized by very low breakthrough, good recovery, good reproducibility, and field blanks that are generally in the sub-nanogram per sample range. The biota method exploits the comparatively low tissue/air partition coefficient by using an active head space approach to purge the D5 out of a heated sample slurry and trap it on an ENV+ cartridge. The method characteristics include large sample volumes, minimal exposure of the sample to air during analysis, simultaneous homogenisation, extraction and clean-up, and clean extracts. The method detection limit achieved was ~0.3 ng/g wet weight.

Mineralogical, chemical and toxicological characterization of the air particles

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Residents of industrialized and densely populated regions are exposed to the ambient air pollution arising primarily from the industrial activities, heavy traffic and combustion sources. However, the organic pollutants are also emitted from various secondary sources such as contaminated soils, buildings or equipment. The health hazard of ambient air is determined by conventional gaseous pollutants (ozone, nitrogen oxides) and particulate matter (PM). The fine and ultrafine size fractions, i.e. < 2.5 and < 0.1 micrometer of size, have been identified to carry the highest hazard potential as they reach deeper into the human respiratory tract and, for ultrafine particles, even into the lymphatic and blood circulations. The chemical composition of the particles themselves, as well as the variety and amount of compounds sorbed to their surfaces, represent other factors expectedly responsible for the health effects. In spite of growing attention devoted to the effects of particles on human health, there are few studies linking the toxicological effects of particles to their size dependent chemical composition. An integrative approach applied in this project includes site-specific detailed characterization of the chemical composition and mass size distribution of atmospheric aerosol particles as a key parameter for understanding the transport and sink processes of substances bound to or carried by particles as well as for the assessment of health hazards of the ambient air. A combination of methods was used to describe a morphology and sorption potential of various particulate size fractions, to determine the chemicals associated with their surfaces and related toxicity of the individual size fractions. Properties of each size fraction of the airborne particles were assessed. Finest fraction (<0.45 µm) showed to have the highest mass, highest active surface, highest amount of associated PAHs and also highest direct and indirect genotoxic potentials. While 43% of PAHs were associated with the fine fraction (< 0.45 µm), 20 % was found in the fraction between 0.45 and 0.95 µm and around 10 % in each of the remaining fractions. This distribution is in a very good agreement with estimated specific areas coming out from mineralogical analysis. The coarse fraction included abundant spores and plant fragments along with rock-forming minerals, such as quartz, feldspars, mica, illite-smectite, chlorite and kaolinite. The intermediate fractions consisted mainly of clay minerals, e.g. kaolinite, illite-smectite, dolomite, calcite and gypsum. The finest fractions (<0.95 µm) were dominated by carbonaceous PM, most probably soot flakes, droplets and films, poorly crystallized quartz, gypsum, lead and copper sulfates. SOS chromotest was used to study direct and indirect (without and with metabolic activation) toxicological potential of each particular fraction. All samples reached statistical significance of direct genotoxicity (Induction Factor >1.5), and genotoxicity increased with decreasing particle size.

Current state on research and research needs on the topic of pharmaceuticals in the environment

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During the last ten years, numerous reports have been published on the occurrence of pharmaceutical residues in river water that receives discharges from waste water treatment plants (WWTPs). The conclusion of these studies is that pharmaceuticals are ubiquitous compounds downstream the treatment plants. It has also been shown that the concentration of pharmaceuticals decreases as the distance between the sampling point and discharge point increases. This decline in concentration is partly due to dilution, but also due to sedimentation and transformation reactions.

There is a huge gap in our knowledge of the environmental fate and impact of pharmaceuticals. Therefore, we are not able to grasp the seriousness of the pollution. For example, more work is needed on the determination of the fate, the possible bio-accumulation and the aquatic toxicity of the compounds.

Since the optimal conditions for biotransformation/biodegradation prevail in the WWTPs, further biotransformation in environmental waters is most likely a rather slow process. A more significant process is transformation initiated by energy up-take from the sunlight, i.e. photolysis. However, phototransformation is seldom a process that causes degradation of the pharmaceuticals, but rather a process that converts parent drugs to new compounds. It has been reported that photolysis of pharmaceuticals may produce compounds of higher environmental concern than the parent compounds. Consequently, more work should be devoted to the study of phototransformations.

Bioaccumulation of pharmaceuticals has been the subject of only a few studies. Work in our laboratory and elsewhere show that fish may accumulate pharmaceuticals and form different metabolites. The effects on the fish physiology are at most unknown, with the exception of the feminization and sterility caused by the ethinyl estradiol. But, should pharmaceuticals cause behavioral changes in fish and make them more vulnerable to predators, especially birds, there may be a risk that the residues are carried over to the predators. Such a scenario may have a deleterious effect on species at a higher level of the food web.

An increasing number of publications deal with the aquatic toxicity of environmentally relevant level of pharmaceuticals. Till now, these publications are concerned mainly with the parent drugs. Common to the findings is that the tested compounds have an effect on the test organisms at surprisingly low concentrations. The compound that has gained most interest in this aspect is the contraceptive ethinyl estradiol, for which a no-effect concentration of 0.35 ng/L has been proposed. But since the drugs are present in the aquatic environment as complex mixtures of parent compounds, metabolites and transformation products, the testing and the risk assessment should be done on mixtures. And due to the chronic exposure, long-term testing is needed. The challenge is to determine quantitatively and qualitatively the appropriate constituent of the mixture, i.e. which compounds should be included and what should be an appropriate amount of the individual compounds?

Minimizing the sample volume for the analyses of PAHs, BTEX and chlorinated hydrocarbons in melted snow

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Fast and simple analytical methods for determination of PAHs (polycyclic aromatic hydrocarbons), BTEX (benzene, toluene, ethylbenzene, xylenes) and chlorinated hydrocarbons (CHs) (1,1,1-trichloroethane, trichloroethene, tetrachloroethene) in melted snow of low sample volume were developed and optimised. The methods were based on Solid-Phase Micro Extraction (SPME) and Purge & Trap (PT) followed by gas chromatography-mass spectrometry (GC-MS).

19 PAHs were extracted by direct immersion (DI) (SPME) from samples of 5 ml. Various SPME fibre coatings were tested. The method detection limits (LOD) and precision ($n=4$, concentration 10 ng/L) for individual PAHs ranged between 0.3 and 2.9 ng/L (derived from the blank values) and between 1.6 and 15.0 %, respectively. These are the values for the polydimethylsiloxane-divinylbenzene (PDMS/DVB) fibre, which showed the highest responses for PAHs and was therefore used for analysis of environmental samples.

BTEX and CHs were extracted using a headspace (HS)-SPME and PT with the sample volumes of 15 ml and 5 ml, respectively. Extraction of BTEX and CHs by PT using a tenax/silica gel/cms trap showed higher responses for individual compounds than HS-SPME. LOD for PT-GC/MS ranged between 10 and 90 ng/L for the compounds showing blank values, i.e. BTEX and trichloroethene. For 1,1,1-trichloroethane and tetrachloroethene no analytes were detected in the blanks. LOD for both compounds calculated at signal to noise ratio of 3:1 were 1 and 3 ng/L, respectively. The precision of the PT-GC/MS method for all BTEX and CHs determined at concentration of 100 ng/L ($n=6$) varied between 0 and 14.9 %.

DI-SPME was used for the analysis of PAHs, and PT for the analysis of BTEX and CHs in the snow samples from Antarctica (both, surface snow and 3 year-old vertical profile of a firn core). The PAH levels ranged between 14 and 188 ng/L in all samples, with the light PAHs showing the highest abundance (blanks subtracted). The concentrations of BTEX and CH ranged from 22 to 140 ng/L in all samples (blanks subtracted). Tetrachloroethene, the compound with the highest octanol-water partitioning coefficient ($\log K_{ow}$) of 3.4, was detected in majority of samples.

Atmospheric lifetime and long-range transport of DDT over central Europe

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Dichlorophenyltrichloroethane, DDT, and its major metabolites dichlorophenyldichloroethylene, DDE, and dichlorophenyldichloroethane, DDD, are long-lived in the environment (persistent) and circulate since the 1950s. They accumulate along food chains, cause detrimental effects in marine and terrestrial wild life, and pose a hazard for human health. DDT is a multicompartamental substance with only a small mass fraction residing in air. Decreasing concentration trends are recorded in Europe, where the substance has not been used since ≈1988 (Holoubek et al., 2007). Transport in the free troposphere is expected by models (Lammel & Semeena, 2005; Semeena et al., 2006), but no observations in the free troposphere had been reported in Europe. The degradation rates of DDT, DDE and DDD are uncertain. In particular, the hydroxyl radical reaction rate coefficients in air are unknown.

DDT monitoring data in air at a central European continental background station, Košetice, Czech Republic, were used in combination with back-trajectories (HYSPPLIT model, NOAA) to localize DDT sources in central, western and northern Europe. The decreasing trend continued during recent years, 2004-06. However, *p,p'*-DDD does not show a trend and *p,p'*-DDT in summer only.

During two campaigns at a high mountain site in the Alps (Zugspitze, 2650 m a.s.l.) mean concentrations of 0.23, 0.63 and 0.08 pg m⁻³ of DDT, DDE and DDD, respectively, were measured in summer and 0.73, 2.22, and 0.52 pg m⁻³, respectively, in winter. The levels were not lower in free tropospheric air than in boundary layer air. Transport and residence times in air were quantified using Lagrangian particle dispersion model retroplume analyses (FLEXPART model; Stohl et al., 1998). During a stable anti-cyclonic situation photochemical lifetimes corresponded to $k_{OH} < 1.5 \times 10^{-12}$ cm³ molec⁻¹ s⁻¹ are found for *p,p'*-DDT, $k_{OH} < 0.75 \times 10^{-12}$ cm³ molec⁻¹ s⁻¹ for *p,p'*-DDE and $k_{OH} < 1.0 \times 10^{-12}$ cm³ molec⁻¹ s⁻¹ for *p,p'*-DDD. The k_{OH} values for DDE and DDD are significantly lower than estimated (QSAR).

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Sustainable Chemistry for the WEEE management

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Waste Electrical and Electronic Equipment (WEEE) is an emerging problem given the volume generated and the content of both toxic and valuable material in it. WEEE has been identified as a priority waste stream by the European union (EU): it constitutes the fastest growing waste stream (around 14 WEEE/inhabitant/year produced), with a growth rate almost three times higher than that of average Municipal Solid Waste (MSW, 3-5% annually) [1]. About 75% of European e-waste is not disposed correctly. In response, the European Commission adopted three directives: 2002/95/EC on restrictions of certain hazardous substances used in electrical and electronic equipment (RoHS); 2002/96/EC and 2003/108/EC on WEEE disposal; and 2005/32/EC on the eco-design of energy using products (EuP) [2-4]. WEEE contain both many toxic substances and substantial quantities of reusable materials such as metals, plastics and glass, which can be recovered in the form of secondary raw materials. In this work chemistry fundamentals are exploited as tool to find a correct WEEE management, in particular:

- for metals: a new environmental friendly process was developed in order to detach the gold coating from printed circuit boards by selective leaching of the supporting metal. Two etching solutions were tested and evaluated with regard of etching time and recovery of the etchant.
- for plastics: according to RoHS directive, bromine content must be evaluated and limited. BFRs content quantification was performed by several kinds of techniques: IR spettroscopy, XRF fluorescence, EDS analysis.....Solvent and solvent mixture with different polar nature such as metanol, ethyl acetate were considered for their extraction. Moreover different extraction parameters (type of extractive solvent, extraction time and temperature and particle size), are evaluating to optimise the extraction of BFRs from the WEEE plastics.
- for glass: by considering the technological properties of WEEE glass from both Cathode Ray Tube and fluorescent lamp (chemical composition, thermal and thermomechanical behaviour.....), experimental tests have been performed in the field of both ceramic glazes and tile bodies production cycle.

Hydrolysis of polyphenolic glycosides in hot water by immobilized thermostable β -glucosidases

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Each year agricultural-, food and forestry industries produce tons of waste material and by-products, such as onion skin, carrot waste and birch bark. Today, these waste and by-products can be used in animal feed or for composting, incineration or anaerobic digestion. High-value compounds can however be extracted from these sources. In the case of onion skin, an extractable high-value compound is quercetin, mainly present as quercetin glycosides¹. By hydrolysis of extracted quercetin glycosides to quercetin, the quercetin yield is increased, and quantitative determination is simplified. A commonly used method for this extraction/hydrolysis is solid-liquid extraction with aqueous-methanol and high concentration of hydrochloric acid². A problem, using hydrochloric acid is the harsh conditions applied, which may lead to breakdown of extracted compounds³. We have previously published an environmentally sustainable alternative extraction/hydrolysis method using pressurized hot water extraction at 120°C and 50 bar in combination with hydrolysis by a thermostable β -glucosidase⁴. Use of water as extraction solvent and enzymatic hydrolysis is a more environmental friendly alternative compared to the conventional method and handling of toxic chemicals is avoided. Calculations showed that our method is to prefer regarding environmental impact categories and it is mainly the shorter extraction time and smaller volumes of solvent that makes the method more energy efficient. Another advantage is that the onion waste still can be used in animal feed after extraction and hydrolysis. To further improve the method, catalyst modifications are investigated, involving development by mutagenesis, as well as use of immobilized forms. The β -glucosidase showed low activity towards one of the glycosylated forms, *i.e.* quercetin-3-glycoside (Q-3), and the gene was mutated to evaluate possibilities to modify specificity. One mutant enzyme showed increased catalytic efficiency towards Q-3 but also towards Q-4'. The next step is immobilization of the enzyme to allow recycling. Initial studies are made on epoxy-activated support materials; a cryogel (acrylamide-based supermacroporous monolith), and Eupergit C (acrylic beads). By immobilizing the enzymes, an on-line mini-flow system with pressurized hot water extraction and enzymatic hydrolysis can be built. Generally, an on-line system brings the advantages of less sample handling, less solvent usage and most importantly, shorter total process time.

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Zinc released from roofing materials and its environmental interaction. Results from a 10-year field exposure in Stockholm

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Zinc and zinc-based materials are essential for the infrastructure of the society and extensively used in different outdoor applications such as crash barriers, lamp poles, buildings, facades and roofs. The diffuse emission of zinc from these and other zinc-based applications and sources in the society has been subject for special attention during the last decades. Triggered by significant knowledge gaps and the need for accurate data on release rates of zinc, an aspect of atmospheric corrosion not traditionally considered, a major interdisciplinary research project was initiated in 1998 together with a majority of European zinc and galvanized steel producers. The main objective of this effort was to generate relevant exposure assessment data focusing on zinc release from roofing materials induced by atmospheric corrosion and its environmental interaction through parallel interdisciplinary long-term field and laboratory investigations. The research project has provided a unique in-depth understanding of the zinc release process, its correlation to surface characteristics and environmental fate, data essential for sustainable decisions, legislative actions and accurate risk assessment and management.

Generated results from the 10-year urban field exposure will be presented and discussed from a metal release rate perspective also addressing issues related to corrosion rates and patina constituents, and to chemical speciation, bioavailability, ecotoxicity and environmental fate of released zinc.

Nitrogen doped tetrahedral amorphous carbon thin films for metal tracing

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Human activities have released toxic metals such as mercury (Hg), lead (Pb) and copper (Cu), etc into the environment. Nowadays, the presence of toxic metals in the aquatic ecosystem implicates directly to biota and indirectly to human being [1]. Therefore, fast detection and determination of trace heavy metals are a tough challenge for analysts. In the past, Hg was used extensively for electroanalytical purposes but its disposal and cost are major issues [2]. Chemical and mechanical robustness of boron doped diamond (BDD) thin film electrodes has made them suitable for working in various corrosive media. However, a requirement of high film deposition temperatures has confined such an application of BDD film electrodes [3]. Recently, it was reported that nitrogen doped diamond-like carbon (DLC:N) thin films could have similar chemical characteristics to those of BDD films. In addition, DLC:N films can be fabricated at low temperatures [4]. This paper is to investigate the ability of nitrogen doped tetrahedral amorphous carbon (ta-C:N) thin films produced by a filtered cathodic vacuum arc (FCVA) technique for detecting trace heavy metals such as Pb, Cu and Hg by using linear sweep anodic stripping voltammetry (LSASV) in KCl solutions. The ta-C:N thin films were deposited on p-Si (111) substrates ($1-6 \times 10^{-3} \Omega\text{cm}$) by FCVA with a nitrogen flow rate of 20 sccm. The ta-C:N film coated samples were then used as working electrodes to detect trace heavy metals such as Pb, Cu and Hg by using LSASV in 0.1 M KCl solutions (pH 1). The results showed that the current response of the ta-C:N film electrodes was significant to differentiate all the tested trace metal ions (Pb^{2+} , Cu^{2+} , and Hg^{2+}) and the three ions (Pb^{2+} + Cu^{2+} + Hg^{2+}) could be simultaneously identified with good stripping peak potential separations.

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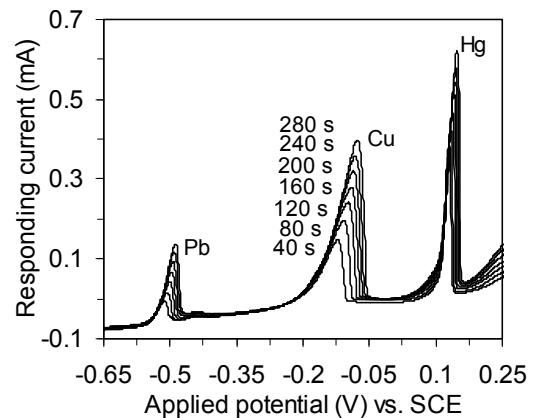


Fig 1. Anodic stripping voltammograms obtained from a ta-C:N film electrode (20 sccm N_2) in a 0.1 M KCl solution containing 8.9×10^{-6} M Pb^{2+} + 2.5×10^{-5} M Cu^{2+} + 9.2×10^{-6} M Hg^{2+} as a function of deposition time [5].

Assessing mixtures by considering comparative ecotoxicity of pharmaceuticals and their transformation products

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Transformation products of active pharmaceutical ingredients (APIs) formed within sewage treatment plant (STP) or receiving waters occur as complex mixtures that may undergo temporal and spatial variations in the natural environment. The transformation products are usually predicted to be less toxic to aquatic species than parent substances¹. However, there is increasing concern on that environmental transformation products may be more toxic than the parent APIs. Regulatory guidance for the environmental risk assessments of pharmaceuticals² makes specific reference to the use of such data for refinement of the environmental risk assessment. However, little guidance is provided on how such information will be used and expert judgement is needed. The majority of published data describes procedures based on the identification, isolation and ecotoxicity testing of individual components. By comparison, few studies have reported direct measurement of comparative biological effects of parent API versus degraded mixtures. Although technically challenging, we believe results from the later approach are more robust and realistic for hazard and risk assessments of pharmaceuticals.

In this study, a framework was developed to guide the testing of aquatic toxicity of APIs versus degraded mixtures. Selected APIs were subjected to biodegradation and phototransformation using modified OECD Test Guidelines 302B and 316. Comparative toxicity of APIs and their degraded mixtures were measured using algal (*Pseudokirchneriella subcapitata*) and rotifer (*Brachionus calyciflorus*) screening tests. Overall results demonstrated a reduction in toxicity of degraded mixtures. Chemical analysis of effect test solutions confirmed that the reduction in toxicity was due to the loss of APIs via biodegradation and phototransformation. Such results provide useful insights into the environmental risk assessment of APIs by taking into account their transformation products in mixtures.

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ATMS (Automatic Trace Metal System) for early warning and short term event in polluted rivers

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Contaminated mine drainage water represents a major hydrogeological and geochemical problem linked to mining and metal refining industry. Mine drainage waters in *e.g.* Scandinavia is often characterized by low pH, high metallic and sulphate contents. This is particularly the case for the old mine at Løkken Verk (Norway), which was one of the greatest cuperous-pyrite deposits in the world based on a FeS₂–CuFeS₂–ZnS ore body in greenstone bedrock. Like most of the metal sulphide mines, Løkken Mine has had contaminated water discharging from tailings, waste rocks, and adits. After 333 years of mining industry, the Løkken Mine was closed down in 1987, and the tailings and mine workings were flooded to reduce sulphide oxidation¹. The flooding of the mine workings greatly improved the water quality of effluent streams for almost 20 years, however recently the actions made in 1987 seems to decline and a significant pH change and increase in metal concentrations has been observed and seriously threatens the important salmon river course Orkla. This area is polluting freshwater stream with metals generated by sulphide mineral oxidation, which is accelerated by exposure of metal sulphides to air. Monitor of the quality of drainage water and local streams in mining regions are normally carried out through periodically manually sampling and analysis in the laboratory. However, artefacts may occur during such sampling, like *e.g.* contamination and adsorption and precipitation processes which affect the chemical equilibrium in the samples and importantly alter the labile fraction of the metals, which is often the most interesting one from a biogeochemical point of view. In this contribution an original voltammetric monitoring system is presented, in order to test the robustness of long time sensor deployment in the field. Using this system, measurements have been performed every 120 minutes by DPASV over a period of several months in two different rivers in Norway for measuring metals like zinc, iron², and copper downstream to Løkken Mining area, and to point out the use of such system for early warning and daily cycling. In addition to these analytical considerations, geochemical behaviours of Fe, Zn and Cu in the water stream are considered by using complementary techniques like DGT, direct samplings and thermodynamic equilibrium calculations, in order to provide complementary information on metal speciation³ and toxicity of these water bodies. Parameters like pH, conductivity, oxygen, etc. have also been collected and the results discussed against the metal concentrations. Another example of trace metal monitoring will be also displayed and focused on the river Deûle at Auby (Northern France), which was heavily polluted during the last century by Pb and Zn smelting plants.

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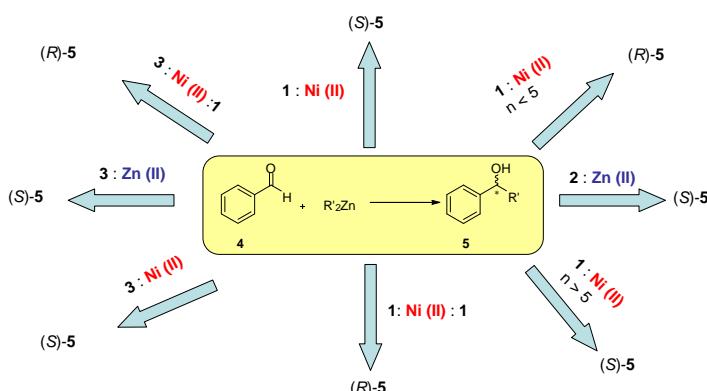
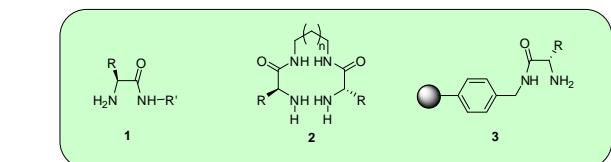
Simple and versatile enantioselective catalysts derived from aminoacids

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The search for new ligands in asymmetric catalysis is a field of continuous interest from the perspective of developing environmentally, friendly chemical processes for the synthesis of fine chemical. In this regard, the use of nitrogen-containing ligands in catalysis has received increasing attention in the last years.^[1] These ligands seem to appear as promising ligands for several reasons: (i) they can be easily prepared by standard synthetic protocols; (ii) they contain two nitrogen atoms with different coordination capabilities connected through a chiral backbone; (iii) their steric properties can be easily tuned by the selection of the appropriate R and R' substitution (iv) they can form robust metal complexes with transition metals under the appropriate conditions.

In this context we have found that very simple α -amino amides like **1** or **2** can act as very efficient and versatile ligands for chiral transformations. An important outcome has been the ability to control, in many instances, the topology of the major isomer just by controlling the stoichiometry of the catalytic complex^[2] or the nature of the non-chiral components of the structure (i.e. the value of n in compounds **2**).^[3] Polymer-supported equivalents have also been prepared with the aim of developing stable and reversible catalysts with a bigger impact in terms of sustainable chemistry. Those were prepared either from gel type or monolithic polymer. Additional results of interest were found, as the immobilization provided the access to active and enantioselective catalysts from species that were essentially non-selective under homogeneous conditions. This is one of the most remarkable effects reported up to now for supported species for which the opposite behaviour is most often reported. On the other hand, the immobilization provided us with new ways to control the final topology of the products.



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Dimensional distribution and environmental importance of antimony(III) and antimony(V) in PM

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During the last decade there has been a growing attention towards the environmental diffusion of antimony, because of its potentially harmful effects. Antimony concentration has been suffering high increase in environmental matrices and some recent studies show that antimony is now the most present trace element in the urban atmosphere. As with other elements, the Sb oxidation state influences the physiological and toxicological behavior of antimony. Particularly, Sb(III) compounds are about 10 time more toxic than Sb(V) species. All the studies on the separation of the two inorganic antimony forms in soils and waters report the Sb(V) prevalence and suggest the spontaneous oxidation of Sb(III) in these matrices. Identification and quantification of the antimony species in PM samples has been attempted only in a few research works, in which a very low number of real samples were considered. Furthermore, no studies were addressed to the dimensional distribution of the two species and to identification of their emission sources.

Our work concerned the optimization and the validation of a quick and sensitive analytical method able to separate and quantify Sb(III) and Sb(V) in particulate matter (PM) by ion chromatography - inductively coupled plasma - mass spectrometry (IC-ICP-MS). The procedure has been applied to PM10 and size segregated samples. Both Sb(III) and Sb(V) species were detected; contrasting with the results from other environmental matrices, in some PM10 samples the Sb(III) concentration resulted higher than the Sb(V) one and ratios Sb(III)/Sb(V) ranged from 0 to 1.5. Furthermore, the spontaneous oxidative conversion between the two species in the atmosphere resulted negligible. The analysis of the size segregated samples, collected by a 13 stages impactor, allowed us to draw some conclusions on the Sb(III) and Sb(V) sources. These two chemical forms are detectable only in particles with aerodynamic diameter higher than ca. 1 μm , that are generally related to mechanical abrasion mechanisms. The most probable source for coarse antimony is related to brake pads abrasion. Preliminary tests on these materials showed a high variability of the Sb(III)/Sb(V) ratio as a function of the blend production and, in some cases, Sb(III) resulted the predominant species.

Recovery percentages of the IC-ICP-MS analysis of PM₁₀ samples, calculated with respect to the total Sb content determined on the same solution by direct ICP-MS analysis, showed an high variability, with values ranging from 30% to 70%. A series of experimental tests were addressed to the comprehension of the reason of these low and variable recovery values. All the tests suggested the presence in the analysed solutions of nano-particles aggregates, that are able to reach the plasma torch in the case of direct ICP-MS analysis, but are detained by the chromatographic column when the IC-ICP-MS method is applied. Furthermore, the aggregation state of these nano-particles seems to be easily altered when they are suspended in the water solution. A similar behaviour could be hypothesized when the aggregates are in contact with biological fluids and their health effect would then deserve further investigations.

Development of a standardised method for the monitoring of persistent organic pollutants in gull eggs

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The presence of Persistent Organic Pollutants (POPs) in birds has been documented in many countries. POPs are transferred from the mother bird to her eggs, therefore eggs have been proposed as matrix for the biomonitoring of various POPs. Although a lot of research has been carried out on eggs, the sampling and measuring methods differ greatly. To make the comparison between data from different studies possible, a standardised biomonitoring method needs to be developed. This method should include all steps from sampling through analysis until the end. The aim of the study was to design a standardised bio-monitoring protocol for POPs in gull eggs. During the analytical method development spiked chicken eggs were used. All the POPs mentioned in the Stockholm convention, including the candidate compounds, were analysed in the eggs.

The perfluorinated chemicals (PFCs) were extracted from wet samples with solid-liquid extraction using acetonitrile. The extracts were cleaned with ENVI-carb and then measured with UPLC-MSMS. The extraction of aldrin, isodrin, dieldrin, endrin and the PBDEs was also done with liquid-solid extraction after freeze drying, but with a hexane and dichloromethane mixture, followed by clean-up with florisil and measurement with GS-MS (NCI). The dioxins, furans, PCBs, PBDEs and organochlorinated pesticides (OCs) other than drins were Soxhlet extracted with toluene and purified with an automated clean-up system. The dioxins, furans, planar PCBs and PBDEs were measured with GC-HRMS, whereas the OCs and non-planar PCBs were measured with GC-ECD. The recovery rates for the PFCs were between 95 to 122 % for samples spiked with 5 ng/g ww of each of the PFCs, 84 to 120 % for those spiked with 100 ng/g ww and 80 to 115 for those spiked with 250 ng/g ww. The perfluoro sulfonates had lower recoveries (84 - 112%) than the perfluoro carboxylic acids (105 – 120%). For aldrin, isodrin, dieldrin and endrin the average recovery rates were between 70 and 85%. The recovery rates for the PBDEs were between 86 and 115%. For the dioxins, furans, PCBs, PBDEs and OCs the recovery rates were between 40 and 120%. Method sensitivity, overall robustness of the developed methods and the various problems and solutions encountered will be discussed. Finally, to test and validate the protocol, Yellow-legged gull (*Larus michahellis*) eggs from nature reserves in Spain and Portugal have been analysed to evaluate the occurrence and distribution of target analytes.

Structural analyses of Au/Pd bimetallic nanoparticles supported on TiO₂ and their promotion effects for photocatalytic activities

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Designing nano-morphologies is expected to be one of the most promising approaches to develop the novel high performance catalysts. Using chemical effects of ultrasound, bimetallic nanoparticles consisting of Au-core and Pd-shell can be obtained [1], and noble metal nanoparticles can be immobilized on the surface of metal oxide supports [2]. In this study, we report sonochemical preparation of Au/Pd bimetallic nanoparticle-supported TiO₂ photocatalysts and their photocatalytic activities.

Au-core/Pd-shell bimetallic nanoparticles dispersions are prepared by the sonochemical method [1]. TiO₂ (P-25) was added to the dispersion, and followed by the sonication (200 kHz, 6 W / cm²) under air atmosphere to immobilize noble metal nanoparticles on the surface of TiO₂ (sample A). TEM images of sample A are shown in Figure. The mixtures of Au and Pd monometallic nanoparticles individually prepared were also immobilized by the same methodology (sample B). On the other hand, by annealing sample A, the core-shell structure was broken and changed into ordered state where Au and Pd atoms were homogeneously located in each particle on TiO₂ (sample C) [3]. Neither sintering of the supported nanoparticles nor growth in their sizes was not observed after the annealing. ICP analyses showed that the content elements were almost same between sample A, B, and C.

Ar-purged ethanol aqueous solutions containing the prepared photocatalysts were illuminated with a Xe lamp in a closed glass vessel with a quartz window. The amounts of evolved H₂ depended on the wavelength region of illuminated light and the nanostructure of the supported nanoparticles (Table). These results suggest that the nanostructures of the supported bimetallic nanoparticles govern the photocatalytic activities.

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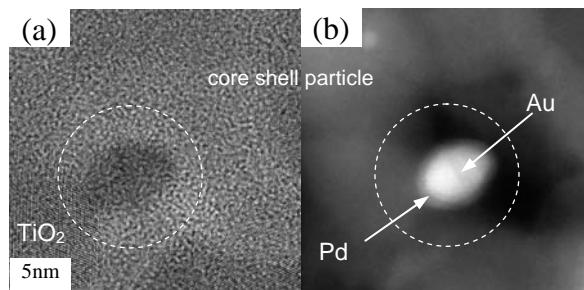


Figure. (a) HRTEM and (b) HAADF-STEM image of Au-core/Pd-shell bimetallic nanoparticle supported TiO₂.

Table. H₂ evolution over sonochemically prepared photocatalysts

Sample	H ₂ evolution / micro mol h ⁻¹	
	UV illumination ^a	VIS illumination ^b
A (Au-core/Pd-shell)	89	132
B (Au-Pd mixture)	135	98
C (Annealed)	48	77

^a 250 – 385 nm. ^b 385 – 740 nm.

Determination of total organic fluorine by defluorination of perfluorinated compounds followed by reversed-phase chromatography of fluoride

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Mass balance study of organic fluorine, based on comparison of results obtained for specific target compounds and total organic fluorine, provides more complete image of sample content considering fluorinated substances and may suggest presence of unknown fluorinated species [1, 2]. Major aim of this research was to develop a procedure for total organic fluorine determination, incorporating defluorination method using sodium biphenyl reagent (SBP), followed by determination of formed inorganic fluorides. Considering commonly present HPLC equipment in analytical laboratories, fluoride determination was planned to employ reverse-phase liquid chromatography (RP-HPLC) with spectrophotometric detection.

Developed method consists of following sub-procedures: 1) Preconcentration of perfluorinated substances from a large sample volume (1L), using solid-phase extraction with carbon based material as a solid sorbent. 2) Defluorination with SBP of preconcentrated compounds directly on sorbent bed or after back extraction and solvent evaporation. 3) Derivatization of obtained inorganic fluorine with triphenylsilanol and finally 4) RP-HPLC determination of the reaction product - triphenylfluorosilane.

Results obtained for the separate sub-procedures indicate satisfactory efficiencies of defluorination reaction as well as fluoride derivatization tested for perfluorocarboxylic acids with 6, 8, 10 and 12 carbons in molecule. The limiting process seems to be the preconcentration of a large sample volume. The complete procedure for the mixture of the 4 model compounds in concentration of $0.1 \mu\text{g L}^{-1}$ each, resulted in recoveries of $125 \pm 25.0\%$ ($n=7$) for standards and $98.1 \pm 9.49\%$ ($n=2$) for spiked tap water samples. Complete procedure was applied for total organic fluorine determination in river water samples.

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Noncovalent interactions between dissolved humic and fulvic acids and aromatic compounds: Mechanisms and impact on enzymatic availability

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The solubility and bioavailability of aromatic compounds are modified through noncovalent interactions with dissolved humic and fulvic acids (HA and FA). However the exact mechanisms of these noncovalent interactions are poorly characterized, and as a result, it is unclear how the association with dissolved HA and FA specifically modifies bio- or enzymatic availability of aromatic compounds. Noncovalent interactions between the fluorescent probe 6-propionyl-2-dimethylaminonaphthalene (PRODAN) and dissolved Norman Landfill leachate fulvic acid (NLFA), Suwannee River fulvic acid (SRFA), Suwannee River humic acid (SRHA), and Leonardite humic acid (LHA) were examined as a function of pH, HA and FA concentration, and solvent polarity using steady-state fluorescence spectroscopy. Static quenching processes, as indicated by linear Stern-Volmer plots and high K_d values, were positively correlated to the % aromaticity of the HA and FA, as well as to solution pH. Results illustrate that for FA molecules with relatively low % aromaticity values, solvophobic interactions between PRODAN and FA are the primary interaction mode. For HA molecules with higher % aromaticity, PRODAN engages in both solvophobic interactions and $\pi - \pi$ interactions, in particular electron donor-acceptor interactions, via condensed aromatic, election accepting moieties inherent within HA molecules.

In the context of the fluorescent spectroscopy results, the mechanisms by which dissolved HA and FA alter the degradation kinetics of aromatic substrates by oxidoreductive enzymes were hypothesized to be that dissolved HA and FA: 1) deactivate the enzyme; 2) act as a competitive substrate; or 3) protectively sequester the aromatic substrate. The degradation of pentachlorophenol (PCP) by purified laccase isolated from *Trametes versicolor* at 28°C and pH 5.0, in combination with Aldrich humic acid (AHA), LHA, SRFA, or Waskish peat fulvic acid (WFA), was used as a model system to quantitatively test and compare these three mechanistic hypotheses. Catechol assays demonstrated that the four HA and FA did not deactivate laccase. Slower PCP degradation rates by laccase in the presence of HA and FA were found to correlate with higher inhibitor binding constants (K_i , ranging from 3.63 ± 0.78 to $6.47 \pm 1.07 \mu\text{g/mL}$) and sorption coefficients (K_{dom} , $\log K_{\text{dom}}$ ranging from 4.09 to 4.81). Comparison of experimental PCP degradation rates in the presence of dissolved HA and FA with predicted degradation rates of just the freely dissolved PCP phase (i.e., PCP not associated with dissolved HA and FA) indicated that dissolved HA and FA modified the PCP degradation by laccase at low concentrations through protective sequestration as predicted by fluorescence spectroscopy. However with increasing concentrations, HA and FA additionally modified the enzymatic availability of the PCP by acting as a competitive substrate.

Selection criteria for ecomodel reactions for reactivity-persistence correlation

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Model reactions of five types were proposed for assessment of persistency through reactivity: reduction, oxidation, photolysis, radical and hse(hydrolysis/substitution/elimination). This classification is inconsistent: reduction, oxidation, and, in part, hydrolysis/ substitution/elimination and photolysis are determined by the result, e.g. structure of end product. Radical reaction and, in part, hydrolysis/substitution/elimination and photolysis are determined by the nature of reagent[1]. However, one reagent with different substrates may cause different reactions. For instance, reaction of organohalogen compounds with S-nucleophiles may lead to substitution or to reduction products.

Photolysis may give reduction, oxidation or elimination while having free-radical mechanism. Therefore more meaningful set of reactions should be determined by reaction mechanism, or more precisely, by the type of reagent on rate-determining step:

Hard nucleophile (POP + OH ⁻)	Hard electrophile (POP + H ⁺)
Soft nucleophile (POP + HS)	Soft electrophile (POP + Hg ⁺⁺)
Nucleophilic radical (POP + R·; + M(0)·)	Electrophilic radical (POP + R ₂ NH ⁺ ·; + Cl ⁻)
Electron transfer (POP + e ⁻)	Electron abstraction (POP - e ⁻)
Metal complex (OxAd; POP + M)	Direct photolysis (POP + hν)

Model reactions in the table are just examples.

How to select the best model reaction for development of reactivity scale? The primary criterion must be a correlation of model reactivity and observed persistence for well-studied POPs[2], especially within congeners. The secondary, confirmation criterion can be isotope effect(s), the internal characteristics of an elementary step of any chemical reaction [3].

How many reactions are, in fact, responsible for degradation of a given POP in the environment? Classification of Bergman and Green (5 reactions, 4 media)[1] gives 20 reactivity parameters. Suggested set of 10 reactions doubles this number to 40 reactivity parameters. Both the difference in reactivity of a given POP towards different reagents and, *vice versa*, reactivity of a given reagent towards different POPs exceeds 40 orders of magnitude. Therefore it seems likely that only one reaction pathway in one media will be responsible for major part of degradation of any given POP in the environment.

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Artificially aged silk analysed with chemical and physical methods to find an adequate substitute for 17th century silk

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The aim of this project is to evaluate conservation methods for historic costumes. The project is run by the Royal Armoury in Stockholm and the Institute of Conservation at the University of Gothenburg in cooperation with the Department of Fibre and Polymer Technology, the Royal Institute of Technology, Stockholm. The Royal Armoury collections consist of objects associated with the Swedish court from late 1500 until today. The museums large number of 17th century men's garments is exceptional in terms of both quantity and quality. The dominating material is silk and many of these costumes are in need of conservation. Knowledge of the advantages and disadvantages of methods used in textile conservation is of vital importance for the preservation of our historic textiles. As it is impossible to use authentic artefacts in experimental work, artificially aged standard silk must be used as a substitute.

The first goal of the study was to lay a scientific ground for proposing an optimal accelerated ageing procedure, simulating as far as possible the nature of degradation found in naturally aged silk from the seventeenth century. In order to be able to compare the type and extent of degradation in artificially and naturally aged silk it was necessary to identify analytical markers for chemical and physical degradation of silk. Standard silk samples were artificially aged by exposure to different environmental conditions (thermo-oxidation, UV radiation, pH immersion, and relative humidity). To validate the artificial ageing methods against the properties of seventeenth century silk material, the chemical and physical properties of historic silk samples and artificially aged samples were evaluated using analytical markers assessed by Attenuated Total Reflection – Fourier Transform Infrared Spectroscopy (ATR-FTIR), Size Exclusion Chromatography (SEC), and tensile tests. The development of a method to simulate the natural ageing of silk will result in adequate substitute sample specimens for historic costumes, when the conservation methods are further evaluated.

Standard silk samples were artificially aged by exposure to different environmental conditions. To validate the artificial ageing methods against the properties of seventeenth century silk material, the chemical and physical properties of historic silk samples and artificially aged samples were evaluated using analytical markers assessed by Attenuated Total Reflection – Fourier Transform Infrared Spectroscopy (ATR-FTIR), Size Exclusion Chromatography (SEC), and tensile tests.

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Ionic catalysis vs. radical oxidation: A new chemistry for organic compounds in atmospheric aerosols

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Atmospheric aerosols contain a wide range of material but mixtures of sulfate salts, ammonium salts, and organic compounds dominate their internal composition.¹ Until about 10 years ago the main fate of organic compounds in aerosols was thought to be radical oxidations, mostly mediated by OH radicals. But in the last decade the importance of ionic reactions in these media has started to emerge. A peculiarity of these ionic reactions over radical oxidations is that they can produce C-C, C-O-C, or C-N bonds, i.e. products larger than their parent compounds. Some of these products have strong optical properties and can affect the direct contribution of aerosols to climate. These reactions are also expected to produce Secondary Organic Aerosol (SOA).

This presentation is an overview of this new aerosol chemistry and of the latest advances. In particular, new catalysts making these ionic reactions important in tropospheric aerosols, sometimes faster than OH reactions, have been identified in the last few years: amino acids^{2,4} and simple inorganic ions.^{5,7} These results reshape the understanding of aerosol chemistry by showing that inorganic material ubiquitous in aerosols, such as ammonium sulfate, is not inert towards organic compounds as previously thought but triggers important transformations. These results are supported by numerous observations, such as the presence in aerosols of light-absorbing compounds similar to the products of these ionic reactions,⁸⁻¹⁰ and the uptake of glyoxal and formation of SOA in Mexico City.¹¹

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Selection of appropriate source tracers and APCSA modelling for the source apportionment of particulate matter

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Source apportionment (SA) of airborne particulate matter (PM) by Factor Analysis techniques (FA) has the main advantage that it does not require any *a priori* knowledge of sources, since source identification is based on evaluating the mutual correlations between chemical variables at receptor sites. However, it is also known that source identification by principal component – factor analysis can suffer of physical inconsistency due to likely arbitrariness of factors extraction. An appropriate selection of analytes to be included in the data matrix is thus of key relevance. It is acknowledged [1] i.e. that identification of PM sources is improved by evaluating the solubility of trace elements, as their soluble/insoluble forms can be contributed by different sources. On the other hand, interpretation of factors can also be supported by investigation about the *site* specificity of analytes. This can be performed by Fisher's Linear Discriminant Analysis (LDA), which provides an absolute and independent measure of the discriminating ability of each single variable between different categories (sites). In this work, a combined FA - LDA approach is presented, for to the identification of local / non-local character of source contributions. The FA-LDA method has been applied to different data set of chemical characterization of PM samples, including soluble/insoluble forms of trace and major elements obtained by chemical fractionation [2]. In example, application to a large data set [3] including 40 analytes and about 200/site PM₁₀ and PM_{2.5} daily samples collected at different locations over the region of Lazio (Central Italy) led to select 21 of initial 40 variables. Analytes linked to local sources show highest values of Fisher's LD, while the role of Cr, Ni, Mn and Zn as selective tracers of two non local sources is only evidenced by FA.

APCSA modeling was thus performed with only selected variables. This allowed the identification and apportionment of overall seven (local and non local) sources at five sites (road dust, crustal, secondary aerosol, marine salt, soluble Cr and Ni, Mn and Zn, combustion). Moreover, by APCSA chemical profiles have been estimated of analytes both included and not included in the 21 selected of 40, showing a good provisional potential for this linear – multivariate approach.

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Application of accelerated solid phase dynamic extraction for analysis of biogenic volatile organic compounds

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Over the last few years there has been a great interest in volatile organic compounds (VOCs) emitted from vegetation. Atmospheric oxidation of biogenic volatile organic compounds (BVOCs) and their reactions with ozone (O_3), hydroxyl (OH^-) and nitrate (NO_3^-) radicals are considered as important processes in tropospheric formation of ozone and secondary organic aerosols [1,2]. Commonly used techniques for measurement of BVOCs include: sorbent tubes, solid phase microextraction (SPME), headspace sorptive extraction (HSSE). The aim of this work was to investigate the applicability of accelerated solid phase dynamic extraction (ASPDE) to analyze BVOC emissions from trees.

An innovative, portable ASPDE device which can be also apply in field experiments was used. A dilution system for standard gaseous mixture of monoterpenoids was constructed in order to optimize the sampling and desorption parameters of ASPDE and to compare the reproducibility of three sampling techniques: ASPDE, SPME and sorbent tubes. The compounds that were studied are: isoprene, sabinene, α -pinene, β -pinene, limonene, linalool, and (Z)-hexenyl acetate. Using the dilution system it was possible to produce a stable flow of the standard mixture of mentioned compounds at concentration ranging between 2.5 and 500 ppb.

All seven investigated compounds were detected in samples from sorbent tubes. In contrast, six analytes were identified in SPME and SPDE samples, namely sabinene, α -pinene, β -pinene, limonene, linalool, and (Z)-hexenyl acetate. Using these sampling techniques, isoprene could not be detected due to its high volatility (BP 34°C) comparing to the other analytes (BP 155-196°C). The peak areas obtained with SPDE were 2-8 times higher than the peak areas obtained with SPME which can be explained by larger volume of polydimethylsiloxane (PDMS) coating on the SPDE needle wall compared to SPME fiber. It was also found that desorption of SPDE samples at high temperature (230°C) led to the formation of artifacts, which were not observed at the desorption temperature 100°C. Further experiments revealed that the additional compounds appearing during desorption of SPDE samples were monoterpenoids which were degradation products of linalool.

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Organic chemical pollutants in China with focus on the Yangtze River delta

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Currently, the general situation of environmental pollution with respect to organic chemical pollutants in China does not allow people to be optimistic. China had produced and used large amounts of e.g. organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) before they were banned. The economic development and urbanization during the past three decades exacerbated the organic chemical pollution in China, especially in rapidly developing regions. The Yangtze River Delta, with an area of 99,000 km² and a population of 75 million, located in central-eastern China, is one of the most rapidly developing regions in China and one of the most densely populated regions on the Earth. The delta region comprises only 1 percent of China's land area and 5.8 percent of China's population, but generates about 18.7 percent of the country's gross domestic product (GDP). Accompany with its fast development, it suffers from a common problem faced by many regions in China: the organic chemical pollutants is threatening its environment.

In this review, literature statistic was first carried out with respect to organic chemical pollutants studies in China published both in Chinese and in English. It was found that only 39 papers in Chinese and no paper in English were published before 1979. In 1980s, more than three hundred Chinese articles dealing to OCPs and PCBs studies in the environment could be found but English articles remained very few. In 1990s, besides hundreds of Chinese articles, 24 English articles concerning OCPs and PCBs appeared in SCI source journals. After the year 2000, there came a boom of organic chemical pollutants relating papers published both in Chinese and in English, which make up 1732 and 339 articles, respectively, according to our statistics. It was not until 2004 the first paper was published on PBDEs and the China environment. In addition to the statistic numbers, this review will also provide an overview of the general occurrence and distribution of OCPs, PCBs and PBDEs in air, soil, water, sediments and organisms of China with focus on the Yangtze River Delta. Sources of these chemicals, the relationship between the pollutant concentration and the economic development level, as well as the agricultural and industrial pattern in different regions will be discussed.

Gas-particle partitioning of persistent organic pollutants generated during the conflict situation in the Western Balkan countries

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Concentration levels of persistent organic pollutants / PAHs, PCBs, dioxins and furans / in the atmosphere, surface and ground water, sediment and soil, have been significantly increased during the war conflict and NATO operation in former Yugoslavia, as a result of the explosions, fires, combustion processes and direct releasing of the substances into the environment. In the atmosphere, persistent organic pollutants are found in the gaseous phase or sorbed to the solid particles. Atmospheric distribution controls removal and atmospheric degradation processes and has a severe impact on long-range transport and environmental fate of POPs.

As the result of the air sampling campaign, conducted in 2003 and 2004, concentration levels of PCBs, OCPs and PAHs in gaseous and particulate phase of 129 ambient air samples from 24 background, urban and industrial sites, including hot spots, were determined. Active air sampling method with high-volume samplers containing quartz and polyurethane foam filters was used to collect atmospheric particles and compounds in gaseous phase. At each sampling site, 3-10 samples were taken. Analytical determination of seven polychlorinated biphenyls, organochlorine pesticides and 16 EPA polyaromatic hydrocarbons in all samples was carried out in laboratories of Research Centre for Environmental Chemistry and Ecotoxicology (RECETOX), Masaryk University in Brno, Czech Republic.

Concentrations of selected POPs in particle and gaseous phase were converted into the particle-bound fractions, ϕ . These fractions were highest in Bosnia and Herzegovina due to the elevated levels of total suspended material in ambient air.

Experimental values of particle-associated fraction were compared to the Junge-Pankow model. A model for urban/industrial environments provided a better prediction of partitioning behavior than a model for background and rural background sites. That is probably because the total amount of atmospheric particles is higher in the Balkan region than found in the previously published studies.

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Combination of synthetic chemicals and natural products (CHEMONAP): Ecologically safe approach to develop novel antibacterial agents

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Microbial diseases are now more frequent than during the last few decades being still difficult to control the emergence of resistant strains. Despite the tremendous progress made in development of different classes of antibacterials, there is still a need of expansion of antibacterials in terms of their target spectrum, minimizing the toxicity associated with their synthesis, emergence of resistant mutants etc.

This situation highlights the need for advent of effective, novel and safe antibacterial compounds. In this regard earlier we have proposed the use of combination of effective synthetic compounds and more biocompatible natural products.

Encouraged by the results we have extended our study by preparing 38 new formulations using α,β - unsaturated carbonyl compounds in combination with Natural products (Neem Oil and *Nicotiana tabaccum*) and screening them against MTCCB 96 *Staphylococcus aureus* and clinically isolated multidrug resistant *Enterococcus faceium* by disc diffusion method.

Intuitively attractive results were obtained showing synergistic interaction between inactive synthetic and inactive natural product. It is mentionable that although synergism between two antibiotics is well documented in literature against bacteria but studies focused on combination of natural product and synthetic compounds, are less in practice and can bring revolutionary development in medicinal world.

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Modelling of heavy metal transfer from soil to vegetation in a cattle manure application scenario

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Soil is essentially a non-renewable resource and a very dynamic system that performs many functions and delivers services vital to human activities and ecosystems survival (European Commission, 2006). Soils are critical environments where solids, air and water interact. Consequently, they are subjected to a number of pollutants released in different anthropic activities (industrial, agricultural, transport, etc.). When considering the different kinds of contaminants, heavy metals are especially dangerous because of their persistence and toxicity (Adriano, 2001). In particular, agricultural soils can be a long-term sink for heavy metals stem from the application of manures, sewage sludge disposal or aerial fallout from industrial activities. This can result in a loss of soil functions concerning environmental quality protection, maintenance of human health and productivity, which are relevant aspects of soil quality. The implications for the quality of agricultural soils range from phytotoxicity at high concentrations to the transfer of heavy metals to the human diet, from crop uptake or soil ingestion by grazing livestock.

In Galicia (NW Spain), the application of cattle droppings as fertiliser in pastureland is a common practice, which may increase total and bioavailable metal contents in the soil. The estimation of chemical concentrations in soil and in plant foliage by multicorrelation models is often needed in risk assessments of contaminated sites. With that aim, soil-plant regression models were developed in this work for Mn, Fe, Zn, Cu, Cr, Co, Ni, Cd and Pb. Concentrations in vegetation were related to soil concentrations (total and assimilable), manure concentration, soil properties and manure properties. In most cases the models obtained resulted significant at 0.05 or 0.01 level, except for Zn. The R^2 values for the significant models ranged from 0.50 for Co to 0.93 for Pb. In this study, Standard Deviation Error of the Estimate (SDEE) was used to represent the 95% upper and lower confidence limits, since no external validation data were available.

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Development of novel green processes for the continuous extraction and drying of food antioxidants from natural origin: the WEPO® process

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In the search of green processes to obtain valuable compounds from natural sources, the extraction with subcritical water has been shown as one of the most selective and environmentally friendly technique. However, the extracts require later freeze or hot drying, and this is the major limitation, as it is energy and time consuming.

On the other hand, particle formation based on supercritical fluids have raised different solvent-antisolvent processes that can be interpreted as a way to dry pure compounds from organic solutions. In the case of aqueous solution, these processes are not suitable for drying due to the low solubility of scCO₂ in water. At the moment, only CAN-BD (Carbon dioxide assisted nebulisation- bubble dryer) process have been applied to obtain powders from pure proteins [1, 2], vaccines [3], antibiotics, antiviral [4] and other water soluble drugs [5]. However, regarding to complex extracts, there is only one publication by PGSS process [6].

In this work, we have developed a new process combining subcritical water extraction plus particle formation on-line, as a novel way to obtain dried complex extracts from natural sources in one step. This process has been patented as WEPO® meaning for (Water Extraction and Particle formation On-line).

As an example of this promising technique, we have carried WEPO with several aromatic herbs such as rosemary and oregano, leading to dried particles with intact antioxidant properties. These particles could be used as functional ingredients to develop functional foods.

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Sulfur accumulation in wood of shipwrecks with implications for fossil fuels

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Considerable accumulation of sulfur in reduced forms, organic sulfur compounds (thiols, disulfides) and iron(II) sulfides including pyrite, FeS_2 , has been found to occur in marine-archaeological wood preserved in seawater. At least 2 tons of sulfur in different reduced forms is present in the timbers of the famous historical shipwrecks *Vasa*, Stockholm, 1628, and the *Mary Rose*, Portsmouth, 1545 (see Fig. 1). Organic sulfur compounds were localized chiefly within the lignin-rich middle lamella between the wood cells by synchrotron-based sulfur x-ray absorption near edge structure (XANES) spectroscopy and scanning x-ray (S K-edge) micro-spectroscopy (SXM). In addition, particles of iron(II) sulfides and pyrite, formed when iron(II) ions from corroding iron objects reacted with bacterially produced hydrogen sulfide, were found in cavities in the waterlogged wood. The sulfur isotope depletion, from $\delta^{34}\text{S} = 21\text{\textperthousand}$ in marine sulfate to $\delta^{34}\text{S} = 6\text{\textperthousand}$ and $1.8\text{\textperthousand}$ for reduced sulfur and sulfate in a *Vasa* wood sample, respectively, is typical for bacterial transformation. Oxygen access into the moist marine-archaeological wood can cause severe acidity by oxidization of the sulfur compounds, particularly in the presence of iron ions that acts as general oxidation catalysts. Laboratory experiments aiming to simulate the seabed conditions of the shipwreck of the *Vasa* (from 1628) were performed on fresh pine wood blocks submerged in media containing sulfate and iron(II) ions inoculated with erosion (EB) and sulfate-reducing bacteria (SRB) obtained from seawater. The sulfur content increased more than 10 times within two years, mainly as thiols (R-SH) in the lignin-rich middle lamella. In another series, after four years anaerobic treatment with active inoculums from marine archaeological wood, considerable amounts also formed of inorganic iron sulfides, Fe_{1-x}S , which oxidized at atmospheric exposure. SXM-maps of the sulfur and phosphorous distributions indicated that the scavenging SRB penetration producing hydrogen sulfide *in situ* was restricted mostly to the EB-degraded parts of the wood structure. The two types of sulfur accumulation in marine archaeological wood, as reactive iron sulfides and as organic sulfur, have important implications for the conservation strategy. The specific biogenic accumulation of organic sulfur within lignin-rich parts of waterlogged wood also has geochemical significance for fossil fuels of marine origin, as lignin-rich humic matter is important for the diagenetic formation of kerogens from anoxic marine sediments.

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Fig. 1 (left) The *Vasa* in the *Vasa* Museum; (right) The *Mary Rose* hull sprayed with PEG 200 in aqueous solution.

How do we understand, evaluate and avoid environmental persistence of chemicals?

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Persistence describes how long the presence of a chemical in the environment lasts once the chemical has been released. Persistent chemicals have time to be distributed in the environment and to cause adverse effects at the sites that they reach as a result of environmental transport, be it toxic effects in organisms or chemical effects such as ozone depletion in the stratosphere. Since the 1970s, persistence has been a key indicator in the environmental hazard assessment of chemicals. The importance of persistence in the assessment of chemicals is, e.g., reflected by the regulatory focus on persistent chemicals that is set by the Stockholm Convention on Persistent Organic Pollutants (POPs), the Aarhus Protocol on POPs, and REACH, the new chemicals legislation of the EU (persistent, bioaccumulative and toxic chemicals are considered as Substances of Very High Concern under REACH).

Assessing the persistence of a substance in the environment requires knowledge of the processes that lead to transformation and eventual breakdown of the substance's chemical structure. These processes include, e.g., biodegradation, hydrolysis, photolysis, and reaction with hydroxyl radicals. Data on these processes are available for several 100 or 1000 chemicals but for many of the approximately 100,000 chemicals that are on the market worldwide, only very limited or no data at all are available. Improving our *understanding* of the environmental persistence of chemicals includes several aspects: identification of the most persistent chemicals among the large number of chemicals currently on the market; a better mechanistic understanding of the different degradation processes and how they are influenced by the chemical properties of a substance; further development of the test methods for reactivity and degradability of chemicals; and improved methods for estimating degradability based on chemical structure. In the lecture, these different aspects will be illustrated.

The *evaluation* of persistence also has different aspects, ranging from fundamental considerations of the meaning of persistence to specific questions about numerical threshold values used in different legislations: In what way should persistence be combined with other indicators in a chemicals assessment scheme? Is high persistence even in the absence of knowledge about toxicity an unwanted property of a chemical? What is the basis and rationale of the threshold values for environmental degradation half-lives as they are used for the evaluation of persistence under REACH and other legislations? Possible answers to these questions will be discussed in the lecture.

Finally, *avoiding* environmental persistence would require a systematic design of chemicals based on degradable building blocks. Such a "design for degradability" is one of the goals of Green Chemistry. A key question is to what extent such a design process is feasible for industrial chemicals that need to have a high performance in technical applications. Examples of chemicals designed for degradability will be given in the lecture.

In the last 15 years, persistence has become an increasingly important factor in the regulatory context, but to what extent is persistence (or the goal of avoiding persistence) also a driver for innovation in the chemical industry?

Biomass smoke –a major contributor to ambient particle levels in Europe

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Airborne particulate matter has become one of the major issues in air quality management. To reduce ambient particle concentrations, knowledge about the magnitudes of individual source contributions is necessary. Emission inventories help to understand the relative contribution of primary emissions. However, large contributions from fugitive sources as well as from secondary formed aerosol are generally not accounted for in emission inventories. Therefore, for the analysis of source contributions, methods based on the analysis of the ambient PM10 aerosol combined with special data evaluation techniques have been emerged.

In two larger studies, CARBOSOL and AQUELLA, a macro tracer model was applied to derive source contributions from Diesel emissions, wood combustion, biogenic material, mineral dust, secondary organic and inorganic aerosol to particulate matter on the European level (Puxbaum et al., 2007). Results of both studies were based on emission tests at the Vienna University of Technology (Schmidl et al., 2008a) and showed that biomass smoke is the major primary source of fine particles during winter at background as well as urban sites in Europe. Furthermore it was shown, that relationships among the three main saccharidic tracers occurring in biomass smoke allow a discrimination between soft- and hardwood, as well as softwood leaves contributions in the smoke (Schmidl et al., 2008a, 2008b).

Source apportionment techniques using tracers for calculating source contributions are based on chemical source profiles. We therefore investigated the emission characteristics and source profiles from a number of wood combustion facilities from small-scale log-wood stoves in the low kW range to mid-scale boilers up to 50kW – with different types of fuels. For this a dilution sampling system was designed that allows to collect 8 filter samples simultaneously in pre-selected size fractions, e.g. PM10 or PM2.5. Sampling is performed on quartz fibre and cellulose ester filters, in parallel at near room temperature. All samples were analysed for selected organic and inorganic compounds. From the obtained dataset source profiles for different wood and application types were developed and analysed with respect to differences and similarities. Results from our study help to reduce the uncertainties in apportioning biomass smoke contributions to atmospheric PM levels for mid-European sites.

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Influence of fatty acids coatings on the reactivity of NaCl(100) with NO₂ under humidity: a laboratory model for marine aerosol chemistry

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Despite their relatively low concentration in the air, aerosol particles are known to have a big impact on the environment and with less certitude also on climate because of their effect on chemical, photochemical and optical properties of the troposphere. The uptake of trace gases such as NO₂ by these particles is a critical step in heterogeneous atmospheric processes. Many studies investigated on the interaction of NO₂ on mineral particles such as alkali halides (Finlayson-Pitts, 2003, Rossi, 2003), but only recently the presence of an organic coating has been considered as important (Tabazadeh, 2005). Oceans are the main source of sea salt particles mainly composed of NaCl. In the marine atmosphere lower molecular weight (C₁₄-C₁₉) fatty acids (LFAs) are known to be present on sea salt particles and their presence can be possibly explained by the high marine biological activity during spring and summer (Mochida *et al.*, 2002).

In the present work, we focus our laboratory study on a well-known reaction between gaseous NO₂ and NaCl as a function of relative humidity and of a fatty acid coating. Palmitic, stearic and oleic acid from ethanol solution are deposited on the NaCl surface via dip-coating technique.

The interaction of NO₂ with the uncoated or coated NaCl surface is investigated at ambient pressure and varying relative humidity (RH= 0-80%) in static conditions inside a reactor coupled with FTIR spectrometer. The gas-phase composition is monitored in real time and the uptake coefficients (γ) of NO₂ on NaCl are calculated. After reaction the NaNO₃ amounts are measured using IR absorption spectrometry. The surfaces are characterized by Atomic Force Microscopy (AFM) and Raman imaging.

The heterogeneous reaction generates mainly gaseous ClNO and solid NaNO₃ at the surface of NaCl for RH values in 0-70% range.

The NO₂ uptake and nitrate formation is found to increase with RH. The presence of the organic coating hinders the reaction. The spatial distribution of NaNO₃ microcrystal formed at the surface is given by Raman imaging, while morphology of the surface reorganization after reaction derives from AFM analysis. Thanks to a reactivity model fitting the experimental concentration profiles of the gaseous phase, we are able to indicate in which process the organic coating interferes.

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Metabolic effects of PFOS/A in mice

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Environmental pollutants, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) cause a dramatic reduction in the size of the major adipose tissue depots in mice. Uncoupling protein 1 (UCP1) expressed in brown adipose tissue dissipates energy of fatty acid oxidation as heat and could contribute to rapid fat utilization caused by PFOS/A. Here, we described the influence of PFOS/A on UCP1 activity, oxidative capacity and fatty acid oxidation in brown-fat mitochondria. Additionally, to answer the question whether UCP1 is responsible for the decrease of mouse white adipose tissue depots after treatment with PFOA/PFOS, we utilized UCP1- knockout (KO) mice to specifically identify the UCP1-dependent effects. These experiments provided some evidence for involvement of UCP1 in the mechanism of PFOS/A effect. However, it could be secondary to a lowered food intake. Fat utilization in brown adipose tissue is under control of the beta-adrenergic system. We used beta-3 KO mice to determine whether the PFOA effects are mediated by activation of the sympathetic nervous system and we found that body fat content decreased to a much smaller extent in beta-3 KO mice as compared to wild-type mice. Similar findings in PPAR-alpha receptor KO mice supported the concept that PPAR alpha-mediated signaling was involved in the PFOA effect. In conclusion, metabolic effects of PFOS/A may include brown adipose tissue activation.

Catalytic oxidation of ethanol by the reuse of chromium - containing Y zeolite

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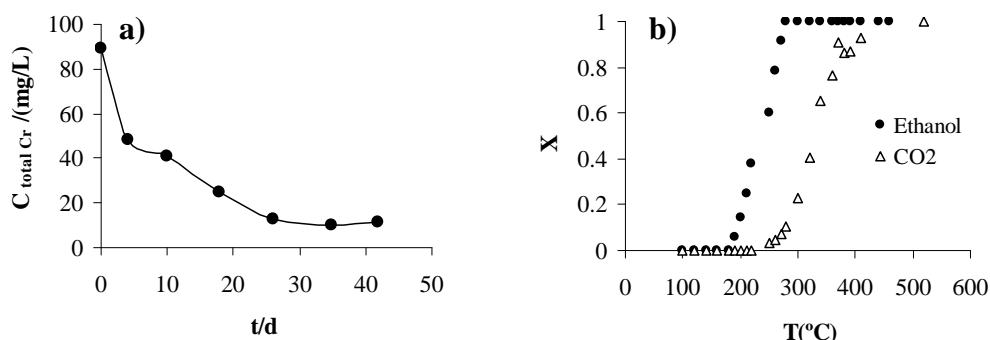
Volatile organic compounds (VOCs) can be considered as a major source of air pollution and are emitted from many industrial processes and transportation activities. Among the different treatment technologies, catalytic oxidation over solid catalysts can be considered the most effective way for reducing the emissions of VOCs from stationary sources. The catalysts based on noble metals are the most commonly used in the treatment of gaseous emissions contaminated with VOCs. The use of low cost transition metals such as chromium (Cr), to replace the noble metal in the catalysts, is a cost-effective alternative compared to the traditional catalysts. As reported in previous work [1], a low-cost system combining the biosorption properties of a microorganism with the ion exchange properties of a zeolite, was able to remove hexavalent chromium from contaminated water. After the biosorption process, the Y zeolite loaded with Cr can be used as competitive and selective catalyst to be applied in catalytic oxidation of volatile organic compounds [2]. The aim of this study was the reutilization of the chromium-containing NaY zeolite obtained by biorecovery of chromium from water, in the oxidation of ethanol.

Figure a) presents the total chromium concentration during experimental time, being achieved a removal efficiency of 88.6 % for total chromium at the equilibrium.

The bulk chemical analysis revealed a content of 0.9 % (w/w) of Cr in the zeolite after the biosorption process.

The ethanol conversion and the conversion into CO₂, as a function of the reaction temperature, are shown in Figure b). The Cr-loaded zeolite showed a good activity as catalyst for the oxidation of ethanol. The results reveal that ethanol was completely converted at 280 °C, while 100 % conversion to CO₂ was achieved at higher temperature.

As conclusion, this work demonstrates that the chromium-loaded Y zeolite obtained from biosorption treatment can be reused as an effective catalyst for the oxidation of ethanol.



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Glyphosate and metal-glyphosate speciation in solution and at solution-mineral interfaces

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A detailed understanding of the bioavailability, toxicity, transport and deposition of trace metals and inorganic/organic ligands in natural aquifers requires knowledge of their chemical speciation. While the importance of solid/solution interfaces is well recognized, the ability to characterize their structure and properties and the processes they mediate is a great scientific challenge. An understanding of interfacial phenomena at the molecular level remains unclear for all but the simplest systems. At the heart of the problem is determination of the surface binding sites and chemical species involved in the interfacial processes. Therefore, ideally, the study of interfacial phenomena must involve measurements that give insight into which species that are present in solution and at the surface. Furthermore, possible dissolution/precipitation processes of the bulk solid phase and surface precipitates must be taken into account.

Glyphosate (N-(phosphonomethyl)glycine, PMG, H₃L) is a widely used organophosphorous herbicide. It interacts with metal ions and mineral surfaces, which may affect its mobility, degradation and bioavailability in the environment. However, so far these interactions are far from fully understood.

This paper is a discussion on the complexation of PMG with metal ions in aqueous solution and the adsorption of PMG and Cd(II) on different mineral surfaces. ATR-FTIR, and XPS measurements showed that PMG adsorbs to the surfaces of goethite (α - FeOOH), aged γ -alumina (γ - Al₂O₃) and manganite (MnOOH) through one oxygen of its phosphonate group to singly-coordinated OH-surface sites.

The coadsorption of PMG and Cd(II) on the surfaces of the different mineral systems results in the formation of ternary mineral-PMG-Cd(II) surface complexes, as suggested from EXAFS results. Surface complexation models consistent with the different spectroscopic results will be presented and discussed.

Metal ion-chelation strength assessment of potential biodegradable ligands

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Aminopolycarboxylates (APCAs) (such as EDTA and DTPA) are very good, water soluble, complexing agents for di and trivalent metal ions. This property triggered the synthesis of several APCAs for sequestering metals and preventing unwanted side reactions. These chelating agents are used in domestic products and industrial applications. As most of the chelating agent's applications are water-based, the disposal of these ligands is made in wastewater, reaching frequently sewage treatment plants where they are not readily biodegradable. Therefore, their accumulation in the environment is becoming a matter of great concern.

In this context, N,N'-ethylenedi-L-cysteine (EC) and N,N'-ethylenedi-methylimidazol (EMI) (Figure 1) were synthetized and metal ion-chelation strength assessment of these ligands was evaluated. Both compounds are ethylenediamine disubstituted derivatives with two secondary nitrogen atoms in the molecule, which are potentially biodegradable [1].

In the case of EC synthesis, starting from L-cysteine hydrochloride monohydrate, the precursor L-thiazolidine-4-carboxylic acid was prepared. Then, EC was prepared by reaction of this precursor with sodium metal in liquid ammonia. In the case of EMI, starting from imidazole-4-(5)-aldehyde and ethylenediamine monohydrate, the precursor bis(imidazole-4-(5)-aldehyde)ethylenediiimine was synthetized; then EMI was prepared by palladium hydrogenation of this precursor.

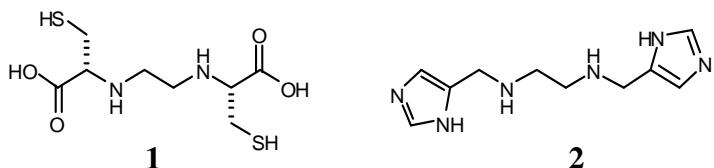


Figure 1. Structure of the synthesised potential biodegradable ligands: (1) N,N'-ethylenedi-L-cysteine and (2) N,N'-ethylenedi-methylimidazol.

Metal stability constants were determined by glassy electrode potentiometry in 0.1 M KCl at 25 °C. Then, to evaluate the metal-chelating strength of both ligands, conditional stability constants values were calculated for several metal ions [Ca(II), Cd(II), Co(II), Cu(II), Mg(II), Ni(II) Pb(II) and Zn(II)] and compared with values calculated for EDTA and NTA. Assuming conditional stability constant values of six or higher, this comparative study has shown that EC and EMI are efficient chelating agents for all metal ions, unless Ca(II) and Mg(II), for pH values higher than 5 and 6, respectively.

These facts suggest that EC and EMI can be suitable complexing agents in technical applications, whereby the presence of major ions [such as Ca(II)] is unavoidable or even essential and whereby complexing of specific metal ions is required.

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Progress in global multicompartamental modelling of DDT

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Dichlorodiphenyltrichloroethane, DDT, and its major metabolite dichlorodiphenyldichloroethene, DDE, are long-lived in the environment (persistent) and circulate since the 1950s. They accumulate along food chains, cause detrimental effects in marine and terrestrial wild life, and pose a hazard for human health. DDT was widely used as an insecticide in the past and is still in use in a number of tropical countries to combat vector borne diseases like malaria and typhus. It is a multicompartamental substance with only a small fraction residing in air.

A global multicompartment chemistry-transport model (MPI-MCTM [1]) is used to study the environmental distribution and fate of DDT. For the first time a horizontally and vertically resolved global model was used to perform a long-term simulation of DDT and DDE. The model is based on general circulation models for the ocean (MPIOM [2]) and atmosphere (ECHAM5). In addition, an oceanic biogeochemistry model (HAMOCC5.1 [3]) and a microphysical aerosol model (HAM [4]) are included. Multicompartamental substances are cycling in atmosphere (3 phases), ocean (3 phases), and vegetation surfaces. The model was run for 40 years forced with historical agricultural application data of 1950-1990.

The model results show that the global environmental contamination started to decrease in air, soil and vegetation after the applications peaked in 1965-1970. In some regions, however, the DDT mass had not yet reached a maximum in 1990 and was still accumulating until the end of the simulation.

Modelled DDT and DDE concentrations in atmosphere, ocean, and soil are evaluated by comparison with observational data. The evaluation of the model results indicate, that degradation of DDE in air was underestimated. Also for DDT, the discrepancies between model results and observations are related to uncertainties of input parameters. Furthermore, better resolution of some processes could improve model performance.

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Profiles of dechlorane plus and new related compounds in a Lake Ontario sediment core

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Dechlorane Plus (DP), a highly chlorinated flame retardant manufactured since the early 1970s, was only first reported in 2006 detected in biota, sediment and the atmosphere. Little information exists on its environmental occurrence even though DP is sold worldwide including Europe and the Far East. Annual importation of DP into the European Union from the sole manufacturer, OxyChem (Buffalo, NY) was estimated to be 1.1 million pounds while total production volume is estimated to be 10 million pounds. The US EPA has classified this flame retardant additive as a High Production Volume (HPV) chemical. For this reason, DP is a target compound on the Canadian Domestic Substances List, but not ranked highly in terms of risk for bioaccumulation because of its high molecular mass (648 Da) and high log K_{ow} (9.3). However, our previous work demonstrated DP's biomagnification potential for certain trophic relationships within food webs from Lake Winnipeg and Lake Ontario, Canada. Additionally, OxyChem's submission to the voluntary EPA HPV Challenge Program indicated that DP may possess ecotoxicological effects in fish and affect sediment bearing organisms due to its adsorptive properties.

To investigate DP's historical deposition pattern from the Niagara River into Lake Ontario, we analysed a core taken from the Niagara River bar, an area where sedimentation from the Niagara River first deposits into Lake Ontario, downstream of the manufacturing facility. DP was initially detected in 1971 (7.2 ng g⁻¹). The concentration of DP in surficial sediment was 3.6 ng g⁻¹ with a maximum concentration of 925 ng g⁻¹ occurring between 1976-1980. During the course of our research 4 additional compounds with an exact mass (GC/HRMS, R=10 000) to that of DP were detected; 2 identified as products from impurities existing in DP's starting material, 1,5-cycooctadiene (1,5-COD). Both the identified and remaining unknown compounds followed the same core profile as DP suggesting a relationship to the chlorinated flame retardant's production. Furthermore, these compounds also exist in the commercial DP mixture in quantities <0.01 % to that of DP. However it is interesting to note that concentrations in the Niagara River bar core are as high as 10% relative to DP.

DP, a Diels-Alder diadduct of hexachlorocyclopentadiene (HCCPD) and 1,5-COD, under certain conditions can undergo a *retro* Diels-Alder reaction resulting in the monoadduct. Our laboratory Diels-Alder reactions using HCCPD with both 1,5-COD and a known impurity, 1,3-COD resulted in solutions each producing their respective monadduct. The sediment core samples exhibited the same monoadduct compounds although not entirely matching DP's core depth profile, suggesting other possible sources. Further studies are required to determine the fate and occurrence of these lesser chlorinated compounds in the environment; in particular lake food webs.

Sampling and analytical methods of VOCs discharged from natural gas vents in volcanic and geothermal systems

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The presence of non-methane volatile organic compounds (VOCs) has to be regarded as a common and remarkable feature of fluids released from natural emissions in geothermal and volcanic systems (e.g., Isidorov et al., 1990; Tassi et al., 2009). Most of these compounds are of great environmental concern because of their demonstrated negative effects on atmospheric chemistry, climate and human health. Nevertheless, reliable estimations of the VOC contribution to the atmosphere from medium-to-high enthalpy natural systems still remain a challenge, being the composition of the organic gas fraction in thermal fluid discharges rarely determined. The analysis of VOCs in air is usually performed by thermal-desorption GC/MS procedures on samples collected via either i) traps constituted by stainless-steel tubes filled with solid adsorbents or ii) cryogenic concentrators (e.g., McCaffrey et al., 1994; Harper, 2000). The headspace SPME can be envisioned as an alternative non-destructive technique based on the distribution of the various analytes between the liquid/gas sample and the stationary phase coated on fused-silica fiber. The fiber is then transferred into the split/splitless injector port of a GC-MS, where the analytes are thermally desorbed and analyzed (e.g., Chai and Pawliszyn, 1995). In this study, three phase (Carboxen B-Carboxen C-Carbosieve S111) absorbent tubes and DVB-Carboxen-PDMS SPME fibers were both used to pre-concentrate VOCs discharged from fumaroles with outlet temperature of 150-160 °C at the Solfatara crater (Phleorean Fields, Italy). Gases were collected as dry phase by using a sampling device consisting of a titanium tube inserted into the fumarolic vent and connected to a glass condensing apparatus cooled with water. The condenser allowed a more efficient VOC absorption avoiding any interference by water vapor, CO₂ and acidic gases, such as H₂S and HCl, typically present at relatively high concentrations in these fluids (e.g., Todesco et al., 2003). Up to 25 different species were determined in the range of 40-400 a.m.u. (atomic mass unit), showing that the results provided by the two methods were largely consistent. The SPME sampling, which is a simple and rapid technique, can conveniently be used to perform expeditious surveys, whereas trap tubes, allowing the collection of a large quantity of gas, should be preferred when a high sensitivity for specific analytes at very low concentrations is required.

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Bioaccumulation of decabromodiphenyl ether and its metabolites: a mesocosm study

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The degradation of decaBDE under laboratory conditions is now well established. Studies have shown that lower brominated, potentially more toxic congeners can be formed from decaBDE under photolytic conditions, by anaerobic microbes and in fish. While degradation under laboratory conditions has been well established, the potential of decaBDE to debrominate in the natural environment remains largely unknown. To address this data gap, four 10 m diameter mesocosms in the littoral zone of a remote oligotrophic, temperate lake were installed at the Experimental Lakes Area in Ontario, Canada (2008). The mesocosms are open to the atmosphere and sediments and contain a natural littoral food web consisting of seston, periphyton, zooplankton, benthic invertebrates and juvenile yellow perch. Known amounts of technical decaBDE were added to three of the mesocosms while the fourth mesocosm, which received no decaBDE, was used as a control. Biota were sampled and are being analyzed to test whether decaBDE is being debrominated in the aquatic environment and whether these lower brominated metabolites are being accumulated fish and zooplankton. To our knowledge, this is the first study to examine the bioaccumulation and bioavailability of decaBDE and its debrominated metabolites in a natural environment.

What are the main pathways for consumer exposure to PFOS and PFOA?

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Perfluorinated compounds (PFCs) are used on a wide range of consumer products to make them stain, grease, and water repellent. Whereas PFOS has been directly applied as active ingredient in e.g. impregnation sprays, PFOA has mainly been used as process aid in the production of fluoropolymers such as polytetrafluoroethylene. As PFOS and PFOA possess toxic properties such as developmental toxicity and are found ubiquitously in human blood, it is important to understand the pathways of consumer exposure to those substances.

Here we review five studies that evaluate the importance of different pathways for consumer exposure to PFCs [1-5]. Two of them focused on total exposure and aimed to cover all relevant pathways [2, 3]. Whereas Trudel et al. [2] focused on the direct exposure to PFOS and PFOA, Vestergren et al. [3] also included the exposure to precursor substances such as fluorotelomer alcohols and applied a biotransformation factor to derive the internal doses of PFOS and PFOA. The other three studies investigated only a selection of pathways: Washburn et al. [1] focused on exposure to PFOA via the contact with treated consumer products (carpets, apparel). Fromme et al. [4] investigated exposure via contaminated foods, drinking water, air, and house dust but did not include exposure via contact with retail products. Björklund et al. [5] only included exposure to dust and foods. All studies (except [1]) found food intake as an important source of exposure to PFOS and PFOA, but the reported levels differ by almost a factor of 10 for exposure to PFOS. In addition, in high exposure scenarios (realistic worst cases) other pathways such as ingestion of dust, contact with treated carpets, or inhalation of impregnation spray droplets (PFOA only) can significantly contribute to the exposure to PFOS and PFOA [2, 3]. The finding that ingestion of dust might be an important source of exposure is supported by the studies [4] and [5]. The study of Washburn et al. [2] backs up the assumption that also treated carpet might be of relevance.

For the food pathway, we investigate possible reasons for discrepancies between the different studies. We conclude that food is likely to be the major pathway of exposure to PFOS and PFOA, but other pathways such as ingestion of dust might contribute to the consumer exposure to PFOS and PFOA in high exposure scenarios.

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High-pressure fluids in sustainable chemistry

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Production of solvents that are used in industrial processes has a large environmental impact. For a sustainable development it is of high priority to replace traditional organic solvents such as methanol, acetone and acetonitrile with more environmentally friendly alternatives. For instance, water is a clean solvent, which production and distribution has negligible environmental impact [1]. To improve its efficiency as a solvent, the temperature can be increased to near or above the boiling point while applying a pressure to maintain water as a liquid. This is what we call a subcritical solvent. In our research group, subcritical water has been used to extract health-beneficial molecules such as anthocyanins, polyphenolic glycosides and other antioxidants from byproducts and wastes in agricultural and forestry industry [2-5]. The use of byproducts and wastes as raw materials for high-value molecules does not only bring the advantage that chemical reagents for synthesizing compounds can be avoided, but it is also wise from a sustainable chemistry point-of-view to more efficiently utilize biomass wastes from agricultural and other industry. In this presentation, optimization strategies to obtain an efficient extraction procedure will be discussed, as well as the issues on stability of thermolabile compounds during the extraction. Another solvent that is considered sustainable is supercritical carbon dioxide (SC-CO₂), as this compound is a byproduct from distillation of air, and it can be pressurized and used, depressurized and recycled unlimited number of times. In our research group, SC-CO₂ is used as a solvent in extraction of unpolar molecules such as carotenoids from plant materials, but more interestingly, as an antisolvent to produce particles of antioxidants off-line or on-line with subcritical water extraction [6]. Selected research challenges and results will be presented in this lecture.

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Pharmaceuticals in the environment – properties, occurrence and environmental fate

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Residues of human pharmaceuticals have been reported in waters from rivers and lakes world wide [1, 2]. The biological potency of pharmaceuticals has raised many questions regarding potential environmental effects. This issue of concern for pharmaceuticals has added a large number of diverse substances to what is often referred to as “new emerging contaminants”.

The detected concentrations in natural waters are most often at trace levels, typically 0.001 – 1 µg/L. However, concentrations close to sources such as outlet from waste water treatment plants (WWTPs) reach concentrations in the 1 – 100 µg/L. Reported concentrations in treated effluent from production units were in the mg/L range [3]. The efficiency of the WWTPs to degrade or remove API’s is found to depend on many factors and no clear correlation with chemical properties or class of pharmaceuticals has been shown so far [e.g. 4].

Among the 1.200 active pharmaceutical ingredients (APIs) on the Swedish market very diverse chemical structures can be found and thus with diverse physicochemical properties. The persistency in the environment can be assessed in relation to the design of resistance for metabolic degradation which in many cases is one prerequisite for the human application of pharmaceuticals. Calculation of log P for 800 APIs revealed an average of 1.85 and values that ranged from 10 to -10.

This presentation will discuss new challenges in the assessment of the environmental behavior and fate of pharmaceuticals. More specific, the presentation will discuss aspects of persistence and bioconcentration in the light of diverse physicochemical properties of pharmaceuticals. Further, discuss occurrence in natural waters in back ground areas as well as close to potential sources, including removal efficiency in WWTPs.

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Bioaccumulation of metals in *P. scaber* as a measure of the EDTA remediation efficiency of Zn, Pb and Cd polluted soil

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Remediation technologies, such as soil washing/leaching, remove metals from the soil; the result is enhanced by using chelating agents as ethylenediaminetetraacetic acid (EDTA). Metals in soil are speciated in different ways, which results in different solubilities. They are not entirely accessible to chelating agents and they are consequently only partially removed. Residual metals left in soil after remediation remain present in chemically stable species bound to non-labile soil fractions. Different selective *in vitro* chemical extraction techniques are used to assess the risk that metals pose in contaminated and remediated soils by estimating metal fractions differing in their availability to organisms. However, chemical soil extraction cannot fully comprise the bioavailable fraction, due to the dynamic and complex nature of metal-soil and metal-organism interactions. The aim of our study was to use the metal accumulation capacity of terrestrial isopods (*Porcellio scaber*, Isopoda, Crustacea) as an *in vivo* assay of metal bioavailability in soil before and after remediation. The hypothesis was that isopods accumulate metals from the soil in proportion to the metal available fraction determined by selective chemical extractions.

Soil industrially polluted with Pb, Zn and Cd (4600, 1800 and 30 mg kg⁻¹, respectively) was leached in a bench-scale experiment with different EDTA concentrations (2.5, 10, 40 and 4-times 40 mmol kg⁻¹ EDTA). Altogether, 6, 41, 54 and 73% of initial Pb, 3, 13, 20 and 23% of initial Zn and 17, 54, 66 and 74% of initial Cd were removed. The metal mobility (Toxicity Characteristic Leaching Procedure), phytoavailability (diethylenetriaminepentaacetic acid extraction) and oral-bioavailability (Physiologically Based Extraction Test) were reduced by 85-92%, 68-91% and 88-95%, respectively, indicating that leaching the contaminated soil with EDTA was successful. After feeding on metal contaminated soil for two weeks, *P. scaber* accumulated Pb, Zn and Cd in a concentration dependent manner. Correlations between the concentrations of metals accumulated in *P. scaber* and the concentrations of mobile, phytoavailable and oral-bioavailable metals indicate that the pool of available metals decreased with the remediation (EDTA concentration) intensity. However, intercept values (extrapolation of metal concentration in *P. scaber* to the null concentration of chemically extracted metals indicate that metals that were otherwise unavailable for chemical extractions were available and were accumulated by *P. scaber*. Contrary to expectations, we also observed constant (Pb, Zn) and even higher BAFs (Cd) in remediated soil when compared to soil before treatment. When the bioavailable fraction is assessed solely on the basis of the results of chemical extraction tests, one would expect much lower amounts of bioavailable metals than indicated by BAFs.

We suggest the chemical extractions to be supplemented by *in vivo* bioaccumulation tests with isopods *P. scaber* for assessing the efficiency of remediation and for a more relevant picture of availability of metals in soil both before and after remediation.

Hexabromocyclododecane – Analysis, pitfalls and method comparisons

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Hexabromocyclododecane (HBCD) is applied as an additive brominated flame retardant (BFR) used in polystyrene. In 2001, the world production totalled 16,700 ton. HBCD predominantly consists of 3 diastereomers (α -, β - and γ -HBCD). γ -HBCD predominates in the technical product, whereas α -HBCD predominates in biota. HBCD can leach to the environment during production, application in products, in-service life (use of the product) and after disposal. HBCD is omnipresent in the environment and it was found in sediments, biota and humans world-wide. γ -HBCD predominates in the technical product, whereas α -HBCD predominates in biota.

Gas chromatography (GC) and liquid chromatography (LC) coupled with mass spectrometry (MS) are both used for the analysis of HBCD. An important advantage of LC-MS is the separation of individual diastereomers. This allows the use of mass labelled internal standards, which improves the accuracy of the results. The advantage of GC-MS is the simultaneous analysis with other BFRs such as polybrominated diphenyl ethers (PBDEs). However, until now severe discrepancies were found between GC-MS and LC-MS results. Several experiments were conducted to evaluate performance of both methods: (i) check of degradation of HBCD in the GC; (ii) measuring of HBCD response factors in the GC-MS; (iii) application of a rapid resolution column for LC separation, (iv) sensitivity test of different instruments and (v) the evaluation of GC vs. LC for the analysis of fish samples. This provided the following insights:

- In GC, degradation of HBCD diastereomers occurs, resulting in the formation of the degradation products pentabromocyclododecene and tetrabromocyclododecene. This leads to erroneous HBCD results. In addition, the degradation products can disturb the analysis of major PBDEs (e.g. BDE 49 and 99).
- The GC response factors of the diastereomers are different when using electron capture negative ion MS. This leads to serious quantification errors as the diastereomer profiles in standards and samples are different.
- In LC-MS, the use of a rapid LC-column reduced the run-time (5-fold) and improved sensitivity (4-fold).

Comparative studies in fish showed that GC results are (on average) 4.4-fold higher than the LC results. Research is not conclusive which of the methods delivers biased results (GC-MS or LC-MS or both), and this should be further elucidated. However, because of several advantages of the LC-MS method (i.e. determination of individual diastereomers, the use of mass labelled standards, good sensitivity, no thermal degradation, and simultaneous analysis with tetrabromobisphenol-A) LC-MS is currently the preferred method of analysis.

The role of models in comparing the behavior of different organic contaminants in different organisms, food chains, and ecosystems

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Environmental organic chemists seek to understand, describe and predict how organic contaminants behave in the physical and biological environment, with the aim to anticipate and quantify chemical exposure of organisms, including humans. Increasingly, they rely on mechanistically based models in these endeavours. We will argue that much is to be gained from a comparative approach that contrasts the modelled behaviour for different chemicals and for different systems.

The practice of comparing the environmental behaviour of different organic contaminants is well established. Environmental fate is being related to chemical characteristics in order to address the question: “What chemicals are most hazardous by virtue of having the potential for causing high exposure?” Tools have been developed that facilitate the comparison between chemicals of variable distribution and degradation characteristics. In particular, the practice of displaying various results of environmental chemical fate models as a function of the chemical partitioning space has proven invaluable in constraining the attributes of organic chemicals that are subject to important exposure-relevant contaminant amplification processes in the physical and biological realm. Examples are the identification of chemical properties that favour global¹ and mountain cold-trapping², or bioaccumulation in the human food chain³. Most recently, this approach has formed the basis for the screening and ranking of chemicals in terms of potential hazard^{4,5}.

Less common is a complementary perspective that seeks to relate chemical fate to systems characteristics in order to address the question: “What systems are most vulnerable to organic chemical contamination?” Systems here comprises different organisms, food chains and ecosystems, and simulation models are well suited to compare chemical behaviour in such systems. Ongoing efforts contrast the bioaccumulation potential of organic chemicals in different food chains^{6,7} and the cold-trapping potential in different mountain regions. Model simulations also suggest that the reversibility of persistent organic contamination may differ widely between environmental systems. Various examples will be presented and the potential insights gained from the comparison highlighted.

Enlightened chemical regulation that proactively anticipates and mitigates the potential for, rather than reacts to observation of, high chemical exposure should stand to gain the most from further advances in the model-based comparison of the environmental behaviour of organic contaminants.

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Membrane extraction of pesticides – an example of environment-friendly sample preparation

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Microextraction techniques, which become more and more popular in analytical sample preparation, include membrane-based extraction techniques [1]. A membrane is defined as a selective barrier between two phases, the donor phase (sample) and the acceptor phase, which often consists of an aqueous or organic solvent (acceptor phase). When driving forces are applied, such as concentration or pressure gradients, the analytes permeate from the sample through the membrane into the solvent. Separation is achieved when some compounds permeate the membrane more readily than others. Due to the barrier between the sample and the solvent in membrane extraction, several advantages such as good matrix separation and strong potential for automation are combined. An important benefit of membrane extraction is the small solvent consumption; usually less than 1 mL solvent is needed. This work describes the application of a polymeric membrane extraction technique called Membrane-Assisted Solvent Extraction (MASE). In recent years, MASE has been applied for different groups of organic compounds, among others triazines, PCBs, OPPs, PAHs, chlorinated benzenes, phenols and VOCs [2,3]. Due to the usage of cyclohexane and ethyl acetate as acceptor phase, MASE is conveniently combinable with gas chromatography (GC-MS or GC-electron capture detection) and the extraction and injection process can be fully automated.

The current investigations deal with the combination of MASE with HPLC-MS/MS for the analysis of pesticides in a polarity range between $\log K_{OW} = 1.7$ (metalaxyl) and $\log K_{OW} = 3.5$ (prometryne). An adaption of the extraction parameters (e.g. extraction solvent) was necessary to meet the demands of the analytical system. With the fully validated procedure several real water samples with analyte concentrations in the ng/L range were analysed. The results were compared with a common extraction procedure (solid phase extraction) used in pesticide analysis. Benefits and drawbacks of both techniques are presented.

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PCDD/F source apportionment for Baltic surface sediments using receptor modelling

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Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) continues to be an environmental problem for the Baltic Sea environment, with levels in fatty fish exceeding the regulatory limits for EU member states. A large number of off-shore and coastal Baltic surface sediments sampled along the Swedish coast were previously analyzed for all *tetra*- through *octa*-substituted PCDD/F congeners¹. A number of hot spot areas were identified, and most of these are located in the vicinity of pulp and paper industry or other wood related ongoing or historical industrial activities.

In order to trace and apportion PCDD/F sources for these sediments, source-to-receptor modelling was applied by using Positive Matrix Factorization³ (PMF). PMF is a multivariate technique that, similarly to Principal Component Analysis (PCA), simplifies the data by describing the matrix in a few new variables instead of the large number of original variables. For PMF, two matrixes are used, concentrations and measured/estimated uncertainties for each data point. In this case, both matrixes were normalized to the total concentration of PCDD/Fs of each sample.

The results of the receptor modelling showed a complex PCDD/F contamination situation in several of the coastal areas, suggesting ongoing release or leakage from historical emissions from up to 6 different source types. The suggested source types were identified by comparing the modelled fingerprints with known source fingerprints. It was shown that previous use of chlorophenol agents for wood preservation and a previously unknown source dominated by HxCDDs and associated to pulp and paper industry, are of significant importance in some regions, while the classical chlorine bleach source is of minor interest today.

For offshore and other pristine areas, the model suggested high importance of atmospheric loads, in line with other recent studies³⁻⁵. It appears as the atmospheric inputs can be divided into several source types, of which one is proposed to reflect long range transported (weathered) PCDD/Fs pollution, while the others show similarities to high temperature process emissions.

This study demonstrated the strength of combining comprehensive congener patterns with receptor modelling when tracing sources of PCDD/Fs in the environment. By this approach, not only apportionment of various sources could be suggested, but also clear spatial trends were shown, such as differences between sub-basins and between pristine and coastal areas.

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Visualising chemical fate within the environment

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When characterising the environmental fate and behaviour of chemical pollutants, such as polycyclic aromatic hydrocarbons (PAHs), there is a need to know not only how much chemical is in a system, but exactly where that chemical is, for instance in a leaf cuticle or cell wall. The micro-scale behaviour and location of a pollutant can have important implications for its long term environmental fate, storage, degradation and potential toxicity. This is not only true of many persistent organic pollutants, such as PAHs, but also emerging pollutants such as nanomaterials. To understand how chemical location effects environmental fate we developed a 3D visualisation technique utilising Two-photon Excitation Microscopy (TPEM) and autofluorescence to directly observe the location, fate and behaviour of organic chemical pollutants within living environmental systems, from vegetation, bacteria and fungi, to atmospheric particulates and nanotubes. TPEM is a form of laser scanning microscope, it uses a pulsed scanning laser to excite fluorophores within a sample, this creates fluorescence, which is detected to produce an image. The sample is only excited within a sub micrometer volume at the focal point, producing a single thin optical section; by adjusting the position of the focal point, multiple optical sections can be generated and combined to produce a 3D reconstruction of the sample. TPEM can be used for real time analysis over scales of 100s nanometres to 100s micrometers.

TPEM-autofluorescence utilises the intrinsic natural autofluorescence from the sample, and compounds of interest under study. Different cellular structures, or chemicals of interest, have distinct and unique fluorescent signals, by which they can be identified. In this way, a range of xenobiotics have previously been identified, monitored and tracked within different in-vivo plant, fungal and bacterial cellular structures including the cell wall, membrane, nucleus or vascular tissues. This means that for the first time cellular uptake can be directly observed, degradation pathways and sites of metabolism determined and long term storage and toxicological implications assessed. This has opened up many new avenues of research, offering an unprecedented level of understanding into pollutant environmental fate which previously had not been possible.

PAH atmospheric deposition to vegetation has been visualised, chemical movement from particulate matter into plant cuticles has been characterised, and complex chemical uptake and cellular storage patterns, fates, and behaviours directly monitored. 3D PAH root interactions, modes of cellular uptake, degradation pathways, and specific sites of cellular metabolism have been visualised alongside PAH fungal interactions and PAH bacterial interactions. In these systems, novel chemical clustering was visualised. It was observed that chemicals such as PAHs form micro-scale clusters within cellular compartments, these increase in size and number with time, and have significant implications for our understanding of organic chemical fate and behaviour within the environment, potential toxicity, modelling and regulation. These observations have spurred research into potential new pollutants such as nanomaterials and their role in modifying the fate and behaviour of traditional pollutants. Here we have observed how carbon nanotubes can act as significant sorbents of PAHs, both reducing uptake to root systems, whilst acting as carriage vehicles directly into cells pierced by the nanotubes, providing new scope and insights for further research. Understanding environmental chemical fate through this highly visual and accessible technique can open up new research pathways whilst helping to clarify and corroborate previous theory.

Efficient and improved aluminium triflate mediated organic transformations

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Metal triflates are useful in Lewis acid-mediated organic reactions. They are water stable, often recyclable and frequently tolerate water in the reaction mixture. They catalyse several different types of organic transformations either in their own right or as co-catalysts with a transition metal catalyst and can be used in green chemistry applications.

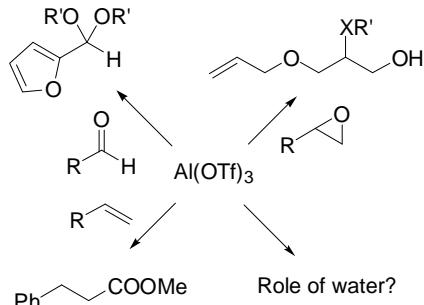
We have been investigating the usefulness of Al(OTf)₃ in epoxide ring-opening reactions (Scheme) with various oxygen and nitrogen nucleophiles [1,2]. Catalyst loadings as low as the ppm levels are possible with nucleophiles being present in as little as 1.2 equivalents in reactions yielding greater than 90% of the desired products. The catalyst is recyclable over several cycles without loss of activity. This work is now being applied to the synthesis of several physiologically active compounds.

We also established Al(OTf)₃ as an highly efficient catalyst for the solventless generation of acetals from various aldehyde and ketone substrates, using an orthoester in only 1.1 equivalents excess in the presence or absence of relevant alcohols [3]. This highly atom efficient approach also allows the catalyst to be recycled without loss of activity.

In transition metal catalysed reactions, Al(OTf)₃ was for the first time found to replace Brønsted acids in the Pd-catalysed methoxycarbonylation reactions of styrene and 1-pentene [4]. The catalysts so generated are more active than traditional catalysts. In such reactions, ligand quaternisation is a significant problem, and the system to hand suppresses this reaction, meaning that significantly less ligand is required and consumed in the reaction.

We have started investigating the fundamental role of water in metal triflate-mediated reactions. Preliminary studies indicate that in some instances reactions that are believed to be Lewis mediated are in fact Brønsted-type acid-mediated while in others the Lewis acid is the catalyst.

The studies described above will be highlighted in the presentation.



Scheme

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Real-time monitoring of VOCs by Proton Transfer Reaction - Mass Spectrometry (PTR-MS)

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Proton Transfer Reaction - Mass Spectrometry (PTR-MS) is a highly sensitive, real-time analytical technique for detecting volatile organic compounds (VOCs) in air, which was developed in the mid-1990ies in the laboratories of the Institute of Ion Physics at the University of Innsbruck. PTR-MS combines the concepts of soft, non-fragmenting chemical ionization (via proton transfer reactions with H₃O⁺ reagent ions) and of highly sensitive and quantitative product ion formation in an ion drift tube. Since its inception PTR-MS has become a leading technology in on-line VOC analysis, spanning a number of research fields that include environmental chemistry, food science, and life sciences. A series of recent technical improvements have greatly improved the instrument's capabilities. A 5 to 10-fold increase in sensitivity has been obtained with current detection limits ranging from 10 to 100 pptV (3σ, 1 sec signal integration time). The PTR-MS response time has been lowered to ~ 100 ms, making it one of the fastest currently available VOC sensors. The implementation of sophisticated mass spectrometric equipment (time-of-flight MS, linear ion trap MS, triple quadrupole MS) has led to a gain in duty cycle and in analyte specificity (MS/MS capability). Optimized modes of PTR-MS operation have been developed for the detection of gas-phase ammonia and formaldehyde. This talk will cover the basics of PTR-MS, recent instrumentation developments and selected applications in the field of environmental chemistry.

Or 100

Analytical Methodology

Poster abstracts

Ana P1-P68

Naturality of ascorbic acid: Chemometric analysis of ^{13}C NMR spectrum and IRMS

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As a tool against the illegal sale of industrially manufactured ascorbic acid in place of the natural product, the origin of vitamin batches was authenticated by stable isotope analysis, an analytical technique which has become more and more reliable for food control quality over the past few years.¹

^{13}C NMR (Nuclear Magnetic Resonance) and IRMS (Isotopic Ratio Mass Spectrometry) on carbon-13 were used to classify ascorbic acids coming from either natural or industrial sources. Natural samples were obtained from tropical fruits (acerola and camu camu) by means of a new extraction procedure. Industrial samples were provided by chemical suppliers such as Sigma-Aldrich and Carlo Erba.

A quantitative ^{13}C NMR procedure was optimized to calculate isotopic relative abundance on each molecular site;² NMR data were evaluated according their integrals and provided a matrix data set treated by a chemometric method. As reported in Figure 1, natural vitamins were well-discriminated from industrial ones.

Samples were also analyzed by IRMS coupled with gas-chromatography/combustion and elemental analysis devices (Figure 2). The combined use of these techniques enabled us to validate the origins of ascorbic acid batches issuing from different sources.

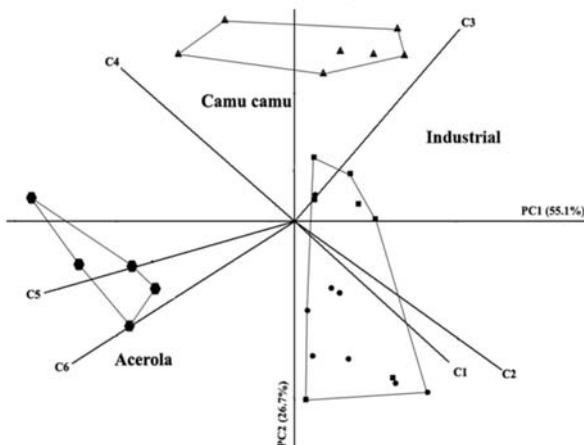


Figure 1

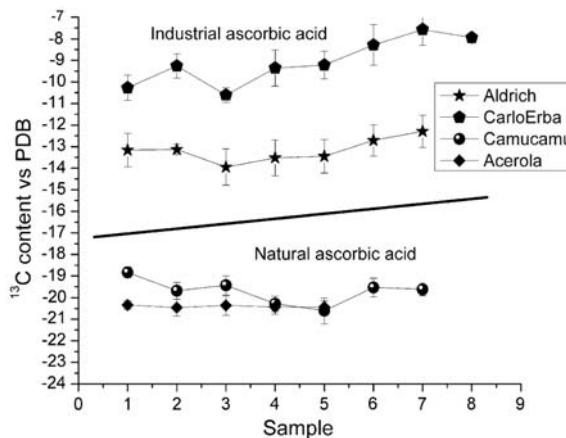


Figure 2

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Identification of dissolved organic species in non-drinking tap water by solid phase extraction and gas chromatography-mass spectrometry

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A method is presented for qualitative identification of dissolved volatile organic compounds (VOCs) in non-drinking tap water samples based on applications of both solid phase extraction (**SPE**) and gas chromatography-mass spectrometric (**GC-MS**) techniques. Water samples were collected and passed over a micro-column packed with acid treated active silica gel phase (pH = 2.6) for adsorption of dissolved organic species under this pH-condition. Silica-bound-organics were then divided into equal portions followed by suspension into organic solvents of different polarities as methanol, ethanol, butan-1-ol, ethyl acetate, diethyl ether and chloroform. These suspensions were then automatically shaken for one hour at room temperature. The organic extracts were subjected to **GC-MS** analysis under temperature programming conditions. The mass spectrum of each eluted chromatographic peak was library searched or manually interpreted to identify the correct name and structure. Blank solvent and silica samples were also subjected to the same **GC-MS** analysis for comparison.

Molecularly imprinted polymer treatment applied to the determination of the residual mass of atrazine and metabolites on an agricultural catchment (Brévilles, France)

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Despite the stopping of atrazine (At) application in the watershed since April 1999, the groundwater of the Brévilles spring still exhibits in the years 2005 and 2006 a recurrent contamination by At and desethylatrazine (with concentrations of $0.19 \pm 0.7 \mu\text{g/L}$ and $0.59 \pm 0.18 \mu\text{g/L}$ ($n= 133$), respectively (Baran et al., 2007 and unpublished data). In addition, a marked spatial variability appears in the contamination of the GW sampled from the network of 7 piezometers distributed within the 3 km^2 catchment (Baran et al., 2007). One of the hypotheses raised to explain these observations is the existence of a stock of At and DEA in the soils of the recharge area that would continuously feed the infiltrating water with these two substances. The estimation of the residual mass of pesticides in the soils is hindered by problems of detection limit for determining these substances in solid matrices.

Atrazine, desethylatrazine and desisopropylatrazine have been measured in the soils of Brévilles watershed. Pressurised liquid extraction technique was used for extraction followed by purification with terbutylazine molecularly imprinted polymers (Pichon 2007). This clean-up procedure allowed to remove interfering compounds from the sample extracts. This selective sample treatment for soil extracts allowed limit of quantification (LOQ) of 0.03 ng/g for atrazine, and 0.05 ng/g for metabolites.

The concentrations in soil samples ranged from 7.1 ng/g to < LOQ for atrazine and from 2.5 ng/g to <LOQ for metabolites.

The total cumulated mass was estimated at 1.4, 0.52 and 0.25 kg for atrazine, desethylatrazine and desisopropylatrazine, respectively. A fraction of this mass available for leaching could generate water infiltrating with concentrations higher than the drinking water limit, 7 years after the last application of atrazine.

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PAH determination in particulate matter by liquid chromatography: development of a validated method

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The particulate matter (PM) is an air pollutant consisting of a complex mixture of substances suspended in the atmosphere in solid or liquid state. The PM varies in size, composition and origin. The chemical composition may vary widely as a function of its major emission sources and the subsequent chemical reactions which take place in the atmosphere.

The polycyclic aromatic hydrocarbons (PAHs) are a class of complex organic chemicals. The United States Environmental Protection Agency (US EPA) has considered 16 priority PAHs based on their toxicological profile. The best known PAH is benzo[a]pyrene (B[a]P), which may be adopted as a marker for the PAHs mix, because this compound makes a consistent contribution to the total carcinogenic activity of the mixture. The heavier PAHs with three or more aromatic rings are almost totally adsorbed onto PM. The directive 2004/107/EC fixes an annual target value of total content of B[a]P in the PM10, 1 ng/m³.

The air matrix is complicated and the concentration of the PAHs in PM is very low, so the pretreatment of sample is a very important step. A comparison between the different concentration-extraction and clean-up techniques for 16 priority US EPA PAHs analysis in PM is presented.

Several pretreatment procedures are tested: extraction with soxhlet for 9h or total reflux boiling for 20 minutes (recommended by UNE-ISO 16362) and concentration with N₂ blowdown or rotary evaporation. The clean up step is carried out with an automatic system (Power Prep, Fluid Management Systems, Inc), the sample is added to a several 10g neutral silica columns deactivated at 10% and 15%, and it is eluted with n-hexane and dichloromethane/n-hexane (40:60 v/v). The chromatographic analysis is performed by high-performance liquid chromatography coupled with diode-array and mass detector. The proposed analytical method are validated in terms of recovery (%) and limit detection (ng/m³) with an airborne standard reference material, SRM 1649a "Urban dust" and with doped filters.

Sohxlet extraction with toluene, N₂ blowdown concentration and 10% deactivated neutral silica clean-up provided the best results. The experimental results show that the proposed method fulfills the requirements for the validation as an equivalent standard method of UNE-ISO 16362 "Ambient air. Determination of particle-phase polycyclic aromatic hydrocarbons by high performance liquid chromatography". The proposed method is applied for the determination of PAHs in PM10 and PM2.5 of an urban background monitoring station in the coastal city of Santander, northern Spain.

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Quantitative structure-Activity relationship study of some anti-tubercular drugs using chemometric methods

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Quantitative structure–activity relationship (QSAR) methods represent an attempt to correlate structural and/or property descriptors of compounds with biological activities. It is now widely used for the prediction of biological activities in chemical, environmental, and pharmaceutical areas [1,2]. In conjunction with the spread of HIV infection, tuberculosis is today amongst the worldwide health threats. Drugs for treating tuberculosis (TB) have been available for over half a century, but the total number of deaths and TB cases is still raising due to population growth [3,4]. In this study, QSAR has been applied to the modeling and predicting the Log (IC_{50}) indices of a series of anti-tuberculosis (4-quinolylhydrazones and 4-quinolylhydrazines) drugs. Four hybrid approaches of stepwise-multiple linear regression (S-MLR), stepwise-artificial neural networks (S-ANN), genetic algorithm-MLR (GA-MLR) and GA-ANN were used for prediction of Log (IC_{50}) indices of model compounds. Superiority of GA-ANN model over the others indicates the strengths of GA as variable-selection method and ability of ANNs in mapping the features for predicting the nonlinear phenomena such as cytotoxicity. Selection of two types of Burden matrices, Moran index and local dipole index by GA reveals the importance of the molecular size, topology of molecules and electronic interactions in the mechanism of cytotoxicity of compounds. For GA-ANN model, the relative mean square errors (RMSEs) for the calibration and prediction sets are 0.107 and 0.160, respectively.

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Investigation of occupational exposure of iron mine workers to some heavy metals as monitored through hair and nails analysis

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Environmental contamination and exposure to heavy metals is a serious growing problem throughout the world. The heavy metals determination in human tissues has been critical issue in environmental and clinical chemistry [1]. Due to many advantages such as, relatively high concentration of some heavy metals, easier sample gathering, transfer and storage, an increased interest in the use of human keratinized tissues such as hair and nails to determination heavy metals has been observed [2,3]. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for the determination of nine heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn) concentrations in hair and nail samples. To this purpose, samples were collected from a population group (N=61) of male worker from an iron mine in the center of Iran and a controlled group (N= 66).

The effects of different variables as age, occupation, habitat and habits on the elements concentration in the samples were studied. The major statistical analysis focuses on determining analysis of variance by t-test ($P < 0.05$) and Pearson correlation coefficients. We found some differences in hair and nails element concentrations between each group on the basis of occupation, age and individual habits (e.g. smoking). Our data were compared with those existed in literature about other countries. Then Pb, Cd, Fe and Cu assess by a three-column system. Analytical tools employed for separation and determination were based on a continuous system including solid phase extraction by C18, cation exchanger (Dowex 50x8) and anion exchanger (Dowex 2x8). The determinations of these species were carried out by flame atomic absorption spectrometry (F-AAS).

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Determination of phytoestrogens at trace levels in environmental samples using liquid chromatography-mass spectrometry

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Phytoestrogens are natural estrogenic compounds found in a diverse number of plants. These compounds have similar structures to estrogens and have both estrogenic and anti-estrogenic effects. Some papers are available concerning the estrogenicity and potential adverse-effects of phytoestrogens and their occurrence in vegetables. The occurrence of phytoestrogens in the aquatic environment has been less investigated and there are very few literature reports in this area.

This poster presents the development of a reversed phase liquid chromatography/mass spectrometry method for the simultaneous quantification of isoflavones (Daidzein, Formononetin, Genistein, Biochanin A, Glycitein, Daidzin, Genistin, Equol) lignans (Enterodiol, Enterolactone) and coumestran (Coumestrol) in environmental samples.

The chromatographic and mass spectrometry parameters are optimised in order to enhance the sensitivity for the quantification of phytoestrogens compounds. The separation is performed on a C18 column with a gradient of water/MeOH acidified with acetic acid and compounds are detected in both positive and negative electrospray mode.

The extraction is carried out by solid phase extraction. Different cartridges and elution conditions are tested in order to optimise the extraction step.

The developed method allows the quantification of phytoestrogens at nanograms levels in environmental samples.

Use of LC/MS for determination of (amino)nitrotoluenes in soil samples

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The presented work is focused on development of a simple extraction procedure and final analytical HPLC/MS method for determination of a group of 14 nitroaromatics (2,4,6-TNT, 2,3,5-TNT, 2,3,4-TNT, Am-DNTs and DAm-NTs). The retention behaviour of a mixture of TNTs and their metabolites was studied under various chromatographic conditions using different columns with octadecyl stationary phase. The mixture of methanol/water was used as a mobile phase in isocratic and gradient modes. The effect of organic modifier content and temperature of mobile phase has been investigated. The mass spectrometer (MS/MS with electrospray ionization) was used for the detection of studied compounds. The MS parameters were optimized to increase the intensity of signal and decrease the limits of detection. The scan mode (50-350 m/z) was used for selection of precursor ion of each (amino)nitrotoluenes. Subsequently the time-scheduled selected ion monitoring (SIM) was performed for MS detection. The various values and polarity of ion spray voltage and variable fragmentor voltage were used for maximum signal intensity achievement. Optimal conditions were used for identification and/or determination with multiple reaction monitoring (MRM). Different properties of extraction procedures for isolation of trinitrotoluenes and their metabolites from soil were tested. Experimental conditions of Soxhlet warm extraction (extractant type, extraction time) suitable for efficient extraction of individual analytes were studied. Recoveries over 80% for all studied compounds and over 90% for almost all (11 compounds) were obtained in a short extraction time (1 hour). The developed method was used for determination of studied compounds in real soil samples selected in contaminated sites in Czech Republic.

Selective Depletion of Phospholipid Interference Utilizing HybridSPE™-PPT Technology

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Analysis of biological samples is often hindered due to interferences carried through the sample preparation technique. Protein precipitation is a widely accepted sample preparation method for biological plasma samples due to simplicity and gross level removal of proteins. Though widely used, protein precipitation methods often result in chromatographic irregularities due to co-extracted endogenous species such as phospholipids that negatively affect chromatographic analysis. A more thorough sample cleanup can be achieved using solid phase extraction (SPE), but at a cost of time and method complexity.

In this poster a new platform was developed to process various plasma samples using a simplified two-step procedure to produce biological samples depleted of phospholipids prior to LC-MS-MS analysis. The HybridSPE-PPT platform employs the simplicity of standard protein precipitation with the added selectivity of SPE. The platform exhibits a high affinity towards phospholipids while remaining non-selective towards a broad range of basic, neutral and acidic compounds. The methodology and application examples, comparing results of protein precipitation and HybridSPE are displayed, showing cleaner extracts and more reliable recovery for the HybrisSPE for most drug components.

Summary

- HybridSPE-PPT platform demonstrated a high selectivity toward phospholipids while excluding basic compounds.
- Co-extracted phospholipids from rat plasma sample using standard protein precipitation results in severe ion-suppression.
- HybridSPE-PPT enables one step sample preparation with reduced processing time.
- Remove interfering matrix due to co-extracted phospholipids from protein precipitation.
- Decrease variability due to phospholipid interference.
- Increase reproducibility and sensitivity of bioanalytical methods.
- Demonstrated good recovery across a range of analytes.
- Effective phospholipid removal with a broad range of organic and acidic modifiers.

Development of bioinformatics resources for plant metabolomics research

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Recently, metabolomics research becomes a worldwide trend of new omics-based approach for systems biology and agricultural, industrial and pharmaceutical applications. Plant metabolomics is therefore thought to have a great impact on the food and drug supply around the world.

One of the major advantages with metabolomics investigations compared to traditional target metabolite analysis is that metabolomics data can give an unbiased view of changes in metabolism during environmental, genetic or developmental changes. Instead of tracking only a few metabolites, changes in relative amounts in 300 to 1000 or even more metabolites can be recorded and analyzed, covering all major metabolic pathways. This development has accentuated the need to apply and further develop multivariate methodology. Chemometrics provides tools to make good use of measured data, enabling practitioners to make sense of measurements and to model quantitatively and produce visual representations of information. Today, chemometrics has grown into a well established data analysis tool in areas such as multivariate calibration, quantitative structure-retention modeling, pattern recognition and multivariate statistical process monitoring and control.

In chemometrics, there are three basic categories of analysis

- Exploratory analysis which gives an overview of all the data in order to detect trends, pattern or cluster.
- Classification analysis and discrimination analysis, which classifies samples into categories or classes.
- Regression analysis and prediction models are used when a quantitative relationship between two blocks of data is sought.

Our interest is focused on method optimization to determine the new compounds using stationary and mobile phases with different physico-chemical properties in various modes of detection. Evaluation of chromatographic properties of the new stationary phases and description the molecular separation mechanism is done using the quantitative structure-retention relationship (QSRR) method including molecular modelling.

The goal of this study is to develop such system for determination to be able to establish data as bioinformatics resources for plant metabolomics research.

Determination of fungicides in wine by solid phase extraction and liquid chromatography coupled to tandem mass spectrometry

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Grape production, mainly destined for wine, is widespread in Spain. The vineyards are normally subject to fungi attack, which can cause diseases such as downy mildew, powdery mildew and gray mold. Depending on the wine-making procedures, fungicides on the grape berries can pass into the wine or may remain in the must. The European legislation regarding maximum residue limits (MRLs) of fungicides in wine is still limited, but the exposure level of consumers to these products must be assessed in order to prevent potential human hazard [1].

Concentrations of fungicides in wine are usually very low, and therefore, sensitive and selective analytical methods are necessary for their accurate determination in such complex matrix. Different analytical methodologies, based on either GC [2-3] or LC [4-5] analysis, have been developed in the last years for the determination of different types of fungicides in grape, must or wine. Frequently the extraction-purification steps are based on solid phase extraction (SPE) [3,5] or solid phase microextraction (SPME) [2,6].

The purpose of this work was the development of a method for simultaneous analysis of 9 fungicides (diniconazole, difenconazole, flusilazole, myclobutanil, penconazole, propiconazole, tebuconazole, azoxystrobin and metalaxyl-M) in wine. Analytes were selectively determined by liquid chromatography (LC) coupled to tandem mass spectrometry (MS/MS) detection using electrospray (ESI) as ionization source and SPE as enrichment step. Mixed-mode reversed phase SPE cartridges provided enough selectivity to avoid further clean-up steps. The proposed methodology was validated for both red and white wine, and applied to the analysis of different types of wine.

Acknowledgements

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Qualitative analysis of organic compounds- A Cleaner, economical and safer approach

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Identification of organic compounds is an integral part of curriculum for undergraduate and post graduate students of chemistry in most of the universities in India and abroad. The students studying chemistry as their main subject undertake the basic training in qualitative organic analysis in laboratory, which is of immense importance in their research careers in industries. For example in pharmaceutical industries, most of the lead compounds are isolated from natural sources and qualitatively characterized. The conventional methods of analysis (based on test tube chemistry) requires the investment of quite a large amount of reagents, non-renewable energy sources and time. Moreover, the waste produced during the experiment is a complex mixture of organic and inorganic reagents, the disposal or recycling of which is a major challenge.

In view of all this we have developed spot tests for identification of functional groups in an organic compound and carried out test tube chemistry¹ on a TLC plate or a filter paper and a groove tile. Unlike the spot reagents used in past, we have used inexpensive and easily available reagents for the tests. The procedures have been modified and the requirement of a non-renewable LPG gas used for heating is minimized. The problem of wastage and its disposal has also been tackled to a large extent. Tests for the functional groups such as carbohydrates, carboxylic acids, alcohols, esters, nitro, amino, etc. have been successfully carried out, the details of which will be presented

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Occurrence of polycyclic aromatic hydrocarbons (PAHs) in fish products

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Polycyclic aromatic hydrocarbons (PAHs) represent one of the most important groups of environmental pollutants which can be transferred into human food chain. It should be noted that some processing practices such as smoking can also be a source of PAHs human diet. With regard to carcinogenicity, mutagenicity and other adverse health effects, consumers' exposure to these toxic compounds is of high concern.

While for monitoring of environmental pollution, 16 PAHs identified by, the US Environmental Protecting Agency (US EPA) in 1984 as key contamination markers have been routinely used, in food safety control, benzo[a]pyrene has been employed for this purpose for a long time. Recently, in the European Union; a new legislation (2005/108/EC) was adopted thus providing a list of "15+1 EU PAHs" with carcinogenic potential.

As far as environmental matrices according to EPA list are to be controlled, the high performance liquid chromatography coupled with fluorescence detection (HPLC/FLD) is commonly employed. This approach, however, cannot be used for analysis of EU PAHs set since some target compounds, such as cyclopenta[c,d]pyrene, benzo[j]fluoranthene, are fluorescent.

The aim of the presented study was: (i) to validate a new analytical procedure for the determination of 16 carcinogenic and mutagenic PAHs in fish products using GC–MS and (ii) to assess the safety of canned fish products (both natural and smoked) available at the Czech market based on PAHs contamination.

For the extraction of target compounds, pressurised liquid extraction (PLE) was used to reduce sample preparation time and to minimize solvent consumption. The extract was after gel permeation chromatography (GPC) clean-up examined using conventional GC–MS and comprehensive GC \times GC–TOFMS. The latter technique allowed not only resolution of some critical pairs of isomers (e.g. benzo[k]fluoranthene and benzo[j]fluoranthene), but also a decrease of detection limits thanks to (i) compression elution zone during modulation process, and (ii) separation of matrix co-extracts hence reduced chemical noise at particular area of analyte elution. In the final phase of our study, 25 smoked and 25 non-smoked fish products from the Czech market were examined for PAHs content. Detectable levels of PAHs were found in all examined canned fish samples. Significantly higher contamination was observed in smoked products. In 40% of smoked fish samples the concentration of B[a]P exceeded the maximum limit 5 µg/kg which is set by EU for smoked food products.

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Uncertainty in the environmental sampling

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In the past sampling accuracy was rarely taken into consideration. The reason why was that analytical results usually referred to laboratory sample instead of the original one. This approach was probably based on control methodology applied in the industrial field. According to this procedure a laboratory sample was considered representative of the product total mass when constituted by different subsamples randomly taken. On the contrary, in the past 40 years the growing interest in the ecological problems brought to a greater awareness of the availability of representative samples of the ecosystem under control (rivers, lakes, polluted soils, air, etc). Studies on the irregular dispersion of contaminants highlighted the difficulty for the collection of representative samples. One of the first (1) regarding the water compartments has proved that metallic pollutants originated from punctiform sources are spreading in the basins with significant gradients of concentrations. Thus, in 1967 the sampling uncertainty was quoted to be the third of the total uncertainty (2), a value that increased to the half in 1997 (3). Key factors are sampling instruments and sampling strategies. An importance that has been proved by international studies in the different segments of the environment, soils in particular (4-7). Therefore, after a short review of sampling strategies for air, water, soil and waste. The procedures for the quantitative evaluation of the total uncertainty will be considered. Furthermore, the influence of the uncertainty on the respect of decreted limit values will be evaluated.

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Analysis of complex samples by GC/MS/MS – Pesticides and PCBs in marine biota

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The analysis of organochlorine pesticide residues in marine biota samples (mussels) by GC/MS is extremely challenging. Despite accelerated solvent extraction (ASE), followed by size exclusion chromatography and alumina clean-up, the extracted samples still contain large amounts of matrix materials. On a single quadrupole GC/MS system, these materials can interfere with the quantitative analysis in selected ion monitoring (SIM) mode and potentially lead to false negative results. The other analytical issues when injecting these complex samples are related to the chromatography with shifting of GC retention times and decreasing signal intensities. A new highly sensitive and selective method using Agilent 7000A triple quadrupole GC/MS/MS system will be discussed for the determination of PCBs and pesticides in biota and sediments by EI-MS/MS. Comparison of quantitative results will be made with GC/MS single quadrupole measurements and a novel column backflushing technique using Capillary Flow Technologies has also been investigated to provide a robust solution for the analysis of organic contaminants at low ppb concentration levels.

Investigation of the photochemical behaviour of lacking-cyclopropane-ring pyrethroids by Photo-SPME. Part I: Flucythrinate

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In this study, the photochemical behaviour of the pyrethroid insecticide flucythrinate has been investigated by photo-solid-phase microextraction (photo-SPME). In photo-SPME [1-2], fibre is exposed to light after extraction of the target analytes from aqueous solutions. Afterwards, the parent compounds and their corresponding photoproducts, which are generated in the same SPME fibre, are thermally desorbed into the injection port of the gas chromatograph and GC-MS analyses are carried out. Results indicated that, by using 8-W UV irradiation at 254 nm wavelength, flucythrinate is rapidly photodegraded (losses of more than 90% after 15 minutes of UV irradiation) following a first-order reaction kinetics. A large number of photoproducts were detected and some of them were tentatively identified by means of their mass spectra and using the information found in the literature [3]. All the proposed photoproducts involve cleavage of the ester bond; some of them had never been detected before. Photoformation-photodegradation curves of the photoproducts were easily monitored by the photo-SPME technique. Finally, flucythrinate photodegradation pathways were postulated.

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Investigation of the photochemical behaviour of lacking-cyclopropane-ring pyrethroids by Photo-SPME. Part II: Fenvalerate

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The advantages of performing photochemical studies in solid-phase microextraction (SPME) fibers [1-2], photo-SPME, were exploited to investigate the photodegradation of the pyrethroid fenvalerate. Gas chromatography coupled with mass spectrometry (GC-MS) has been employed to monitor the degradation kinetics of the target insecticide, to tentatively identify the photoproducts generated *in situ*, and to follow their photoformation-photodegradation curves. More than 90% of fenvalerate was degraded after 15 min of UV irradiation (8 W, 254 nm). First order kinetic behaviour was demonstrated and kinetic parameters (k_{ap} , $t_{1/2}$) were estimated. Twelve photoproducts were tentatively identified including 2-oxo-2-(3-phenoxyphenyl)acetonitrile, which has been reported to be considerably more toxic than fenvalerate [3]. Photodegradation mechanisms could be proposed on the basis of the identified photoproducts and with the aid of information from the literature.

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Detection of chromium(VI) using a polypyrrole film modified with carbon-nanotubes

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The Water Quality (Dangerous Substances) Regulations were introduced to give further support to the Council Directive 76/464/EEC on pollution caused by dangerous substances discharged into the aquatic environment and also to support the Water Framework Directive (2000/60/EC). The main substances concerned include heavy metals such as Cr(VI). Heavy metals are widely used in industry, are poisonous and tend to accumulate in certain organs once consumed; pesticides have carcinogenic, mutagenic and teratogenic properties and may bioaccumulate in fish and other organisms while volatile organic compounds arise from exhaust emissions of motor vehicles and also from industrial processes that involve organic solvents. The EPA has prioritised the monitoring of these dangerous substances in water in Ireland (STRIVE programme 2007-2013).

To date, the application of polypyrrole and polyaniline-coated substrates in Cr(VI) remediation has received much attention [1,2]. While in recent times, carbon nanotubes have attracted considerable interest in electrochemical applications as capacitor and sensor materials due to their high electronic conductivity, mechanical strength and surface area. In this paper we present conducting polymer films modified with carbon nanotubes as a new material for the reduction of Cr(VI) to the less toxic trivalent state, Cr(III). Various electrochemical methods were employed to monitor their ability to detect Cr(VI).

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Measurement uncertainty of Pb and Cd determination in blood by graphite furnace atomic absorption spectroscopy

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It is well known that various elements are present in our human body in wide concentration ranges and many of them play important roles in blood and organs. Human blood serum is one of the biological fluids most frequently used in clinical analysis for medical diagnosis, because it is collected from man. Therefore, it is important to measure the concentration of elements in blood serum. The determination of trace elements concentration in blood sample by electrothermal atomic absorption spectrometry is a common and well established technique in many chemical testing laboratories. However, the evaluation of measurement uncertainty results is not systematically implemented. An analytical result is not considered to be complete without a statement of the measurement uncertainty associated with it. Electrothermal atomic absorption spectrometry was used for the determination of Pb and Cd in whole blood and evaluation of the expanded uncertainty of these elements determination using ETAAS are described. To calculate the expanded uncertainty Graphite Furnace AAS calibrating with a commercial routine standard was used. In this application the standard calibration technique is used, three calibration solutions (5, 10, 35 µg/l) for Pb and (0.3, 0.6 and 1.2 µg/l) for Cd were used to calibrate the analytical procedure. To estimate the uncertainty of stock standard solutions, the bulk standard solutions of elements were used.

The commercially available Pb and Cd standard solution 1000 ppm has a manufactures stated uncertainty of $1000 \pm 2\text{mg/l}$. The value of the uncertainty is given without confidence level or distribution information, so an assumption is necessary. Without any other information a rectangular distribution is assumed and therefore the semi range is divided by $\sqrt{3}$. So the uncertainty related to stock standard solutions are: $U_{Stock} = 2/\sqrt{3} = 1.055 \text{ mg}$.

Uncertainty of pipette and volumetric flask cab is calculated by combining the major influences of the volume, the calibration, the repeatability and the temperature effects.

$$U_{Pipetter} = \sqrt{(U_{PipeRepeat})^2 + (U_{PipeSpec})^2}, U_{Volumetric} = \sqrt{(U_{Tol})^2 + (U_{Temp})^2 + (U_{Repeat})^2}.$$

The overall expanded uncertainty can be calculated by combining an uncertainty of the precision of the method with the combined uncertainty of the standards. The precision of the method was determined by calculating the SD of a commercially available quality control material that had been analyzed by different analysts, in the same laboratory, on the same equipment over a 5 year period.

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Monitoring of pesticides in water samples with SPE-GC-MS method including an uncertainty estimation of the analytical results

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Growing concern about the possible risks then pesticides pose to human and environmental health have increased the demand for analytical methods that are capable of detecting very low levels of pesticides. Trace levels of pesticides are often difficult to detect in river water and food samples because these samples contain a complex mixture of natural compounds that tend to interfere with detection. A simple preparation step is necessary to extract traces of pesticides from the aqueous medium, bring the analytes to a suitable concentration level before analysis. The choice of the extraction methodology for various types of pesticides and their transformation products from water samples depends on analyte characteristics, such as polarity, ionic character and stability. Several sample preparation methods have been developed for pesticides extraction, mainly liquid –liquid extraction (LLE) and solid-phase extraction (SPE). Nowadays, there is considerable interest in developing new selective methods and materials for extracting and isolating components from complex environmental matrixes. The selectivity of sorbents is an important parameter taken into account when compounds are to be extracted from surface water samples, since the main objective is to remove interferences and facilities further analysis by conventional analytical methodologist such as gas chromatography (GC) or high-performance liquid chromatography (HPLC).

In this work the procedure include solid-phase extraction of pesticides and subsequent analysis by GC-MS. A solid phase extraction method was applied with retention of analytes on a mini column of XAD-4 resin mixed with activated carbon as a sorbent to allow preconcentration of the target analyt from water sample. Determination of analyst was carried out with a GC capillary gas chromatograph coupled to mass spectrometer. The influence of various analytical parameters including the amount of solid phase, pH and volume of sample solution on the extraction efficiency of analytes was investigated. A detailed analysis of the uncertainty estimation is included. To estimate the uncertainty of analytical result obtained, we propose assessing trueness. Proportional and constant bias are calculated in the assessment of trueness. Nested design applied for calculating proportional bias and Youden method to calculate the constant bias.

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Investigation of environmental data from Lake Como Basin and watershed (Italy) by multivariate data analysis methods

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Lake Como (or Lario) is located in Lombardy, northern Italy, at 198 m a.s.l. It is the deepest alpine lake (down to -410 m), with an extension of 145 km², a volume of 23372 km³ and a catchment area of 4508 km². It is surrounded by mountains that reach the maximum altitude of 2609m with Legnone Mountain.

It has several tributaries, among them the most important is Adda river which flows into the lake in the northern part. It is also the only emissary: it flows out from Lecco branch to River Po. Como branch, with no emissary, shows a peculiar situation.

Beside the wonderful landscapes appreciated worldwide that Lake Como offers, it represents an important drinking water reservoir as well as an environmental and economic resource for the population living in NW Lombardy.

In 2001 an investigation involving lake waters, tributaries waters, lake sediments and tropospheric composition has started at the University of Insubria in Como with a twofold aim: getting a picture of the present condition of the lake environment and studying its evolution.

Lake waters were characterized with respect to the main ion composition and some trace metals of environmental concern. The investigation was then extended to the tributary waters to get knowledge about the sources of the considered metals. Sediments were then investigated as they are environmental archives and they could give information concerning the evolution of the whole ecosystem. Finally some tropospheric data available from 1999 to 2007 were studied with the aim of getting more information concerning the temporal evolution of the area.

Chemometric data analysis methods such as Principal Component Analysis and multi-way methods PARAFAC and Tucker3 were then employed in the data treatment to rationalize the information hidden in the huge amount of data. An overview of the results will be presented.

Analytical aspects of mercury determination and speciation in environmental samples

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For the centuries, mercury has been hidden by the Nature as an insoluble mercury sulfide called cinnabar. But the beginning of nineteenth century opened several industries where mercury compounds have been used and now, each year, we introduce thousand of tones of mercury into the environment. At this moment the greatest sources of mercury emission are the coal power plants, which are responsible for more than 60% of mercury emission to the environment. As a result of anthropogenic emission many components of the environment are contaminated with mercury. In the human body, mercury accumulates in the liver, kidneys, brain and blood. Mercury may cause acute or chronic health effects. In 1997 the US Environmental Protection Agency established "Mercury Study Report to Congress". In the European Community the reduction of the mercury input into environment is one of the priority of environmental protection policy. In January 2005, the European Commission adopted a Mercury Strategy that envisages a number of actions to protect citizens' health and the environment. Due to this there is a necessity to improve the level of mercury content determination in many components of environment and continuously improve the analytical techniques for its detection, determination and speciation. The most toxic is mercury in the form of organometallic compounds and as a methylmercury (MeHg) in particular. Since most of inorganic mercury compounds are insoluble in aqueous solutions thus these forms are much less dangerous and essentially are not accumulated in the living organisms. More often the determination of the total mercury in environmental samples should be replaced by its speciation. From the analytical point of view the determination of MeHg in environmental samples is a special challenge. The most unstable stage of MeHg speciation is the derivatisation step. Although several derivatisation procedures have been described in the literature, they are usually limited to particular kinds of environmental samples and difficult to apply elsewhere. Other problems are caused by MeHg decomposition during sample preparation. Also equipment for mercury speciation is usually unique and composed for particular case. The method and equipment for mercury determination (speciation) in the form of methylmercury will be presented, discussed and illustrated with the results of mercury contents in the sediments and fish samples. The advantages and disadvantages of environmental sample preparation, derivatisation and detection of mercury in environmental samples will be discussed.

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Determination of parabens, triclosan and triclocarban in water by liquid chromatography-electrospray-tandem mass spectrometry

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The extensive inclusion of bactericides on personal care products has awakened the concern about their potential long-term effects on human health and wildlife. Esters of 4-hydroxybenzoic acid (parabens) show estrogenic activity and have been related with breast cancer, presumably favoured by the use of paraben-containing deodorants. 2-(2,4-dichlorophenoxy)-5-chlorophenol (triclosan, TCS) and 3,4,4'-trichlorocarbanilide (triclocarban, TCC) are known to be endocrine disruptors, and, beside this, they can turn into more toxic and persistent species such as chlorinated phenols, polychlorinated biphenyl ethers, polychlorinated dibenzodioxins and mono- and di-chlorinated anilines¹⁻³. These chemicals are continuously released in the aquatic media through urban wastewater, their main entry route into the environment. Thus, they occur at the µg/L level in wastewater and can still be found at ng/L¹⁻⁴.

The goal of this work was to develop an analytical procedure for the simultaneous determination of TCS, TCC and 7 parabens, including the branched and linear isomers of propyl and butyl paraben (PrP and BuP) in water samples. The method is based on a solid-phase extraction (SPE) step followed by a liquid chromatography-electrospray ionisation-tandem mass spectrometry (LC/ESI-MS/MS) analysis. Oasis HLB (60 mg) cartridges produced efficient retention of the analytes at the natural pH of samples, (without breakthrough even when 1 L of water was concentrated) and easy desorption with only 4 mL of methanol. SPE recoveries were higher than 85% except for raw wastewater, where they fell to 65% for TCC. The performance of the method was investigated with two triple-quadrupole LC/MS instruments from a low/mid and mid/high market range: a Varian 1200L and an API-4000, respectively. The last one provided between 3 and 80 times lower limits of quantification (LOQs) than the first one, in the 0.08-0.44 ng/L range for surface water. Moreover, the comparison of matrix effects on both instruments showed a very different behaviour. Particularly, for parabens, signal suppression was observed in the Varian instrument and signal enhancement with the API-4000. As a result, different calibration approaches were chosen for them and pointed to the need of matrix effect re-evaluation in case of method transfer between different LC/MS systems. The application of the method to real samples showed the ubiquity of methyl paraben (MeP) and n-PrP (at the 1-6 µg/L in raw wastewater) and the coexistence of i-BuP and n-BuP at similar levels (ca. 100-200 ng/L in raw wastewater).

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Detection of gelatinase A and B in sera of patients with cardiovascular diseases

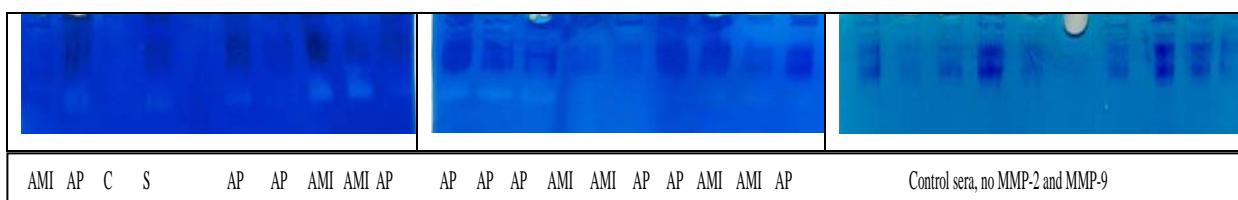
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MMPs are members of a family of at least 21 Zn²⁺ dependent endoproteases which play important roles in many normal biological processes including postpartum uterine involution, wound healing and angiogenesis as well as in pathological processes including inflammation, fibrosis, arthritis and cancer. The main characteristic of MMPs is the degradation of extracellular matrix. Recently there is increasing evidence that 72 KD and 92 KD collagenases (MMP-2 and MMP-9) play a pathogenic role in the development of the atherosclerotic plaques. MMP mediated vascular remodeling is maybe caused through the imbalance between reactive nitrogen and oxygen species generated in diseased vessels by activated vascular cells, found to activate latent MMPs and degrade TIMPs.

This study enrolled 60 patients with ACS (23 with AMI –acute myocardium infarct; mean ± SD age 70,3 ±21, 27 with AP – angina pectoris; mean ± SD age 63,7 ± 14,5 and 10 volunteers; mean ± age 54 ± 11). All patients with cardiovascular diseases were from Clinical Center of Serbia and Clinical Hospital Zvezdara. It were excluded subjects with history of neoplastic, hepatic, infectious and autoimmune diseases. SDS PAGE was performed with 7.5% polyacrylamide gel [1] under no reducing conditions and SDS-PAGE zymography with copolymerized gelatin according to the method of Kleiner and Settler-Stevenson [2]. Regions of proteolytic activity were visualized as clear zones against a blue background after 3 h staining with Coomassie brilliant blue. The zymogram of patients sera on SDS PAGE Coomassie brilliant blue stained gels, show bands on the mass position of 92 KD and 72 KD. The protein molecular mass of 92 KD was detected in 71,42%, and 72 KD in 85,71% of patients with ACS. Molecular mass of 92 KD indicated MMP-9, and 72 KD MMP-2 proteases.



In blood of patients with ACS: MMP-9 was detected in 10 of 14 patients and MMP-2 in 12 of 14 patients. Surprisingly, MMP-9 was not detected in normal subjects. Increased levels of MMP's were documented in patients with ACS. Those findings were associated with development of atherosclerotic lesions. If this prove to be a casual relationship, MMP's maybe a strong candidate for farmacotherapy aimed at stabilizing plaques and preventing AMI.

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Rapid analysis of free melamine in milk products and bakery goods by isotope dilution using UPLC-MS/MS

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Melamine is a nitrogen-based compound (66% nitrogen by mass) with a highly stable structure. It is therefore used in industrial and commercial plastics and also as flame retardant for its heat tolerance property. This compound was not designated to be used in food. Nevertheless, melamine is sometimes added to food products as an adulterant because it increases the apparent protein content (Kjeldahl and Dumas protein analysis). This illegal use has severe health consequences such as kidney failure and in some cases can lead to death (China milk scandal).

In collaboration with the Federal Agency for the safety of the Food Chain, we have developed a rapid method to test different target food matrices for melamine. Previous methods developed several years ago as [1] are based on a GC-MS determination after a derivatization step. These methods are time and chemicals consuming, two parameters that have been considered in the development phase.

This paper details a rapid method that combines a simple extraction-purification step for melamine with UPLC-ESI⁺-MS/MS determination. After an acetonitrile-water (50/50) extraction on only 0.5g of sample, the extract is cleaned from fat with an easy liquid-liquid extraction with dichloromethane. The aqueous upper layer is further diluted (with water) before injection on a ACQUITY BEH Hilic, 2.1 x 100 mm, 1.7 µm. Chromatographic runs are very short ($R_t = 0.89$ min) with a cycle between two injections of 2 min leading of a consumption of 1.4ml of mobile phase per sample. Quantification was performed with isotopic dilution (C^{13} labelled melamine). Two transitions were monitored m/z 127>85 and 127>68 for native melamine and m/z 129>87 and 129>70 for the C^{13} labelled melamine.

It has to be noted that the dilution step with water of the sample before injection is also an advantage: it reduces the risk of interferences, of matrix effects and it avoids an additional clean-up like an SPE which is also time and chemicals consuming.

The method was in-house validated. No matrix effect was observed. Consequently solvent (water)-based standards could be used for the calibration curve ranges from 0.5 ppm to 40 ppm. The calibration function was linear with a determination coefficient of >0.999 (r^2). The limit of detection and the limit of quantification were respectively 0.2 and 0.5 ppm.

The precision of the method was examined by analysing spiked samples at three concentration levels (1 ppm, 10 ppm and 30 ppm). Repeatability and within-lab reproducibility were < 6% RSD. Average apparent recovery of melamine ranged from 97% to 99%. The accuracy of the method was assessed by participating to two inter-laboratory studies on milk powder. Z-scores below and equal to 1 were obtained.

[1] FDA method: <http://www.fda.gov/cvm/gcmsmelamine.htm>

Analysis of phytoestrogens in solid agro-environmental matrices

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Phytoestrogens, such as isoflavones, are weakly estrogenic compounds that occur naturally in a wide range of plants. Particularly legumes, like soybeans (*Glycine max*) and red clover (*Trifolium pratense*) contain high levels of isoflavones (formononetin, biochanin A, daidzein, and genistein,) in the mg/g concentration range (1, 2).

Much research has been undertaken to quantify human and husbandry animal uptake of isoflavones, but environmental occurrence and exposure has not yet been studied systematically. We are investigating the emission of phytoestrogens from an agricultural field cultivated with a red clover-grassland-mixture into the environment. Therefore, analytical methods for the quantification of phytoestrogens in different agro-environmental matrices (plants, soil, manure, and digested sewage sludge) are currently developed. Extraction procedures include liquid-solid, liquid-solid extraction at elevated temperature and pressure (ASE), and Soxhlet-extraction. The extracts were separated and detected by HPLC-MSMS (3), therefore the application of ¹³C₃-labeled phytoestrogen analytes was indispensable. Optimized analytical conditions, method validation results, and applications will be presented.

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Analisis of perfluorinated acids (C9-C11) by use of liquid phase microextraction (LPME) and UPLC-MS

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The widespread occurrence of perfluorinated organic acids and other perfluorinated compounds in environmental samples are documented. The high water solubility's of these compounds indicate that the water column might be an ultimate recipient for these compounds. There are concerns about the persistence and bio accumulativ properties of these compounds, and analysis of water samples might be the first step to understand the persistence and bio accumulative picture of these compounds.

We have developed a sensitive and selective method for perfluorinated carboxylic acids based on the use of LPME and UPLC-MS. In LPME a water immiscible organic solvent is immobilized as a thin supported liquid membrane in pores in the wall of a porous hollow fiber. The lumen of the fiber is filled with a 20 µL acceptor solution, where pH is adjusted to make sure that the analytes are in the ionized state. After extraction, 2 µL the acceptor solution was directly subjected to the final analysis by liquid chromatography-mass spectrometry. The compounds were detected by using the MS-instrument negative Electro Spray ionization mode. For all compounds it was possible to obtain recovery around 90%, which indicated an enrichment factor of around 25000.

Isotope effect as a criterion for ecomodel reaction: $k_{\text{H}}/k_{\text{D}}$ in reduction of Polychloronaphthalenes with Cu and Zn

Elizaveta Igumnova and Vladimir Nikiforov

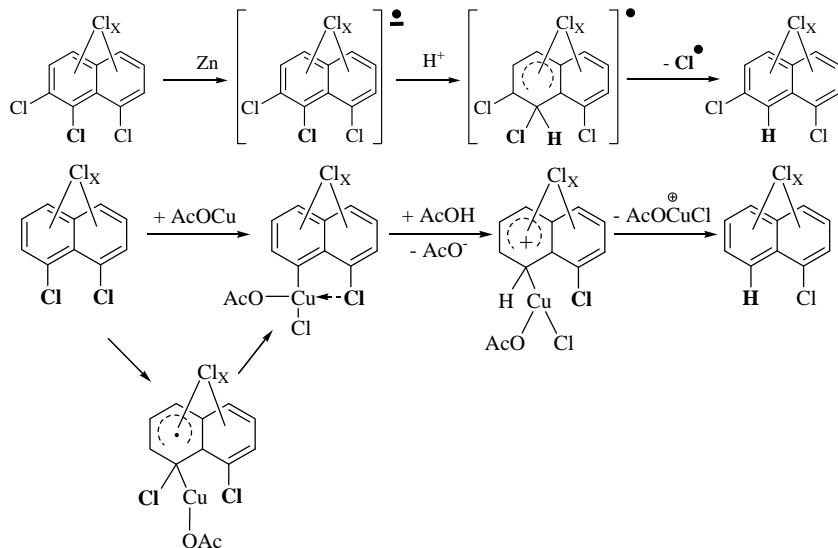
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Kinetic isotope effects of hydrogen ($k_{\text{H}}/k_{\text{D}}$) were determined for hydrodechlorination of a series of polychloronaphthalens (PCN) with Cu or Zn in mixtures of AcOH and AcOD. Significant isotope effect is observed in both reactions. Isotope effect in reaction with Cu is greater (5 – 6) than in reaction with Zn (ca 2).

Table 1. $k_{\text{H}}/k_{\text{D}}$ for hydrodechlorination of PCN congeners with Cu and Zn in AcOH/AcOD

PCN	1,2,3,4,5-PeCN	1,2,4,5,6-PeCN	1,2,4,6,8-PeCN	1,2,3,6,7,8-HxCN	OCN
Cu	5.2	6.1	5.3	5.7	6.0
Zn	1.8				1.9

The difference can be explained by different mechanisms: Single electron transfer with Zn and Oxidative addition or electrophilic attack with Cu as key elementary steps, followed by protonation of a radical-anion or organocopper compound, respectively:



Which reaction is a better model for reduction of PCNs for reactivity – persistence correlation?

Determination of H/D isotope ratios in degradation products of PCNs in the environment and comparison with presented here data of chemical experiments would help to select a relevant ecomodel reaction from these two or two reject both and force to search for a new one.

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Equilibrium sampling using polydimethylsiloxane in fish tissue – possibilities and limitations

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Polydimethylsiloxane (PDMS) has been used for passive sampling in numerous human and environmental matrices, and has recently been applied to fish tissue [1,2]. However, the applications were restricted to lipid-rich tissues [1] or to pre-equilibrium extractions [2]. This work investigated the possibilities and limitations of using PDMS disks for passive equilibrium sampling in fish species of varying lipid content. Polychlorinated biphenyls (PCBs) were used as model lipophilic organic pollutants. PDMS disks of different thicknesses were immersed in the tissues for differing time periods (one hour up to one week), solvent-extracted and the extracts were analyzed using gas chromatography coupled to mass spectrometry. Whether equilibrium had been established was investigated either by assessing kinetics by means of time series or by using PDMS disks of multiple thicknesses (approx. 140 µm up to 620 µm).

Time series showed that equilibrium had not been established within one week of sampling in lean tissues (e.g. pikeperch), whereas equilibration was rapid (i.e. hours) in lipid-rich fish (e.g. eel, Figure 1 A). The latter could also be shown using PDMS disks of three different thicknesses (Figure 1 B), and both methods led to approx. the same amount of sum PCBs sampled per gram of PDMS. The newly developed method was found to be sufficiently sensitive to determine free concentrations of PCBs in lipid-rich fish from the Baltic Sea.

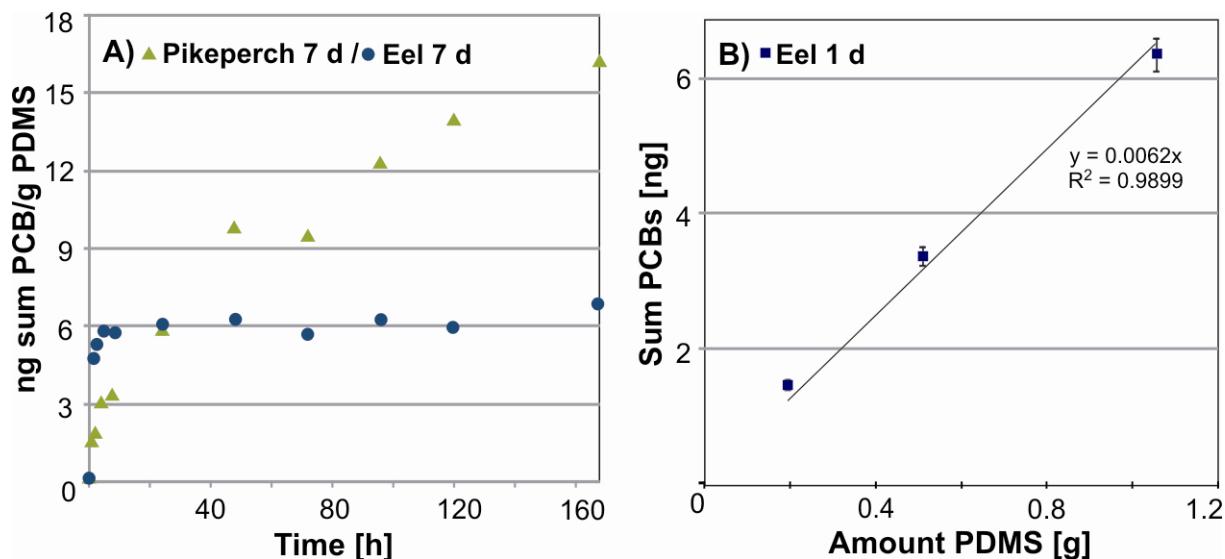


Figure 1. Time series over one week in lean pikeperch and lipid-rich eel (A) and one day equilibrium sampling using PDMS of three different thicknesses in lipid-rich eel (B). The linear regression was forced through the origin, error bars show standard deviations of triplicate samples (B).

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Diffusive sampling for pollutants in wet solid matrices

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Diffusive sampling techniques are applied to wet solid matrices of environmental interest, such as river and lake sediments, soil, sewage sludge, biota and faeces. This leads to very simple procedures and devices involving thin hollow fibers and micrometer thin polymer coatings, which could be immersed in various matrices either in the field or in the laboratory. Different coating and membrane formats can be applied to sample either non-polar compounds (e.g. POP) [1] or more polar, acidic or basic compounds. The latter compounds typically include drugs and drug metabolites, but also many pesticides (e.g. triazines) or other pollutants (e.g. chlorophenols [2], nonylphenol and perfluorinated compounds) and heavy metals [3]. Those substances have been considerably less studied in environmental chemistry with respect to solid matrices than POP. Simpler, cheaper and virtually solvent-free techniques are developed for sampling a wide range of pollutants in solid matrices compared to conventional methodology (e.g. Soxhlet extraction).

In many cases there is a choice to sample either the total pollutant amounts or the freely dissolved concentration. The latter is closely related to chemical activity [4], and the techniques developed can lead to simple measurements of this important parameter for a wider range of compounds than is otherwise possible [5]. This will lead to more detailed information on the speciation of the analytes, i.e. their degree of binding to matrix components, their oxidation state, their bioavailability etc.

This poster summarizes the principles and strategies for diffusive sampling in wet solid matrices together with preliminary results.

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Ecotoxicity estimation of river sediments - case study of sediments from Deûle river

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The Deûle river is located in Northern France, in the department of Nord Pas-de-Calais. For our study the sediment samples from this river were taken near the lead and zinc production plant Metaleurop (near Douai), which is closed since 2003. This Zn-Pb smelting factory was important producer of metals from ores during the 20th century. Because of natural high concentrations of mercury present in the ores used by this factory, its production processes and its waste-water management, the mercury has been progressively introduced in the whole aquatic ecosystem, and finally massively accumulated in the sediments. Nowadays that is a place with an environmentally significant metal contamination.

Two sediment cores have been sampled in November 2003: the first one upstream and the second one downstream the factory. The sediments were analyzed for an amount of anions and metals, sulfides and other physico-chemical parameters. With a view to measure concentrations of mercury and methylmercury, both cores were sliced, dried at room temperature for 48 hours, and finally sieved before analyses. Advanced mercury analyser instrument (AMA254) was used for total mercury (THg) determination. For assessment of methylmercury (MeHg), extracted samples were ethylated with tetraethylborate and injected using an headspace system equipped with Tenax column trap and separated by a gas chromatography with subsequent atomic fluorescence detection.

The toxicity of sediments was determined by standard biotests with *Daphnia magna* and by rapid test using a bioluminescent *Vibrio fischeri*. The 24-hours water leach of the sediment was used for the bioassays with *Daphnia magna* and the values of EC₅₀ after 24 and 48 hours were calculated. Some of the sediment extracts weren't toxic for *Daphnia magna* in contrast to the other ones where the 50% effective concentration reached value of 553 mg l⁻¹ of the sediment (the most contaminated). We applied the *Vibrio fischeri* for contact toxicity testing of the whole sediment. The variation in the sediment toxicity, expressed as IC₅₀ or EC₅₀, are presented. For the evaluation of mercury and methylmercury toxicity of these sediments assays with unenriched and enriched sediments with known amount of mercury and/or methylmercury were carried out. Lastly, correlation analyses between the toxicity results and determined parameters characterizing sediment were done with a view to data correlations to the quantity of THg and MeHg. The toxicity estimation of the sediment is discussed.

Combined analytical method for the detection of chloral hydrate and 1,3-dichloro-2-propanol in water samples

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Chlorination by-products formed during drinking water disinfection are a cause for public health concern, because of their potential harm to human health. Chloral hydrate (CH), a haloacetaldehyde commonly reported in drinking water, has been classified by U.S. EPA as a possible human carcinogen (U.S. EPA, 2000) and is regulated in drinking water by limits set by the European Union (EEC, 1998). 1,3-dichloro-2-propanol (1,3-DCP) is a haloalcohol also used during water chlorination, and has been shown to be carcinogenic, mutagenic and genotoxic, with a high risk factor for human and animal toxicity (Bastos *et al.*, 2002). According to EU directive 91/155/EEC, all formulations which contain more than 0.1% of DCP have to be labeled as toxic and carcinogenic (Chang *et al.*, 2002).

Several analytical methods have been published for the separate analysis of CH and 1,3-DCP in water and other environmental matrices, differing in extraction, sample preparation and end detection techniques. We report a rapid and sensitive method for the concurrent analysis of CH and 1,3-DCP in water samples, by liquid-liquid extraction and GC-MS. CH and 1,3-DCP are extracted from water samples with MTBE, followed by filtration with sodium sulphate, centrifugation and analysis by GC-MS on a 60m HP-VOC column. The mean recoveries ranged from 82% for CH to 104% for 1,3-DCP for spiked water samples. The limit of detection of the method was 1 µg/kg for CH and 0.3 µg/kg for 1,3-DCP.

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QCM-based gas sensory system for VOC's detection

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Quartz Crystal Microbalance (QCM) sensors are widely used in many practical applications in gaseous and liquid medium as mass sensitive sensors, for material characterization, etc. The QCM measurement technique uses the sensitivity of quartz crystal resonator with respect to any mass change at its surface in accordance to Sauerbrey relation [1]. Sensitivity of QCM technique is quite high – mass change of nanogram (and less) scale can be easily observed. When used as chemical sensor quartz surface covered with special coating called sensitive layer. This provides QCM sensor with required sensitivity and selectivity towards gas (or liquid) molecules under study. Polymers, nano-porous materials, macromolecular organic compounds are widely used as sensitive coatings. If several sensors coated with different sensitive layers to collect in array and apply to database obtained from sensors array special statistical algorithm based on multi-component analysis we obtain device designated as “Electronic Nose” (EN). The EN can be used for detection and identification of volatile organic compounds (VOC) using procedure of pattern recognition of chemical images.



Fig.1 Picture of gas sensory system EN-type sampling, valve for switching "sampling" – "purification" and electronics (quartz oscillators, frequency counters, and interfacing with PC). Experiment controlling, data acquisition and process of recognition is being carried out by means of original software. Mode of gas supplying is non-flow type: after injection of analyte vapor cell is cut-off from surroundings. Standard radio-technical quartzes (10 MHz, AT-cut, Ø8mm) covered with appropriate sensitive layers are used as the sensor elements. For purpose of pattern recognition domestic software based on several statistical algorithms (Kmean, PCA, Neural Network, etc.) has been developed and integrated with software for device controlling. Polymers, calixarenes and cyclodextrins are used as sensitive coatings in our device.

Acknowledgments. This research was supported by STCU Project N 3643

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Our team has experience in design and creation of gas analytical sensory systems EN-type. They can be used for analysis of gaseous medium, environment monitoring, detection of hazard pollutants in air, in agriculture and food industry, etc. This work is dedicated to presentation of pilot model of QCM-based chemosensory system (Fig.1). It consists of 8-channel QCM-based sensor array, working cell, gas-supplying pathways, syringe for vapor injection, air filter-drier for providing fresh dry air for purification sensors between

dry air for purification sensors between

The use of multivariate classification techniques for environmental management and quality assessment

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The multidimensional data analysis methods are becoming very popular in environmental studies dealing with measurements and monitoring as well as impact assessment. The complexity and the large variance of environmental sets limits the use of common statistical methods for the assessment of the state of pollution such that the application of geostatistical and multivariate statistical methods is highly recommendable. One of the most often used are the methods based on the compression and rotation of the original parameters. These methods allow to explore complex dataset and extract relevant information from it. Usually, cluster analysis (CA) is carried out to reveal specific links between sampling points; PCA is applied to detect hidden structures in data sets; regression analysis (classical linear or multivariate) is used to create respective trends and prediction models for each contaminant; and finally Partial Least Squares (PLS) modeling helps to find out more detailed connections between variables. From other point of view, the management of environmental systems involves the making of informed choices not only about ecosystem functioning but also about desired levels of economic activities. Information on the economic and ecological effects of measures as well as their spatial distribution is therefore needed.

This contribution is presenting examples of application of multivariate techniques as successful methods for environmental data exploration. First one is focused at finding an alternative method for water quality classification. It was done by means of factor analysis. Such statistics simplifies the representation of sample quality to two factors only. First one is indicating chemical while second biological composition of samples^[1]. Plot of factor scores shows groups of samples with similar character of pollution.

Next example shows the new way for development of possible nutrient reduction scenario within international river basin. It is based on multivariate analysis applied to modeled emission data for seventeen local catchments^[2]. Three major factors describing diffuse (mostly agricultural), erosion and urban sources of emission. Moreover, the results show the key areas where emission of nutrients is related to particular pathway. The idea of such differentiation of catchments can be applied to evaluate new, “pathway-oriented” scenarios for nutrient reduction. Performed analysis can be an easy-to-use tool for support the evaluation of effectiveness of different scenarios aiming the reduction of nutrients.

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Measuring indoor air concentrations of polyfluorinated compounds with passive samplers

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Polyfluorinated compounds (PFC) are toxic, bioaccumulative and persistent and have been found in pristine regions of the earth, indicating that they are distributed by ocean currents and long-range atmospheric transport. Little is known about sources and there is need for research. Outdoor air contaminations have been determined in numerous studies, whereas indoor air has to be scrutinized further. Indoor air concentrations of fifteen polyfluorinated compounds (3 fluorotelomer acrylates, 5 fluorotelomer alcohols, 4 polyfluorinated sulfonamides, 3 polyfluorinated sulfonamido ethanols) have been determined in indoor air applying a passive sampling method developed by Shoeib et al. (2008). Analytes are accumulated on polyurethane foam disks which were impregnated with XAD4- resin to improve sorptive capacities. The sampling media was placed in a protective steel housing. Passive samplers were deployed parallel in buildings representing potential PFC air contaminations such as carpeting shops or outdoor suppliers and five random residential houses. The objective of this study was to compare different PFC air contamination levels. It is expected that contaminations will be the highest in samples from outdoor suppliers. Results will be presented on the poster.

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Continuous membrane extraction – applications for ionizable organic pollutants in aqueous samples

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Introduction: On-line continuous measurements is one way to detect episodic pollution events¹ and membrane-based separation processes are well suited for adaptation to continuous operation². Automated sample preparation can eliminate labor-intensive sampling and improve reproducibility of measurements³. In the current work, different examples of continuous membrane extraction studies are presented.

Theory: An organic liquid is immobilized by capillary forces in the pores of a supporting material, giving a supported liquid membrane (SLM). If the supporting material is a hollow fiber (HF), the method is commonly referred to as liquid-phase micro extraction (LPME). A 3-phase system (aq-org-aq) can be used for selective extraction of ionizable compounds from aqueous samples, over the membrane into a receiving acceptor (extract). pH of the sample and acceptor are set so that analyte is trapped in the acceptor which over time leads to enrichment. The extraction material is cheap, easy-to-use and consumes only minor amounts of solvent. In continuous membrane extraction, pumps are connected to the membrane. The sample is continuously delivered to the membrane, while the acceptor may be stagnant or continuously collected during the extraction.

Applications: A) Using programmable syringe pumps and flat-sheet membranes, completely automatic and portable samplers were constructed. One of these was used for stand-alone extraction to sample 24 h average concentrations of *s*-triazine herbicides in a lake in an agricultural region. B) Using HF membrane contactors, four non steroid anti-inflammatory drugs (NSAIDs; ketoprofen, naproxen, diclofenac and ibuprofen) were extracted. These NSAIDs were monitored in treated sewage water (Lund) at ng L⁻¹ level. C) To assess ecotoxicological risks of pollutants, it is desired to measure freely dissolved concentrations⁴ and LPME has been adapted to this in equilibrium sampling through membranes (ESTM) (e.g. chlorophenols⁵ and metals⁶). Continuous ESTM with HF contactors is suggested as a fast way (experimental equilibration time within 20-40 min) to provide data in studies of interactions between pollutants and sorbing phases. In the presence of 10 mg L⁻¹ humic acids, phenolic analytes exhibited decreased extraction, due to a decrease in C_{free} .

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Ion-pair liquid-phase microextraction of a quaternary ammonium surfactant in a hollow fiber

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Consisting of a hydrophobic and a hydrophilic part, surfactants accumulate at surfaces, reduce surface tension and can form micelles, which have lead to their widespread use in both household and industrial applications. After use, surfactants may reach sewage treatment plants, where they are generally well degraded, but some surfactants have low biodegradability¹. In the mg/L range and even below, many cationic surfactants are acutely toxic to aquatic organisms². Several cationic surfactants are therefore used as biocides and antiseptics^{3, 4}. To manage environmental risks in aqueous compartments, there is a need for development of analytical methods.

A 2-phase hollow fiber (HF) liquid-phase micro extraction (LPME) method was developed for the cationic surfactant dicocodimethyl ammonium chloride in aqueous samples⁵. The target analyte was a quaternary ammonium compound (QAC), which is positively charged in the entire pH-range. Therefore, extraction needed to be performed by forming a neutral ion-pair between QAC and an anionic carrier. The HF was fixed on a metal rod support and impregnated with ~7 µL of organic solvent immobilized in the HF pores by capillary forces. After extraction, the organic solvent was dissolved into 100 µL methanol, which was analyzed by HPLC-MS. LPME parameters that were studied included: selection of organic solvent, fiber length, choice and concentration of anionic carrier, procedure of transfer to methanol, sample volume, extraction time, sample pH and ionic strength. The maximum enrichment factor achieved was 737 times in 750 ml carbonate buffer. For a lower and more practical sample volume of 250 ml, the enrichment was around 400 times. Detection limits of 0.3 µg L⁻¹ in carbonate buffer and 0.9 µg L⁻¹ in industrial process water were obtained.

The compound in the presented study may be seen as a model substance for other surfactants. A similar extraction method for (negatively charged) linear alkylbenzene sulfonate (LAS) has recently been developed. Similarities in LPME extraction of QAC⁵ and LAS (manuscript in preparation) have been observed.

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A method for determination of halogenated phenols and alkyl phenols in marine organisms, analyzed as their pentafluorobenzoyl esters

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A method was developed for the analysis of halogenated phenols and alkyl phenols in marine organisms. The extraction efficiency was evaluated by comparing the recoveries of the lipid content and 13 added phenols from three different marine species (herring, cod and mussel), with the corresponding results from three well-established extraction procedures, the Bligh and Dyer (1), the Smedes (2) and the Jensen (3). The Jensen method and the new method, which applies centrifugation instead of filtration to separate the extract from the protein tissue, gave general phenol recoveries of 80-100% for all species, while the Bligh and Dyer and the Smedes gave relatively low recoveries for the most acidic phenols, with recoveries of only 20-50% for pentachlorophenol (PCP) depending on the species. The new extraction procedure also showed comparable lipid recoveries to the other methods.

The phenols were separated from the lipids and neutral organohalogen compounds through alkaline partitioning. Free fatty acids were converted to their methyl esters (to avoid interferences during derivatization of the analytes) via a simple esterification, using 2% (w/v) sulfuric acid in methanol. Additional clean-up was conducted on a silica gel column (0.5 g).

To increase the sensitivity of the analysis, the phenols were converted to their pentafluorobenzoyl esters, by using a tetrabutylammonium-catalyzed extractive acylation. The reaction was quantitative within two minutes at room temperature, and the formed derivatives were persistent enough to withstand treatment with concentrated sulfuric acid. The introduction of a pentafluorobenzoyl group provides extra response in comparison with non-fluorinated derivatives (e.g. the methyl ethers), especially for low-chlorinated and non-halogenated phenols when working with e.g. electron capture detector (ECD).

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Extraction and fluorescent detection of mercuric ions Hg^{2+} in microsystems using task specific ionic liquid

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Mercury, the most toxic non radioactive metal, is uncommon in natural environment. Its presence is mainly issued from human activity such as industrial or agricultural wastes and extraction of gold. Mercury contamination causes serious environmental nuisance since inorganic mercury can be converted by bacteria into neurotoxic methylmercury, which is bioaccumulated by marine aquatic organisms. The entry of these organisms into human food chain has a dramatic impact on health such as neurological, neuromuscular or nephritic diseases. The level of mercuric ions (Hg^{2+}) in water is therefore the object of strict regulation and should not exceed 1 $\mu\text{g/L}$.¹ Although sophisticated analytical techniques (AAE, AAS and ICP-MS) are currently used, there is a real need to develop fast, inexpensive and real-time monitoring methods for heavy metals detection.

So, to respond to this demand, we suggest an extraction by ionic liquids (ILs) and fluorescent detection in microsystems. Indeed, several authors have demonstrated the extraction of heavy metals by ionic liquids including chelators with very high Nernst coefficients.² One of the most recent developments concerning molten salts is the use of Task Specific Ionic Liquids (TSILs) which possess all ILs advantages including liquid/liquid extraction.^{2,3} Indeed, by grafting a special functional group onto an onium salt, fluorogenic and chelating properties can be obtained. Our microextractor is constituted of two adjacent microchannels separated by vertical micro-pillars. This ECD system performs three functions: (i) extraction of mercuric ions from the carrier fluid through the pillar-stabilized interfaces, (ii) concentration of ions in IL phase due to its very low velocity, (iii) on-line detection via a fluorescence spectrometry.⁴

Thus, we report the synthesis and characterization of a task specific ionic liquid bearing a fluorogenic moiety for sensing mercuric ions. Then, its metal recognition properties are presented. Finally, its use in Hg^{2+} microextraction from aqueous solutions is illustrated.

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Sensing of nitrates at polypyrrole nanowires modified with copper nanoparticles

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The determination of nitrate and nitrite levels and subsequent removal plays an important role in water analysis. In recent years, there has been considerable interest in nitrates with the Nitrates Directive (1991/676/EC) and the EU Water Framework Directive (2000/60/EC) (the nitrate safe limit is set at 30 mg/L i.e. 800 µM). Nitrates are a common groundwater contaminant in irrigation waters and in heavily populated areas. Overexposure to nitrates can lead to a host of medical problems; for example nitrates can combine with amines to form toxic and carcinogenic nitrosamines. Also, nitrates in the form of fertilizers can cause eutrophication of water [1]. The World Health Organisation recommends a maximum daily intake of 0.3 mg nitrate per kg of body weight.

Increasing concern about the rising concentration of nitrate in groundwater has resulted in intensive research in the area of denitrification of drinking water. In this paper, the possible use of polypyrrole nanowires modified with copper nanoparticles for the electrochemical detection of nitrates was investigated. The application of a one-step potentiostatic method was used to synthesise the nanowires at the electrode surface. Once the nanowires were formed they were modified by electrodepositing copper nanoparticles on their surface. The nanowires were characterised using SEM, while various electrochemical methods were employed to monitor their ability to detect nitrate.

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Sucralose – the removal in sewage treatment and recipient concentrations

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Sucralose, an artificial sweetener made from saccharose (cane sugar) by exchanging three hydroxyl-groups to chlorine-atoms, was assessed for ecotoxicological effects as well as occurrence in the environment.

A method for the analyses of sucralose with HPLC/MS-MS was developed, where electrospray together with selected-ion-recording (SIR) as well as multiple-reaction-monitoring (MRM) was used. The sodium adduct ion was used for quantitative purposes due to difficulty in detecting the molecular ion and fragments thereof. The ratio of the chlorine-isotope-pattern was employed to enhance selectivity.

It has been demonstrated that sucralose passes virtually unchanged through a typical sewage treatment plant. To examine if sucralose could be removed in the treatment plant, extended treatment technologies including activated carbon, ozone and UV/H₂O₂ were tested, and the treated sewage water was analyzed for sucralose. The persistence of sucralose in the environment was investigated by analyzing sucralose in the recipient of three sewage treatment plants in the Stockholm area.

Pressurized hot ethanol extraction of carotenoids from waste carrots

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Nutraceuticals and functional food ingredients are known to improve individual health, with especial emphasis to elderly health since their bioactive components are reported to ameliorate or even prevent age related diseases [1, 2]. Carotenoids are known for their antioxidant activity and therefore have a neuroprotective effect. They are known to have effect against singlet oxygen, inhibition of LDL cholesterol oxidation, controlling the risk of range of cancers and improving cognitive development [2]. One of the rich sources for carotenoids are carrots, furthermore, market polices indicates that carrots should meet strict standards of size and shape, this makes about 25% of carrots never come to the set standards. The uncontrollable phenomena of carrot production result in quarter of the harvest to be regarded as waste [3]. The aim of this study was to have beneficial use of waste carrots by extracting carotenoids from them. Nevertheless, established methods for the extraction of carotenoids require the use of organic solvents, which are costly, environmentally hazardous, and require expensive disposal procedures. This fact has extended the objective of this study to optimizing a sustainable technology extraction procedure for carotenoids. Pressurized fluid extraction (PFE) utilizes conventional solvents at controlled temperatures and pressure, it requires less solvent in a shorter period of time, the set up of the technique contain samples in an oxygen and light-free environment makes it preferable for use in the nutraceutical industry [4, 5]. The extraction procedure was optimized by varying time and temperature. The extraction solvent of choice was ethanol since it is generally recognized as safe (GRAS). β-carotene is the most abundant form of carotenes (60 – 80%), and in this study it was used as an indicator for carotenoids content. Preliminary results show that the content in carrots is in the order of 42.6 µg/g DW, which is within the range of the reported values (37 – 78 µg/g).

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Simultaneous analysis of PPCPs in environment samples

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The fate and effects of pharmaceuticals and personal care products (PPCPs) and natural estrogens entering the environment has gained increasing attention. PPCPs include non-prescription and prescription pharmaceuticals for human and veterinary use, and the active and inert ingredients in personal care products. Many pharmaceuticals are not completely removed during wastewater treatment, leading to their presence in wastewater treatment effluents, rivers, lakes, and ground water. Here, we developed analytical methods for monitoring 14 pharmaceuticals from wastewater treatment plants and surface water by LC/ESI-MS/MS. For sample clean-up and extraction, MCX (Mixed Cation eXchange) and HLB (Hydrophilic–Lipophilic Balance) solid-phase extraction (SPE) cartridges were used. The limits of detection in distilled water and the blank surface water were in the range of 0.006 – 0.65 and 1.66 – 45.05 pg/mL, respectively. The limits of quantitation for the distilled water and the blank surface water were in the range of 0.02 – 2.17 and 5.52 – 150.15 pg/mL, respectively. The absolute recoveries for fortified samples were between 62.1% and 129.3%. Intra-day precision and accuracy were 2.7% – 16.4% (R.S.D.) and -12.4% – 31.3% (bias), respectively. In surface wastewater near rivers, chlortetracycline and acetylsalicylic acid were detected frequently in the range of 0.017 - 5.404 and 0.029 - 0.269 ng/mL, respectively. The method could be successfully applied to monitoring WWTP influent and effluent as well as surface water in the major rivers in South Korea. Sulfathiazole and chlortetracycline occurred at high concentration in the influent and effluents of livestock wastewater. Surface water near rivers had higher levels than surface water of domestic treatment plants.

Table . Absolute recoveries, precision, and accuracy for pharmaceuticals (0.01 – 1 ng/mL)

Group	Pharmaceuticals	Recovery(%)	RSD (%)	Bias(%)*
Group I-A	Acetaminophen	77.9 - 86.9	3.5 - 8.1	-0.2 - 4.6
	Carbadox	83.1 - 88.3	2.7 - 8.7	-7.2 - 6.4
	Sulfathiazole	79.7 - 87.1	6.6 - 9.2	1.5 - 2.0
	Lincomycin	62.1 - 7.0	3.9 - 8.0	1.9 - 2.7
	Sulfamethoxazole	81.5 - 92.7	5.3 - 11.8	-1.7 - 8.2
	Trimethoprim	92.2-95.2	7.9 - 10.3	-4.6 - 4.3
	Sulfamethazine	83.9 - 91.1	3.2 - 7.3	-6.9 - 4.7
Group I-B	Chlortetracycline	75.5 - 93.1	11.2 - 12.3	-1.3 - 2.8
	Oxytetracycline	75.6 - 125.4	11.2 - 14.6	-6.1 - 20.6
	Enrofloxacin	72.8 - 82.3	5.5 - 13.9	-4.8 - -0.8
	Ciprofloxacin	84.4 - 96.9	3.2 - 9.0	-12.4 - 3.7
Group I-C	Quinoxaline-2-carboxylic acid	72.5 - 101.7	9.8 - 16.4	1.4 - 31.3
	Acetyl salicylic acid	97.8 - 129.3	1.3 - 9.0	-11.9 - 7.3
	Diclofenac-Na	93.7 - 103.4	8.6 - 11.7	-2.6 - 4.5

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Optimisation of a matrix solid-phase dispersion method for the determination of UV filters in indoor dust by gas chromatography tandem mass spectrometry

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UV filters are compounds designed to mitigate the deleterious effects of sunlight. One of their most known uses is in sunscreens but they are also included in other personal care products (cosmetic, hair dyes, shampoos) and used in the protection of goods, plastics, varnishes and clothes [1]. In the European Union 26 organic compounds have been approved to be incorporated in sunscreens at individual concentrations up to 10%, for most of them [2]. Medium and highly polar UV filters have been often detected in surface and wastewater [1]. More lipophilic species, such as 3-(4-methylbenzylidene) camphor (4-MBC), 2-ethylhexyl-p-methoxycinnamate (EHMC) and octocrylene (OCR) have been found in river and lake sediments [3], sludge [4] and even in biota [5]. In fact, concentrations up to $2 \mu\text{g g}^{-1}$ have been reported for 4-MBC and OCR in fish [5] and as high as $15 \mu\text{g g}^{-1}$ for OCR in sludge [4], suggesting that certain UV filters can be bio-accumulated and concentrated on solid matrices. This information added to reports about the estrogenic activity of some species, such as 4-MBC [6] and EHMC [6] have risen the concern about their effects on wildlife and humans.

Conversely to above studies dealing with environmental samples, for the best of our knowledge, no data are available in relation to the levels of UV filters in indoor areas. The goal of this work is to present a procedure for the determination of a group of selected UV filters: EHS (2-ethylhexyl salicylate), HMS (homosalate), isoamyl-p-methoxycinnamate (IAMC), 4-MBC, EHMC, and OCR, in dust from different indoor environments. Matrix solid-phase dispersion (MSPD) is used as sample preparation and, analytes are determined by gas chromatography in combination with tandem mass spectrometry (GC-MS/MS). The second goal of this work is to provide a first overview of the levels of target compounds in dust samples collected from different environments.

Acknowledgements

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Determination of benzotriazole type corrosion inhibitors in aqueous samples by liquid chromatography coupled to tandem mass spectrometry

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Benzotriazoles are polar high production volume chemicals that find broad application in industrial processes. Benzotriazole itself and the tolyltriazoles, used as a technical mixture of 4- and 5-methyltriazole, are used as corrosion inhibitors in deicing fluids for aircrafts, automotive antifreeze formulations, brake fluids, metal-cutting fluids, and industrial cooling systems.

These compounds have recently been detected in water samples [1-3], due in part to their only partial removal in wastewater treatment plants (WWTPs) and to direct untreated sewage discharge [4, 5]. They have been already classified as emerging pollutants [1]. Due to their polar character, they are often determined by liquid chromatography (LC) coupled to tandem mass spectrometry (MS/MS). Their toxicity is directly dependent on their isomeric structure [6].

The aim of this work was firstly to develop the analytical methodology to determine this type of compounds in aqueous matrices. Solid phase extraction (SPE) was considered as a possible enrichment step previous to the LC-MS/MS analysis using electrospray ionization (ESI). Furthermore, solid phase microextraction (SPME) was also investigated as alternative for preconcentration. Performance of the proposed methodology for very complex matrices such as raw municipal wastewater or industrial wastewater was characterized. The second objective was to apply this methodology to industrial and urban wastewater to evaluate the emission of these compounds from different Spanish industries related to the metal surface production.

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Using e-noses for environmental monitoring

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No preference for **oral or poster** presentation

The environmental problem associated to contaminated soil is pertinent on both a regional and national level. It has been estimated that Sweden alone has about 80.000 contaminated areas. Of the latter, some 13.000 are sites that have been assigned a high priority for after treatment measures. The task of after treating contaminated land areas often requires a long chain of work processes before it is possible to determine the best course of action for minimizing the effects of the contaminants in the soil. Current applied techniques to clean polluted soils include soil washing, thermic destruction, stabilization, leaching and biotreatment. Given today's techniques, the major difficulties facing remediation of soil include: 1) understand a priori which techniques is most applicable for a certain pollutants 2) to monitor the treatment process as it occurs in order to gauge the progress of treatment. The latter case in particular is of utmost importance as it enables important decision making to take place throughout treatment, such as whether to continue the same treatment of a soil, tailor the method, or interrupt the process altogether. Particularly when new methods such as biotreatments are used, continuous monitoring of the process enables both the ability to optimally treat a soil sample whilst developing the application of the treatment method per se.

Unfortunately, current methods for monitoring the remediation of soil are expensive and time-consuming. Currently, the only way to verify soil quality improvement is to examine samples in laboratory. As a result, only at discrete time intervals, over longer periods, are random samples collected and analyze. This may result in missing crucial timeframes to implement new action and as a consequence the cleansing process may be lengthened or retarded unnecessarily. In order for effective remediation to occur, there is a strong need to be able to continuously monitoring the remediation site in real-time as the soil is being cleaned. Such a tool would provide an effective means for improved analysis of the remediation process. In our approach we provide a number of non-intrusive sensors in a network configuration over a particular remediation site. A large quantity of data information is collected which reflect the content and concentration either of the actual pollutants or in some cases bi-products that may emerge as a consequence of the pollutants. Subtle changes in trends in the data are identified to provide early warnings. Techniques which can cope with noise, calibration and sensor fusion are also applied. The sensor technology we use to collect the physical measurements of the chemical compounds is electronic noses (tin dioxide sensing technology), which has been shown to work with the chemicals in question. The novelty of our work is the integration of these gas sensing devices in a sensing network in order to provide continuous readings of concentration levels at soil remediation site, *in situ*. Using state of the art data processing techniques, changes in patterns of the sensor signal could then be detected as soil is cleansed and processed. The continuous flow of information can then be used to chart and evaluate the effectiveness of the remediation techniques.

Synchrotron radiation techniques in environmental science and archaeology at MAX-lab-Present and future activities

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At MAX-lab, the Swedish synchrotron radiation facility, a variety of spectroscopic techniques such as X-ray crystallography and diffraction, infrared spectroscopy and spectromicroscopy, XPS, and XAS are available to both academic and industrial research communities. Collimated beam with high brilliance and broad energy tunability is what distinguishes the synchrotron radiation from conventional X-ray tubes. Synchrotron radiation techniques are often needed to provide information at molecular level about the chemical and biological processes that control the speciation and distribution of chemicals in the complex environmental systems. Some important research areas where synchrotron radiation methods are essential are speciation of contaminants in soil, aquatic systems, and atmospheric particles, and interaction of plant roots with soil particles, as well as interfaces between microorganisms or bio-film growing on mineral surfaces. Synchrotron radiation techniques have also been proven to contribute to studies of archaeological artefacts. Detailed chemical and structural information provides deeper information of the origin and technology behind archaeological artefacts. Furthermore, information on chemical speciation contributes to formulate more effective and scientifically based conservation methods.

The focus of the presentation will be on the synchrotron radiation techniques available at MAX-lab, as well as the techniques required for research in environmental science and archaeology at the next synchrotron radiation facility MAX IV.

Determination of Vx in the atmospheric air in form of the fluoridate derivate by the thermal desorption/gas chromatography with flame photometric detection

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Analytical procedures were developed for the indirect determination of low concentration of Vx in the atmospheric air by the thermal desorption/gas chromatography with flame photometric detection.

The following analysis scheme was implemented:

- Sampling of Vx in water absorbent using an absorber equipped with an inert fluoroplastic insert;
- Vx derivatization in the absorbent resulting the fluoridate derivate - isobutylmethylphosphonofluoridate;
- Extraction of the derivative from the absorbent by the liquid-liquid extraction method;
- Concentration of the derivative in nitrogen current;
- Detection of the derivative by the TD-GC-FPD method.

The detection limit for Vx in air according to this analysis scheme is 2×10^{-7} mg/m³.

The present research work was financially supported by ISTC and was carried out within the framework of the Project # 3320.

Sensing features of modified calixarenes and cyclodextrins layers in monitoring of toxic substances in the environment

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A great attention is now paid to the development of miniaturized, low-cost, robust, smart chemical sensing systems, which provide accurate and reliable online monitoring of the environment. One of the most important problem while elaborating of such systems (known as an “Electronic nose”) is the choice of appropriate sensitive materials for sensor coatings. This work deals with studying of sensitive properties of functionalised calixarenes and cyclodextrins films as sensor layers for detection of toxic volatile organic compounds.

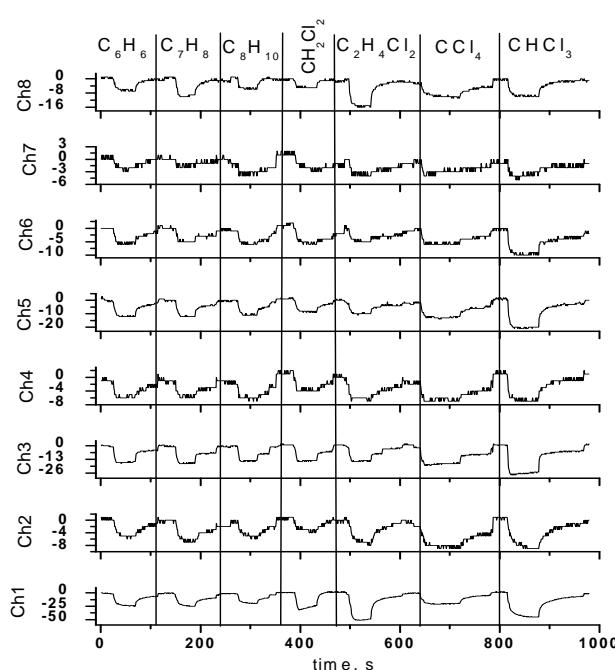


Fig. 1. Kinetic response of sensors (Ch1- Ch8) to injection of 1000 ppm analyte vapors into gas cell.

materials for a sensitive coatings to be applied for gas sensors/sensors arrays. Varying number of aryl and other specific fragments (thus modifying size and shape of the macrocycle cavity) and incorporating a different functional groups into the calixarenes’ upper and lower rims, it is possible to change sensitivity of sensor towards given analyte from virtually insensible to the possibility of registering a very small amount of analytes (less than 10 ppm).

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8-channel QCM sensory system designed in our laboratory has been used in the experiments. Detailed description of device and working mode can be found in our previous publications.

A range of toxic volatiles like benzene (C_6H_6), toluene (C_7H_8), n-xylene (C_8H_{10}) (aromatics), chloroform ($CHCl_3$), dichloroethane ($C_2H_4Cl_2$), dichloromethane (CH_2Cl_2), tetrachloromethane (CCl_4) have been tested as analytes. Kinetic response towards injection of 1000 ppm various analyte vapor is shown in Fig. 1.

Concentration dependences were re-calculated from the kinetic curves and represented good linearity through the all concentration range. Detection limits of every toxic volatile substance under study have been determined.

At the conclusion, it should be emphasized that functionalized calixarenes and cyclodextrins derivatives are the promising

Optical fibre detector for alcohols speciation

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The control of volatile organic compounds emissions in industrial facilities constitutes a very important tool to prevent exceeding safety levels and assuring an acceptable air quality. Although the effort to restrict the emission of these compounds, it is inevitable that vapours will escape into the air and work places with exposure risk by inhalation, ingestion or skin contact. Over-exposure to alcohols such as the isomeric butanols and pentanols causes irritation of eyes and mucous membranes, lacrimation, headache, nausea, dizziness and even central nervous system depression, thus it is of great interest that their airborne concentrations are kept to a minimum.

In the last few years a number of detection devices have been designed to monitoring indoor air quality and help to maintain safe levels of pollutants. In this area, optical fibre analysers have been gaining in popularity, since they show good durability, safe detection, remote and sensitive operation. They have been deployed with different detection systems such as reflection from polymeric films, fluorescence from dye coatings and surface plasmon resonance. An optical fibre polymer-coated detector was developed for a gas chromatograph for the speciation of alcoholic compounds that could be found in industry environments. The sensing principle of developed analytical system is based on the variation in optical signal from the fibre coated with (poly[methyl(3,3,3-trifluoropropyl)siloxane]) as the analyte molecules are adsorbed. The sensitized fibre was positioned in a glass tube which was connected to the gas chromatograph capillary column placed at the opposite end. A laser diode was used to produce the optical signal and a photodetector measured the changes in intensity of this signal in the visible region at 650 nm. The developed methodology was tested with standard solutions of nine alcohols (allyl, n-propyl, sec-butyl, isobutyl, n-butyl and isoamyl alcohol with methyl isobutyl carbinol, cyclohexanol and diacetone alcohol). The alcoholic compounds were well separated with retention times from 1102 to 1432 s, using the Carbowax 20M column with 0.5 µm film thickness, 30 m long and 0.32 mm internal diameter. General figures of merit, such as the analytical time (24 min), analytical error (which varies between 1.3×10^{-2} and 1.3×10^{-1} µg) and analytical performance of GC-OF were similar to those of the classical analytical methods, such as a gas chromatography-flame ionization detector (GC-FID), recommended by NIOSH in the method 1405 [1] for alcohols determination. The analytical methodology was used to analyze five air samples collected from a confined environment at a Portuguese solvent industry by adsorption on coconut shell charcoal. The levels of the nine alcohols were found to be below the recommended NIOSH limits, being the results obtained by the OF and the FID detector very similar. The developed method based on gas chromatography-optical fibre detector (GC-OF) constitutes a much less expensive alternative for the speciation of alcoholic compounds, with high accuracy and detection limits ranging from 0.67 µg for allyl to 0.89 µg for isobutyl alcohol, being most suitable for actual monitoring work on confined environments.

[1] Alcohols Combined: Method 1405, NIOSH Manual of Analytical Methods (NMAM), 4th ed. DHHS (NIOSH) Publication, 2003.

Development of a Laccase Based-Optical Fibre detector for phenolic compounds determination

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Phenolic compounds comprise a wide and diverse group of compounds of natural or anthropogenic origin. Some of these compounds may show toxicological effects as endocrine disrupting on organisms. Therefore, the monitoring of these compounds in environment and food is one of the largest challenges of Analytical Science. Many methods have been developed for the determination of phenolic compounds concentrations, most of these use Gas Chromatography-Mass Spectrometry (GC-MS) and High Performance Liquid Chromatography-Electrochemical Detector (HPLC-ED). However, in recent years optical fibre analyzers have demonstrated interesting properties such as small size, light weight, remote operation or capability of multiplexing, with successful applications in environmental, food and clinical analysis.

An analytical method based on High Performance Liquid Chromatography coupled to a Laccase based Optical Fiber detector (HPLC-OF-Lac), has been developed for separation and quantification of phenolic compounds, namely nonylphenol, bisphenol A and catecholamines such as dopamine, norepinephrine and epinephrine. The developed analytical device is constituted by a PLRP-S 100 Å 5 µm, 150 mm×4.6 mm i.d. reversed-phase column, used to separate phenols and connected to the OF-Lac detection component. This detection system is also constituted by a light source (laser diode) set at 1550 nm and a photodetector to measure the intensity of the modulated optical signal. The application of OF as a detector relies on the reflected optical power detected when the analytes eluted from the HPLC column act as the substrate of the enzyme (laccase) immobilized on a tip of a single-mode OF. The developed analytical system was tested with a standard solution of the five phenolic compounds tested, showing high linearity and stability of the analytical signal. A comparison with the results from an electrochemical detector (ED) revealed that the methods could not be statistically differentiated. The detection limits were of the same order of magnitude, although the OF-Lac ones were slightly lower than the ED values. For instance, those of nonylphenol and epinephrine were 2.9 and 3.5 pg/mL by optical fibre and 3.5 and 4.5 pg/mL by ED. The analytical error, measured as the residual standard deviation of both methods, varied between 1.7 and 2.8 pg/mL. The HPLC-OF-Lac compares much more favourably with HPLC-ED for the speciation of phenolic compounds, due to the lower cost of equipment and high miniaturization potential.

Determination of pentachlorophenol in marine environmental matrices by GC-MS

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Pentachlorophenol (PCP) is one of the most versatile pesticides used today. It is recognized as being destructive to all living cells, because of its multiple routes of action and wide effectiveness.

Due to 2000/60/CE Water Framework Directive and 2455/2001 European Decision about pollutants monitoring, a new fast and simple method is here presented for the determination of PCP in marine environmental matrices (water, sediment and mussel tissue).

PCP extraction by sea water has been carried out by SPE technique, then analysed by GC/MS.

From sediment PCP has been extracted with organic solvent (Ethanol) in an ultrasound bath. The extract is then filtered before injection to the Gas Chromatograph.

PCP from mussel tissue has been extracted by sonication with solvent (Ethanol), then cleaned up on a silica gel column, eluted with dichloromethane, and injected in a GC-MS.

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. 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 method. 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%.

Determination of dimethyl fumarate in desiccant and mouldproof agents

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DMF is a powerful fungicide employed for protecting clothes, footwear and accessories from humidity and mould, which has been found to act as an extreme sensitizer, causing severe acute reactions, and difficult to treat allergic eczemas, when come into contact with the skin of healthy individuals. First cases arose in 2006 from the use of sofas and chairs manufactured in China, and rapidly new cases related to the use of other consumer goods principally footwear were reported [1]. Sachets containing DMF are placed in origin inside clothes and couches, as well as inside shoeboxes, from which it spreads and impregnates the consumer product. A recent Decision adopted by the EU in March 2009 has banned the importation of contaminated products, and those products already on the market need recalling and withdrawing [2]. Hence, it is imperative the availability of rapid, simple and efficient analytical methods for DMF which could be immediately implemented in control laboratories at low cost. Up to now, and to the best of our knowledge, there is a lack of validated analytical methods for DMF in the international scientific literature.

A fast, simple, cheap, and high throughput method has been developed for the determination of DMF. The procedure is based on ultrasound assisted extraction (UAE) followed by GC - μ ECD analysis. The method was conveniently optimized, and the analyte was efficiently extracted from the samples in only 5 min using such a low volume of solvent as 1 mL. The method was validated in terms of linearity, precision, sensitivity and selectivity demonstrating its reliability. Limits of detection and quantification were in the ng g^{-1} level. The proposed procedure was applied to the determination of DMF in several desiccant and anti-mould samples obtained from footwear, footwear boxes, clothes and accessories. Although most of them were labelled as "silica gel", all the samples tested with the exception of three contained DMF, many of them at the high $\mu\text{g g}^{-1}$ level.

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Determination of fragrance allergens in baby bathwater by solid-phase microextraction

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Personal care products (PCPs) are complex formulations that contain a whole host of chemicals. The average baby daily hygiene products include artificial dyes and colours, fragrances, phthalates, preservatives, and harsh chemicals. Hence, the increasing use of unnecessary products in the name of hygiene could be doing children skin more harm than good. Some of these substances might also affect brain and nervous system at low doses, as it has been demonstrated in animal studies. A group of these hazardous chemicals included in most PCPs are the allergen fragrances, 26 of which have been identified to cause contact allergies [1,2].

A method based on solid-phase microextraction (SPME) and gas chromatography-mass spectrometry (GC-MS) has been optimized for the analysis of fragrance allergens in water samples, being the first study devoted to the SPME of this family of cosmetic ingredients. The influence of parameters such as fiber coating, temperature, salting-out effect, and sampling mode, on the extraction efficiency has been studied by means of a mix-level factorial design, which allowed the study of main effects as well as two factor interactions.

The final procedure was based on headspace sampling (HSSPME) at 100°C, using PDMS/DVB fibers. The method showed good linearity and precision for all compounds, with detection limits below ng mL⁻¹. Reliability was demonstrated through the evaluation of the recoveries in different real water samples. The absence of matrix effects allowed the use of external standard calibration to quantify the compounds in the samples. The application of the proposed procedure to the determination of the target allergens in several real samples demonstrated the presence of all the compounds, and, in some cases, at quite high concentrations. The presence and the levels of these chemicals in baby bathwaters should be a matter of concern.

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Development of a multi residue screening method for quantification of mycotoxins in natural waters

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Mycotoxins are naturally occurring metabolites of fungi growing on various agricultural crops in the field or during storage. Hundreds of these filamentous fungi species are known, including genera such as *Alternaria*, *Aspergillus*, *Claviceps*, *Fusarium* and *Penicillium*. Mycotoxins have been studied for decades due to their occurrence in food and feed and, hence, their potential threat to human and animal health. However, the aquatic environment is also exposed to mycotoxins. We quantified deoxynivalenol (DON) and zearalenone (ZON) in drainage water of a *Fusarium* infected wheat field in concentrations ranging from 20 to 5000 ng/L, and not detected to 35 ng/L, respectively [1, 2]. In rivers, we detected these compounds frequently (DON) and occasionally (ZON) [3]. A larger number of mycotoxins is likely to enter the aquatic environment via different pathways due to comparable or even higher amounts produced in wheat and maize [4], and similar or even higher aqueous solubility.

Therefore, we are currently establishing an analytical LC-MS/MS method to quantify 30 to 40 of the most prominent mycotoxins at trace level concentrations (i.e. ng/L) in aqueous samples. The detection of the samples is run in ESI +/- mode. This presentation will report on the analytical method development, where several commonly used SPE materials were tested, and present validation results.

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UPLC automatical method development versus conventional approach - optimization and development of analytical methodology for the determination of fluoroquinolone antibiotics

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Ultra performance liquid chromatography (UPLC) is nowadays new trend for the separation in analytical chemistry. UPLC offers the great advantages over conventional HPLC due to ultrahigh back pressures of up to 15 000 psi (100 MPa) and using the sub-2-μm particle sorbents yielding high separation efficiency.

UPLC method with tandem mass spectrometry detection (MS/MS) using conventional approach was developed for the determination of 5 fluoroquinolone antibiotics (FQs). The separation was performed on Acquity BEH C18 column using 0.1% formic acid and methanol as mobile phase in isocratic mode.

For comparison with conventional approach, an automatical development approach specially arranged for UPLC was used. This approach used changing 4 columns (Acquity BEH C18, Acquity BEH Phenyl, Acquity BEH Shield and Acquity HSS C18), two modifiers (acetonitrile or methanol) and two buffers pH 3 and pH 9 in gradient mode of elution. This automatical approach generates 14 different chromatograms in about 6 hours, including all variables (column, buffer, modifier).

The best results were achieved surprisingly to other studies published with Acquity BEH Phenyl analytical column with buffer pH 9 and methanol as modifier. Further optimization was performed. Based on the results of buffer pH 9 and pK_a values of analytes, ammonium acetate buffer at pH 10.5 was used. This approach gave better separation and peak shape as well. Thus the final conditions for separation of those 5 FQs were using ammonium acetate buffer at pH 10.5 and methanol as mobile phase in gradient mode. Analysis was accomplished in 4 minutes.

These findings are contrary to all published methods where the separation was usually performed at acidic pH of mobile phase using C₁₈ analytical column.

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UPLC-MS/MS method for the determination of tetracycline antibiotics in environmental waters

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The occurrence of antibiotics in environment has lead to the wide increase of antibiotic-resistant bacteria. After administration antibiotics are excreted via urine or faeces into municipal wastewaters very often in unchanged form. Wastewater treatment plants are not able to remove completely these hazardous compounds during treatment process. Therefore antibiotics are continuously released into the aquatic environment and can cause proliferation of resistant bacteria there. In consequence they can have an impact on public health. Hospitals are another very important source of contamination.

The goal of this study was to develop a new method for the determination of 6 tetracycline antibiotics (TCs) in wastewaters using ultrahigh performance liquid chromatography with tandem mass spectrometry detection (UHPLC-MS/MS) technology. Clean-up, solid phase extraction (SPE), UHPLC and MS/MS conditions were studied and optimized.

Our study involved 6 most important TCs: minocycline, doxycycline, oxytetracycline, tetracycline, chlortetracycline and demeclocycline. The chromatographic separation was performed on C18 column with 1.7 µm particle size using mobile phase composed of 0.05% formic acid and acetonitrile. The analysis was performed in gradient elution mode in 6 minutes. MS/MS detection was performed using a triple quadrupole analyzer with electrospray ionization in positive mode (ESI^+) and selected reaction mode (SRM) quantification.

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Identification of β -N-methylamino-L-alanine (BMAA) in marine samples

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The non-protein amino acid β -N-methyl-amino-L-alanine (BMAA) was originally isolated in 1967 from seeds of the cycad tree *Cycas micronesica* Hill (*Cycadaceae*) as a product of endophytic cyanobacteria of the genus *Nostoc*. Since then production of BMAA by other free-living taxa of cyanobacteria was reported. BMAA has been found to selectively kill motor neurons at a concentration 30 μ M by AMPA/kainate receptor activation. Neurotoxic effects of BMAA were studied in the context of neurodegenerative disease amyotrophic lateral sclerosis/parkinsonism dementia complex (ALS-PDC) among Chamorro people of Guam (Western Pacific) exposed to BMAA. Recently the interest in BMAA has grown with the evidence that BMAA is incorporated into proteins. This finding launched speculations about bioaccumulation in the food chain with global ecological and medical implications, since cyanobacterial blooms commonly contaminate water supplies as well as near-shore marine ecosystems. Based on this intriguing hypothesis, BMAA might be a causative agent for increasing morbidity of neurodegenerative diseases in some countries. However BMAA was reported in cyanobacteria, these findings have been questioned and hence have to be verified.

Precolumn derivatisation with fluorescent tag 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (ACQ) and reversed phase HPLC is frequently used for the identification of amino acids. The resulting derivatives (ureas) are highly stable and provide good chromatography with relatively clean chromatograms. Furthermore chemistry of ACQ is well understood and the interactions with cyanobacteria sample matrix have been reported in detail.

The sample work up consisted of acidic hydrolysis (6 M HCl, 24 h at 110°C) followed by cation-exchange SPE. The elution solvent after SPE was evaporated and a sample was redissolved in 0.5 M borate buffer applying conventional derivatisation protocol. The instrument was API 2000TM LC/MS/MS (Applied Biosystems, Foster City, CA, USA) consisting of a binary pump LC-10ADvp, autosampler SIL-10ADvp and benchtop triple quadrupole mass analyser API 2000. LC separation of BMAA and isomeric 2,4-diaminobutyric acid (DAB), also associated with neurotoxic effects and possibly presented in samples, was achieved within 10 min on C₁₈ analytical column (Hypersil Gold, Thermo Scientific, San Jose, CA). Doubly derivatised BMAA and DAB were detected as positive ions using their characteristic fragmentation pattern in selected reaction monitoring (SRM). Sensitivity 70 fmol/injection was achieved for BMAA and 700 fmol/injection for DAB. Difference in retention time together with unique SRM transition was used for identification of both amino acids in the cyanobacteria samples. The future work will be towards analysis of BMAA from marine organisms of dietary importance as well as samples from ALS-PDC animal disease models.

Novel LC-MS/MS for sensitive and selective identification of non-protein amino acids BMAA and DAB in complex sample matrix was developed.

Application of Taguchi method in the optimization of sample preparation for determination trace elements in human hair by flame and electrothermal atomic absorption spectrometry

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Today in developing countries like Iran heavy metals are present everywhere which threatens the health of the people. Necessity of control and determination of them in body, force the analytical chemists to find samples which could be analyzed easily to determine the concentrations of heavy metals in the body precisely. The analysis of human hair is useful in monitoring the levels of certain trace elements in the body and assessing heavy metals environmental exposure. Hair samples can be collected easily and the concentrations of most trace elements are higher in them than other clinical specimens. Unlike other clinical samples, hair is inert and chemically homogeneous, and provides information about a longer period. Sample preparation is the critical step of any analytical protocol, and involves steps from simple dilution to partial or total dissolution. In this study, methods for the pre-treatment and determination of cadmium, lead, nickel, copper, iron and zinc in human hair by flame and electrothermal atomic absorption spectrometry are developed.

The risk of sample contamination during the sampling and digestion was minimized. Prior to analysis, hair samples were washed with 1% (w/v) sodium diethyldithiocarbamate (DDTC). Hair samples were brought into solution by using a mixture of nitric acid and hydrogen peroxide. Taguchi method was employed for sample preparation optimization. Various parameters that influence the sample preparation, namely temperature, digestion time and ratio of acid mixture were studied and optimized. The optimized method has been employed to digest standard reference materials and hair samples of residents of Iran, collected from different age groups and sex. Human hair certified reference materials were used in order to verify the accuracy of the method and the results were in excellent agreement with the certified values.

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Vertical distribution of organic contaminants in air: the use of ultra-light motorized (ULM)

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Volatile organic compounds (VOCs), commonly emitted from both anthropogenic and biogenic sources (Hewitt, 1999 and references therein), are an important class of air pollutants because they are ubiquitous and associated with increased long-term health risks (Mitchell et al. 2000 and references therein). Considerable efforts have been addressed to monitor and regulate public exposure to these chemicals in both urban and rural areas (e.g., Christensen et al., 2000; Barletta et al., 2002; Lee et al., 2002; Moussa et al., 2006). Nevertheless, the distribution of organic air pollutants in the atmosphere is rarely investigated (e.g., Ohura et al., 2006). In the present study an ultra-light motorized (ULM) was used to collect air samples at different elevations above the ground in a highly urbanized and industrialized area in northern Italy. The ULM is to be considered particularly useful for this type of sampling, being able to fly at relatively low speed (110 km/h) and low elevation (from 30 to 300 m a.g.l.). The gas samples, stored into Cali-5-Bond air sampling bags equipped with a 0.75" diameter septum port and having a volume of 45 liters, were flushed through three phase (Carboxen B-Carboxen C-Carbosieve S111) absorbent tubes using a low-flux (200 cc/min) pump. VOCs trapped in the solid phase of the tubes were released at 350 °C in a thermal desorption system (Dani Master TD) and analyzed in the range of 40-400 a.m.u. (atomic mass unit) by GC-MS (Thermo Trace GC Ultra gas chromatograph coupled with a Thermo DSQ Quadrupole Mass Spectrometer). The results showed that most of the VOCs pertaining to the alkanes, aldehydes and alcohols groups, which were measured in significant amounts (up to 25 µg/m³) at ground level, were not detected at 200 m a.g.l. On the contrary, concentrations of aromatics, mainly C₇H₈, and halocarbons, i.e. CCl₄ and C₂HCl₃, were found to be almost independent on the sampling elevation, likely because of their high stability in the atmosphere.

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Quantitative determination of human pharmaceuticals in Baltic Sea blue mussels

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Pharmaceuticals from human and veterinary medicine are constantly dispersed into the environment, recently emerging as an issue of growing concern [1]. Very little is known of the effects of pharmaceutically active compounds, their metabolites or transformation products on non-target organisms in the environment. Pharmaceuticals are, however, deliberately designed to affect biochemical and physiological functions of humans and livestock and are for this purpose, also biologically persistent [2]. Undesirable effects on non-target organisms are therefore likely, especially in aquatic organisms which may be exposed during their entire life, e.g. from effluents from sewage treatment plants (STP) [1]

Baltic Sea blue mussels (*Mytilus edulis trossulus*) were exposed to three human pharmaceuticals as part of a long-term, sub-lethal, ecotoxicological study. The pharmaceuticals used were propranolol, diclofenac and ibuprofen. These pharmaceuticals are produced and sold in large quantities, have a widespread occurrence in the aquatic environment as well as reported to have adverse ecological or toxicological effects [1, 2]. The exposure study was performed at different concentrations, the lowest levels chosen according to natural occurrence in surface water and in STP effluents.

The exposure experiment was carried out for up to 21 days. The pharmaceuticals were administered both individually and as a mixture of two pharmaceuticals. The experiments were carried out in 1 L jars or in 10 L aquaria and conducted in climate rooms. Semi-static systems were used for water exchange. Physiological and behavioural effects as well as potential bioaccumulation was studied.

The physiological responses studied in the blue mussels were filtration rate, assimilation efficiency, respiration and excretion; all combined into a total energy budget, scope for growth (SFG) [e.g. 3], as well as byssus strength, byssus thread abundance and aggregation behaviour. The concentration of propranolol, ibuprofen, and diclofenac was analysed in the blue mussels using liquid chromatography coupled to mass spectrometry (LC-MS) and surface assisted laser desorption ionisation (SALDI) MS. Deuterated internal standards were used for quantification of the pharmaceuticals. The extracts from the mussels were subjected to solid phase extraction clean-up prior to the LC-MS analysis.

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Analysis of trace levels of melamine in foods

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In September 2008 media reported that some infant formula manufactured in China was contaminated with melamine (MEL; 1,3,5-triazine-2,4,6-triamine). Various recalls of Chinese products containing milk powder were prompted by more than 54 000 infants and young children seeking treatment for kidney stones in China. Six deaths have been attributed to consumption of the contaminated infant formula and related dairy products (1).

An analytical method incorporating simple liquid extraction followed by mixed mode cation exchange/reversed phase solid phase extraction, and electrospray positive ionization liquid chromatography-tandem mass spectrometry was developed and validated for the analysis of MEL in various foods. The method was adapted for the analysis of liquid and powdered infant formula, dairy products, soy-based dairy substitutes, egg and soy-containing products, fish, shrimp, and vegetables. Two different MEL stable isotope labelled internal standards are used to monitor analyte recoveries and to account for matrix effects. The method is sensitive (limit of quantitation of 4 ng/g for all matrices), accurate (average 96%), and precise (average CV 7%).

Lower concentrations of MEL could be detected by the liquid chromatography-tandem mass spectrometer but the low level of background contamination of MEL present in reagent blanks prevented confident quantitation below 4 ng/g.

Absolute recoveries of MEL were very dependant upon the matrix being analyzed. For example, average recoveries \pm standard deviation of MEL from two different samples of liquid infant formula fortified at 10 ng/g were $96 \pm 6\%$ and $61 \pm 15\%$. These matrix effects necessitated the use of internal standards.

The method was used to analyze a variety of food samples purchased from major retailers in Ottawa, Canada in order to examine Canadians' dietary exposure to MEL. MEL was detected in many of the food items, including infant formula (nd – 346 ng/g), soy-containing products (nd – 60.6 ng/g), vegetable products (nd – 757 ng/g), and fish products (nd – 1100 ng/g).

1. www.who.int/foodsafety/fs_management/infosan_events/en/index.html; accessed Dec. 31, 2008.

Development of on-line solid-phase extraction coupled to Ultra Performance liquid chromatography/tandem mass spectrometry for evaluation of pesticides in water samples: application example for determination of exposure levels in aquatic mesocosms

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An on-line solid-phase extraction coupled to Ultra Performance liquid chromatography/tandem mass spectrometry (SPE UPLC/MS/MS) assay using SPE column was developed and validated for direct analysis of water samples containing wide variety of pesticides.

The resulting analytical method couples the desired sensitivity (from 10 to 30 ng/L depending on compounds) with ease of use. The method was found to perform satisfactorily for direct water analysis with respect to assay linearity, specificity, sensitivity and accuracy.

This represents a fast, modern and reliable approach for monitoring pesticides over a wide range of polarity. This validated method has been also applied to ecotoxicological study.

A gradient LC condition was applied to separate 20 analytes with a run time for every injection of 15 min. Due to the ruggedness and simplicity of this system, methods can be easily developed and applied to analyze a wide variety of compounds in a high-throughput manner without laborious off-line sample preparation. An example of environmental application is also presented.

The impact of pesticides mixtures in different exposure scenarios is studied on outdoor artificial ponds (mesocosms) of 12 m³ for long-term ecotoxicological studies. In parallel with ecotoxicological measurements, pesticides concentrations are measured to determine exposure levels and the pesticide degradation kinetics. 15 mesocosms are controlled weekly during 18 months, that represent an important number of samples. The input of SPE on line UPLC/MS/MS allows the easy and fast obtaining of the results and by this way, the adjustment of exposure conditions if needed.

Trace residue analysis of Beta blockers and NSAIDs based on SPE with molecularly imprinted polymers (MIPs)

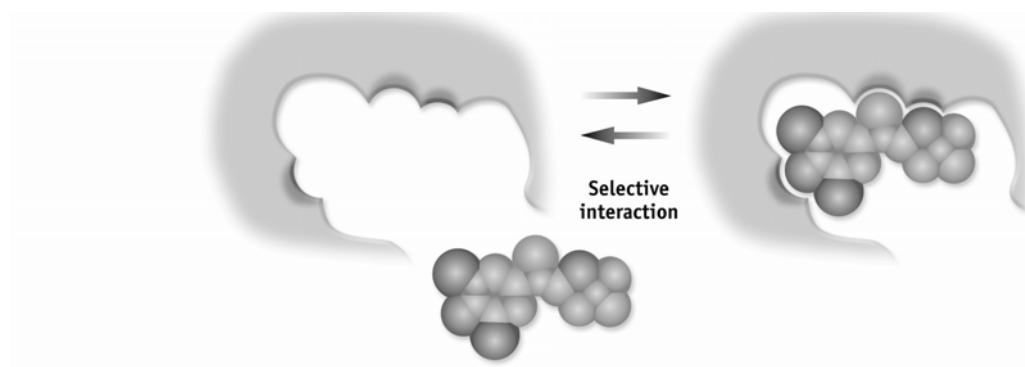
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Extraction of trace residues in sample pre-treatment is often elaborate and time-consuming. Solid-phase extraction phases based on molecularly imprinted polymers (SupelMIPs) obviate the need for multiple clean-up extraction steps, simplifying the pre-treatment procedure.

MIP sorbents contain cavities, complementary both in shape and chemical properties to desired target analytes. This makes it possible to selectively extract the analyte and to get rid of matrix components during the sample preparation. The strong binding of the analyte to the MIP makes it possible to develop robust SPE methods for these phases and the result of this is significant benefits towards reducing the matrix effects during LC-MS analysis, allowing lower detection limits to be achieved and reduced total sample handling times. In this work, two different MIP materials and SPE methods will be presented.

Trace analysis of non-steroidal anti-inflammatory drugs (NSAIDs) in environmental monitoring require reliable, sensitive and easy methods. A MIP phase selective to NSAIDs and SPE method has been developed and evaluated for extraction of Naproxen, Clofibric Acid, Diclofenac, and Ibuprofen from waste water samples. The methods give clean extracts with high recoveries and low ion suppression, facilitating very low detection limits, at ppt level.

In environmental monitoring, sensitive methods for determination of Beta antagonists (Beta blockers) are required. A class-selective MIP material was successfully developed to allow highly selective, simultaneous extraction of Beta blockers. The MIP sample clean-up when used with LC-MS/MS was a powerful combination for confirmatory methods of these veterinary drug residues.



Schematic representation of the function of Molecularly Imprinted Polymers

Advancing endocrine disrupting compound analysis through integrated technology and workflow solutions

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Endocrine disrupting compounds (EDCs) have become important emerging contaminants, due to their presence in environmental waters (following incomplete removal in wastewater treatment or point-source contaminations), threat to drinking water sources, and concern about possible estrogenic and other effects, both to wildlife and humans¹.

Compounds identified as EDCs include steroid hormones and are of special concern due to their potency. These contaminants do not need to be persistent in the environment to cause negative effects since their high transformation and removal rates can be compensated by their continuous introduction into environment. The prerequisite for risk assessment and monitoring is the ability to quantify these contaminants at sub-ppt levels. Flexibility, sensitivity and selectivity, especially for very complex environmental matrices are of paramount importance.

The list is continuously changing due to detection of new compounds and reclassification of emerging contaminants to, for example, POPs. Although emerging contaminants are not directly legislated, they are often candidates for regulation or, increasingly frequently, are self-regulated by the industry.

Innovations in tandem quadrupole mass spectrometry have allowed a rapid analysis of EDCs in environmental waters at ng/L levels to be set-up in an automated fashion. New software tools automate the set-up and creation of methods whilst providing real-time QC decision making on the data as acquisition occurs. During acquisition the unique Dual Scan MRM enables simultaneous matrix monitoring, helping reduce method development timescales and providing essential QC/QA during an analytical run. High performance quantification is complemented by the capability to perform long term studies of trends within results with the generation of electronic control (Shewhart) charts.

DNA-binding studies of doxorubicin in the presence of methylene blue by spectroscopy and voltammetry techniques

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Interaction between DNA and drug molecules is of current general interest and importance [1,2], especially for the designing of new DNA-targeted drugs and the screening of them in vitro. In this way, the interaction of small molecules with DNA is of great importance in many areas [3].

The development of new drugs requires that the underlying mechanism of the drug action at the cellular and molecular levels be better understood.

In this report we explored the interaction of doxorubicin with calf thymus DNA (ct-DNA), using UV-Vis spectrophotometry, differential pulse voltammetry and spectrofluorometry. The aim of this study is to find a relation between the antitumour properties of the drug and the mode of DNA binding. Methylene blue used as a probe for comparing in interaction by DNA. This will help us to design new drugs, which have biological and antitumour activities.

Both UV-Vis spectrophotometry and differential pulse voltammetry studies confirm the intercalation mechanism. The results showed that both doxorubicin and MB molecules could intercalate into the double helix of DNA. The apparent binding constant of doxorubicin with DNA have been found to be $3.2 \times 10^4 \text{ M}^{-1}$. The fluorescence signal of doxorubicin and methylene blue was quenched with DNA addition. The Stern-Volmer equation was plotted base on quenching fluorescence signal of doxorubicin.

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Optimisation of matrix solid phase dispersion for determination of organophosphates ester in fish samples

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The performance of matrix solid phase dispersion (MSPD) for the extraction of several organophosphate esters (mainly employed as flame retardants and plasticizers) from different kind of fish tissue was described. The suitability of different solid supports was tested as well as the effect on the extraction efficiency of the natural fat content in samples. Extraction and clean-up were carried out in a single step and target compounds were determined by gas chromatography (GC) with nitrogen–phosphorus detection (NPD). The main parameters affecting extraction yield and selectivity, such as type of dispersant material, clean-up co-sorbent, rinse and extraction solvent, were evaluated and optimised. Under final conditions, 0.5g of fish tissue were dispersed with 1 g anhydrous sodium sulphate and 2g of Florisil, and loaded on the top of polypropylene cartridge containing 1g of Alumina. The dispersed sample was washed with 5mL of n-hexane dichloromethane 1:1 to remove the least polar interferences and fat content in sample, the target analytes were eluted with 10mL of hexane acetone 6:4. Recoveries of the proposed method for spiked ranged from 78 to 110%, and the day-to-day variability remained between 1 and 9%.

Chemistry in conservation, archaeology and art

Poster abstracts

Art P1-P3

Role of Polymer Composites in Architectural Conservation : Case Study of Shaniwar Wada Pune, India.

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Pune is the second largest city of Maharashtra state of India which posses a rich legacy of historic buildings with outstanding craftsmanship and architecture quality. They form an impressive historical features and heritage of this historic city and need to conserve and preserve because they provide a sense of identity and continuity in a fast changing world for future generations. It has been realized that many historic structures are slowly deteriorating under centuries of exposure to atmospheric condition.

Such kind of deterioration often accelerated by the gaseous and particulate pollutants so common in today's urban environment has led to the development of many novel techniques of preservation. Among those techniques is the application of synthetic organic monomer and polymers for the purpose of repairing consolidating and protecting the stone structures. Many polymers epoxies, silicanes, fluorocarbons, and poly- methyl methacrylate can be used. The monomers penetrate deeply in to the internal surface pores adhere to form a coat, and then polymerize into a tough polymer film with low permeability to water and corrosive gases. In this process water and gas permeability depends on both the solubility and the diffusivity of the penetrating the polymer material. A large number of Polymers are available which can be effectively used in the conservation of historic stone buildings. Such materials must be selected with due consideration to the various parameters with reference to chemical properties of the material, environmental factors and architectural features in the present context.

Present paper is focused on evaluating the use of polymer composites in architectural conservation of stone buildings in Pune, India. It will analyze the effect of different polymers like Isophthalic polyester, bisphenol, A-based polyester, chlorine bearing polyester and vinyl ester resins with reference to their resistant to a wide variety of harsh environment conditions which prevails in Pune by and large. Based on case study of "Shaniwar Wada" it will examine the suitability of this material in the conservation of this historic heritage building belonging to the great Maratha period

Key words: Polymer, synthetic organic monomer, epoxy resin, pollutants, stone consolidation

Bird droppings on outdoor copper and bronze: only an aesthetical damage?

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Bird droppings are often regarded as an agent of decay for outdoor materials and public money are spent annually cleaning up bird excrements from pavements, buildings and statues. The aesthetic and, sometime, the functional damage (i.e. blockage of roof gutters) they can cause on monuments and buildings is undoubtedly evident, but the extent of the chemical damage they are able to induce to the underlying materials is not so clear. So far, there are mixed opinions about the importance of bird droppings in damaging cultural heritage and relatively little research has been done on this topic. Bird droppings are composed mostly of uric acid, a compound sparingly soluble in water and able to coordinate as a bidentate ligand with many divalent transition metals, including copper. The aim of this research is, therefore, to investigate the potential for bird droppings to affect copper and copper alloys, which make such an important contribution to architectural elements of buildings and outdoor sculpture. Laboratory tests have been carried out to assess visual change, erosion and secondary compound formation from uric acid and the presence of real bird droppings in contact with copper. In addition, some observations stains from bird droppings on outdoor copper and bronze statues real cases have been considered. Laboratory tests and analyses on exposed samples show that uric acid chemically affects copper and bronzes, by modifying the metal appearance and forming urates; the corrosive action of uric acid increases when it remains wet. In general, the results of this work suggest that uric acid in bird droppings could cause appreciable damage to copper used in buildings and monuments. Moreover, the role of water in enhancing corrosion by bird droppings seems of particular significance in management, suggesting that cleaning might be particularly appropriate if conditions are likely to remain wet.

Reference:

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Analysis of trace elements in archaeological bones for diet reconstruction

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Archaeological human remains are important witnesses of human life, telling us many details about past populations. As an example, the bones are actually bio-archives, which store information about the lifestyles of the individuals, the place where they lived, the migration habits. In particular, some peculiar trace elements can be considered indicators of the so-called paleodiet, i.e. whether characterized by vegetables, cereals or meat.

An analytical method for the determination of trace elements in bones by quadrupole inductively coupled plasma mass spectrometry (ICP-QMS) was set up. The optimization was carried out on the standard NIST SRM 1486 Bone Meal, dissolved by microwave assisted acid digestion. The methodology was then applied on the buried individuals found in the Neolithic necropolis of St. Giorgio Valdaro (Mantova, Northern Italy), dating back to 3000 b.C.. Unusually for the period, two of them were buried together in a neverending hug, as to be called "the Valdaro's Lovers". Results of ICP-QMS analyses of bones from the site were interpreted by chemometric techniques. The purpose of the study was twofold: to determine trace elements relevant for the definition of the paleodiet and to evaluate the intra-population dietary variability. The preliminary hypotheses are illustrated.

Atmospheric Chemistry

Poster abstracts

Atm P1-P18

Time-resolved measurements of water-soluble micro and trace elements in ambient air particulate matter

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Time-resolved concentration measurements of atmospheric pollutants are a powerful tool for carrying out any detailed study about the dependence of the measured concentration on emission fluxes, deposition processes and meteorological conditions^[1]. Up to now, only a very few studies have been addressed to time-resolved measurements of chemical species in atmospheric particulate matter (PM), mainly because of the high costs of the sampling activities and the very small dimensions of the collected samples.

In this work we optimized and validated a quantitative multi-elemental analytical method able to determine the water-soluble elemental content of PM in 2-hour samples (As, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Sb, Sn, Sr, V). The method, suitable for analyzing conventional low-volume samples collected at 2.3 m³/h on Teflon membrane filters, was applied to a ten-day monitoring campaign carried out in Rome. During the campaign the main meteorological parameters were acquired, including natural radioactivity for the evaluation of the dilution properties of the lower atmosphere^[1].

The temporal profiles of the elemental concentrations allowed us to highlight some interesting correlations among tracers of specific emission sources. A perfect agreement between the temporal profiles of Na and Mg concentrations ($R^2 = 0.99$) was observed during the whole monitoring campaign, confirming the reliability of soluble Mg as a tracer of sea-salt events. Two sea-salt transport events were clearly identified^[2]. Some trace elements of mainly anthropogenic origin (Tl, V, Pb and Zn) showed very different temporal profiles during the two sea-spray events, according to the different back-trajectories of the air masses (Hysplit model). Other relevant information concerned the temporal profiles of some tracers of traffic-related road dust resuspension (Cu, Sb, Mn, Fe, Zn)^[3]. The time pattern of their contribution to PM was compared with the traffic flow and with the mixing properties of the lower atmosphere (estimated by monitoring natural radioactivity). During atmospheric stability days, these elements showed high correlation ($R^2 > 0.9$) and concentration peaks in the evening and in the early morning, when the traffic flow is high and the atmospheric mixing is weak. During the night (weak mixing and low traffic flow) a concentration decrease was observed, probably due to particle dry deposition. A decrease of the measured concentrations was observed also during the warm hours, when traffic emission is diluted by an efficient mixing of the atmosphere.

These examples indicate the potential of time-resolved analytical results for identifying the high number of processes that are responsible for PM time and space variations and for evaluating the relevance of their specific contributions.

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Optimizing aerosol dynamics parametrisations for regional scale chemical transport modeling

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Modeling aerosol dynamics is a multifaceted problem involving microphysical processes that cause high computational demands if solved in detail. The challenge of simplifying these processes in order to make them efficient enough to work in large scale atmospheric models was issued by Kokkola et al. 2008, by developing the Sectional Aerosol Module for Large Scale Applications, SALSA. It was further investigated by implementation of SALSA in the climate model ECHAM5 (Kokkola et al. 2009).

This work, started in SALSA, identified simplifications that are valid for climate modeling but less suitable for regional chemical transport modeling, and advanced it to work within the Multiscale Atmospheric Transport and Chemistry Model, MATCH (Robertson et al. 1999). The extensive chemistry routine of MATCH presently includes 110 thermal, 28 photochemical and 2 aqueous phase reactions.

The MATCH-SALSA system presently works with primary emitted OC, BC, dust and seasalt. The nucleation, condensation and coagulation are optimized by neglecting the processes between, and within, size bins where they are inefficient. Sulfuric acid is so far the only condensing species but the aim is to include HNO₃, NH₃ and secondary organics.

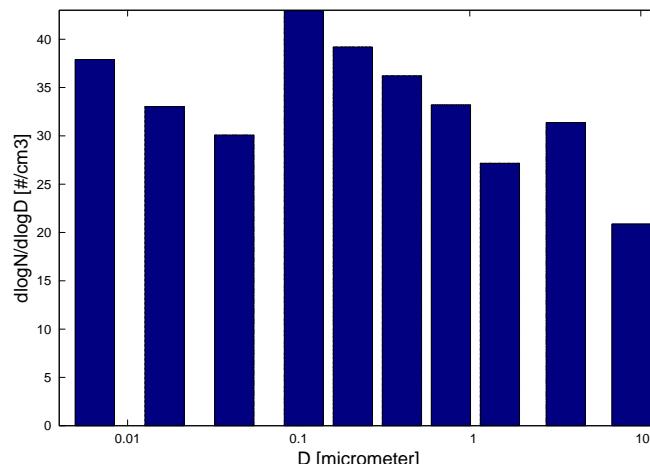


Figure: Preliminary modelled size distribution of the aerosol number concentration. Melpitz, Germany, July 2006.

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Atmospheric concentrations of polyfluorinated alcohols, sulfonamides and sulfonamidoethanols at Station North (north-east Greenland)

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Atmospheric transport of volatile “precursor” compounds is considered to be one of the pathways of transport of perfluorinated compounds (PFCs) to the Arctic environment (Prevedouros et al., 2006). Volatile precursors include the fluorotelomer alcohols (FTOHs) which have been shown to degrade to PFCAs (Ellis et al., 2004) and the perfluorinated sulfonamido alcohols (FOSEs) which have been shown to degrade to perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs) (D'eon et al., 2006). The presence of volatile precursors in the Arctic atmosphere has been confirmed by several measuring campaigns in the Canadian Arctic and the North Atlantic region (Shoeib et al., 2006; Stock et al., 2007).

In the present study we have measured the atmospheric concentrations of FTOHs, FOSEs and FOSAs at Station North, North East Greenland ($81^{\circ}36'$ North; $16^{\circ}40'$ West). Weekly samples have been collected since January 2008. A total volume of approximately $4,500\text{ m}^3$ air is collected on a quartz filter and a PUF/XAD/PUF sandwich. Samples have been extracted and analyzed following the procedure described in Dreyer et al. (2008).

Preliminary results show the presence of 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, N-Me-FOSA, N-Et-FOSA, Me-FOSE and Et-FOSE. 8:2 FTOH is the compound generally found at highest concentrations.

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The metastable liquid state of acidic ambient aerosols in eastern US

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One of the major findings during the Pittsburgh Air Quality Study was the association between the liquid state of the aerosol at low relative humidity (RH) and acidity. The existence of this water could explain the missing mass and has policy and health relevant implications (Solomon et al., 2008). In Pittsburgh, aerosol water content was highest during summer periods when aerosol was often acidic and its composition was dominated by sulfates. The particles appeared to contain water during low RH periods when they were acidic. On the contrary, the aerosol was neutral during the winter and it appeared to be practically dry during low RH periods (Khlystov et al., 2005).

Starting from these observations, we test in this study the hypothesis that the acidity determines the state of ambient aerosol during low RH periods. We investigate the morphology of individual aerosol particles by Scanning Electron Microscopy (SEM) methods in Pittsburgh Air Quality Study samples from both summer and winter periods. Two different shape parameters were automatically measured for more than 30,000 particles together with the corresponding particle elemental composition. High Resolution SEM was also used to confirm the results obtained by the automatic SEM.

Both shape parameters were statistically different for periods when aerosol was acidic and when it was neutral (independently of the season). Lower values for the shape parameters in acidic periods were linked to high sulfur contents and sizes below 500 nm. Acidic aerosol samples had lower shape parameter values because they mainly contained partially coalesced droplets with irregular shapes and partially or totally recrystallized elongated rectangular particles (characteristic from ammonium sulfate or ammonium bisulfate). These results support the hypothesis that acidic atmospheric particles maintain some water even after they are deposited on a filter and are exposed to even lower relative humidity. In addition, SEM evaluation of the filters after some time suggested that part of the acidic aerosols may maintain this partial liquid state after long periods of time (Coz et al., 2008).

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A contribution of microbial substances to cloud formation or precipitation in the atmosphere

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Clouds are the main cooling contribution to climate, yet still the one containing the largest uncertainties. Reducing these uncertainties requires a better understanding of the factors controlling the nucleation of atmospheric aerosols into cloud droplets. A possible role of Life on Earth in these processes has been investigated for decades. In particular, airborne microorganisms have been found to be efficient ice nuclei,¹ but their direct contribution to liquid clouds is less clear because of their large size ($> 1 \mu\text{m}$) and small concentrations in the atmosphere.

This presentation reports recent works investigating the role of substances released by microorganisms that are common at the Earth's surface (continents and oceans), rather than the organisms themselves. The results show that

- 1) these microbial substances have a better cloud-forming efficiency than any aerosol material studied so far, including inorganic salts, as shown by their Köhler curves,
- 2) such substances were present in aerosol samples from four different origins (coastal, marine, temperate forest, tropical forest),
- 3) they were present in these aerosols at concentrations large enough to dramatically lower their surface tension and induce their nucleation into cloud droplets before any other type of particles, including inorganic salt ones.

Thus, microorganisms at the Earth surface could play a role in cloud formation or precipitation (the latter by controlling the cloud droplet size distribution). These effects might explain the correlations between algae bloom and cloud cover reported in the Southern Ocean.² The presence of these substances in all the samples studied also implies that they are common in aerosols and of global relevance, which is supported by the recent identification of organic fractions of better cloud-forming efficiency than ammonium sulfate in aerosols from biogenic origin.³

More generally, these results open new perspectives in the understanding of the Earth's system by identifying a new link between the biosphere, atmospheric processes, the hydrological cycle, and climate. Depending on the responses of microbial populations to climate change, they might also lead to the identification of new climate feedbacks.

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Characterisation of soot in air and precipitation over Southern Asia

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The atmospheric life cycle of soot (light absorbing particulate matter) has been studied over the Indian subcontinent and over the Indian Ocean. This was performed through an integrated analysis of its atmospheric abundance, morphology, transport and deposition at three stations situated in Nepal, India and the Maldives.

The concentration of soot in the air was measured by light absorption using a PSAP (Particle Soot Absorption Photometer) instrument equipped with a dedicated sensor to correct for the scattering part of the light attenuation. The determination of soot in precipitation was based on filtration with polycarbonate membrane filters followed by optical detection with a soot photometer. Morphology and elemental analysis of individual soot aerosol particles used electron microscope techniques. This provided size resolved information on their three dimensional geometry, mixing state, and surface structure.

The temporal distribution of soot in air and precipitation on Maldives showed a distinct seasonal pattern dominated by the Indian monsoon circulation: The dry winter monsoon (November - April), with air influenced by anthropogenic activities such as combustion over the Indian subcontinent, the wet summer monsoon (June – September) strongly influenced by natural marine sources from the Indian Ocean. The analysis of electron microscope images showed a transformation in hydroscopicity of the fresh hydrophobic soot particles emitted over the Indian subcontinent arriving at receptor station, on Maldives, remotely located in the Indian Ocean and served as an explanation for the seasonal similarities in both air and precipitation. When wash out ratios of soot were calculated in parallel with other aerosol constituents they were closely aligned with non sea salt sulphate, although slightly lower.

This presentation will provide an overview of the field program, describing the deployment and shortcomings in using optical determination of soot, and summarizing the observations obtained. The emphasis will be on the atmospheric measurements and possible transformation processes between the source and receptor areas will be discussed.

The case of Spolana Neratovice – Past, present and future problems

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Oral only

The Spolana Neratovice factory is in this time probably the most known source of POPs contamination in the Czech Republic. The chemical factory of Spolana Neratovice is situated approximately 25 km north of Prague at the Elbe River. It produced in the period of 1965-68 the chlorine herbicide 2,4,5-T and chlorinated phenols. A part of 2,4,5-T was even exported to the USA and was applied as the component of "Agent Orange" within the Vietnam war. During the production due to breaking technological conditions, a huge amount of dioxins (in particular, the most toxic 2,3,7,8-TCDD) was formed and former factory buildings containing products, intermediates, installations, etc. belong currently to the one of most POPs-contaminated sites on the globe (mainly by organochlorine pesticides). Moreover, soil in the factory is highly contaminated with produced there, as well. The 2,4,5-T and chlorophenols production was stopped in 1968 when about 80 cases of occupational diseases developed (55 workers were hospitalized mainly with severe chloracne manifestations and porphyria). The production was stopped in 1968 and former producing buildings were closed, but unfortunately did not decontaminated or destroyed up to date.

The Spolana factory including some of the dioxin-contaminated buildings was flooded in 2002 and one can expect dioxin release into agricultural fields and Elbe River and its sediment.

The decontamination and remediation of site started after very complicated procedure at 2005 with using of base catalysed dechlorination non-combustion technology. These processes consist from the decontamination and demolition of 3 buildings, excavation and treatment of surrounding soils of these buildings, treatment of chemicals stored closed to main building, dissemble and treatment of the process unit and backfill and final restoration.

The main requirements for the process of decontamination and remediation were the treatment of contaminated waste in site, final destruction of toxic waste, use of non incineration technology, use of proven technology, protection of environment, safety and health for population. All these steps were monitored by the sampling and analytical methods which respect the international standard and procedures including application of passive samplers as a part of MONET-CZ (Czech national POPs monitoring in ambient air) operated by the RECETOX.

The remediation of this part of Spolana Neratovice was finished in autumn 2008. During the final risk assessment was determined that there this site is still a big potential source of contamination of Elbe river by OCPs and organohalogenated hydrocarbons. Final decontamination of this area is still a big challenge.

**Atmospheric chemistry of a model biodiesel fuel,
 $\text{CH}_3\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3$: Kinetics, mechanisms and products
of Cl atom and OH radical initiated oxidation**

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Relative rate techniques were used to study the kinetics of the reactions of Cl atoms and OH radicals with ethylene glycol diacetate, $\text{CH}_3\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3$, in 700 Torr of N_2/O_2 diluent at 296 K. The rate constants measured were $k(\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3) = (5.7 \pm 1.1) \times 10^{-12}$ and $k(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3) = (2.36 \pm 0.34) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Product studies of the Cl atom initiated oxidation of ethylene glycol diacetate *in the absence of NO* in 700 Torr of O_2/N_2 diluent at 296 K show the primary products to be $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{CH}_2\text{OC}(\text{O})\text{CH}_3$, $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H}$ and $\text{CH}_3\text{C}(\text{O})\text{OH}$. Product studies of the Cl atom initiated oxidation of ethylene glycol diacetate *in the presence of NO* in 700 Torr of O_2/N_2 diluent at 296 K show the primary products to be $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H}$ and $\text{CH}_3\text{C}(\text{O})\text{OH}$. The $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{O}\cdot$ radical is formed during the Cl atom initiated oxidation of ethylene glycol diacetate and two loss mechanisms were identified, reaction with O_2 to give $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H}$ and α -ester rearrangement to give $\text{CH}_3\text{C}(\text{O})\text{OH}$ and $\text{HC}(\text{O})$ radicals. The reaction of $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{O}_2\cdot$ with NO gives chemically activated $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{O}\cdot$ radicals which are more likely to undergo decomposition via the α -ester rearrangement than $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{O}\cdot$ radicals produced in the peroxy radical self-reaction.

Climate change impact of selected 2nd generation CFC replacements

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Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere has led to an international effort to replace these compounds with environmentally acceptable alternatives. One central issue is to develop CFC alternatives with low global warming potentials (GWPs). There are several strategies to increase reactivity towards OH radicals and thereby decrease the atmospheric lifetime and GWP. Two classes of new CFC alternatives are unsaturated fluorinated hydrocarbons and hydrofluoroethers (HFEs). HFEs are compounds which have been developed to replace CFCs in applications such as the cleaning of electronic equipment, heat transfer agents, and carrier fluids for lubricant deposition. Smog chamber/FTIR techniques were used to study the atmospheric chemistry of 2-ethoxy-3,3,4,4,5-pentafluorotetrahydro-2,5-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-furan, which we refer to as RfOC₂H₅. The atmospheric chemistry of this compound is determined by the reactivity of the ethoxy group. Prior to its large-scale industrial use an assessment of the atmospheric chemistry, and hence environmental impact, of RfOC₂H₅ is needed. To address this need the atmospheric chemistry of RfOC₂H₅ was investigated. The atmospheric chemistry of several fluorinated propenes was investigated and the following parameters were determined: kinetics of their reactions with chlorine atoms and hydroxyl radicals, atmospheric lifetimes, atmospheric oxidation mechanisms and degradation products, and global warming potentials (GWPs).

Light duty vehicle non-CO₂ emissions: Assessing the climate forcing

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Global warming is an important issue facing society and all sectors of the economy, including the automotive industry. Society's assessment of global warming may change in the future as the science develops, but the present risk is clear. The climate appears to be changing, the changes appear to be outside natural variation, and the likely consequences will be serious. This talk will provide an assessment of current and future non-CO₂ emissions (HCs, CO, NOx, PM, R-134a, N₂O, and CH₄) from light duty vehicles. Vehicle miles traveled are expected to approximately double by 2050. However, the absolute magnitude of emissions of 'criteria' pollutants (HCs, CO, NOx, PM) is projected to decline substantially (by a factor of approximately 5-10) over the same period. Implications for the light duty vehicle contribution to non-CO₂ climate forcing will be discussed.

Single particle chemical composition and state of mixing of aged Saharan dust

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The Saharan Mineral Dust Experiment (SAMUM) is focussed to the understanding of the radiative effects of mineral dust. The winter campaign of Saharan Mineral Dust Experiment II in 2008 was based in Praia, Island of Santiago, Cape Verde. It was dedicated to the investigation of transported Saharan Mineral Dust. For this work, samples were collected ground-based with a miniature impactor system, a sedimentation trap, and a free-wing impactor. The size-resolved chemical composition was determined by scanning electron microscopy and energy-dispersive X-ray microanalysis of single particles.

The boundary layer aerosol consists of a superposition of mineral dust, marine aerosol and ammonium sulfate, soot, and other sulfates as well as mixtures of these components. During low-dust periods, the aerosol is dominated by sea salt. During dust events, mineral dust dominates the particle mass (more than 90 %). Particles smaller 500 nm in diameter always show a significant abundance of ammonium sulfate.

A more detailed analysis (Fig. 1) shows, that at Praia exists an external mixture of dust, sea-salt and sulfates concurrently with an internal mixture of those. During dust-events, large particles are mainly mineral dust with small amounts of sulfate, some sea-salt particles and a small amount of dust/sea-salt mixtures. The small particles show a broad distribution of dust-sulfate mixtures. In low-dust conditions, the (fewer) large particles are still mixtures of dust and sulfate, but nearly no dust/sea-salt mixtures occur. Sea-salt particles exist in an aged state. The small particles are mixtures of dust and sulfate with a high amount of sulfate-dominated particles. The sulfur content of super-micron aerosol particles scales with the particle surface, indicating the presence of sulfate coatings.

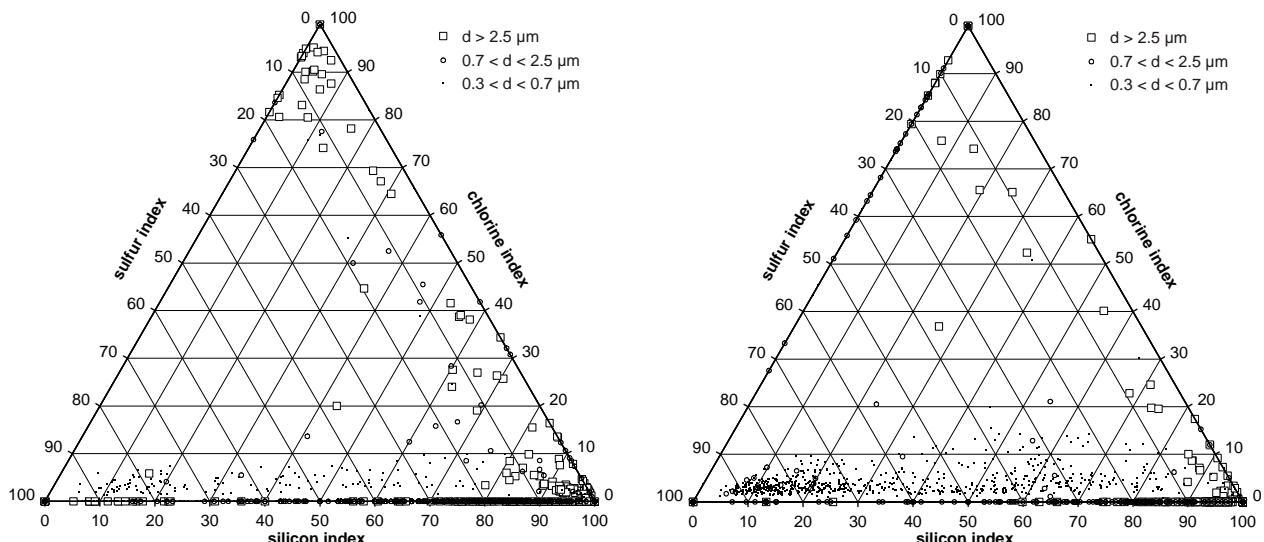


Fig. 1: Ternary diagrams of Si, Cl and S indices* for particles dominated by these elements ($[Si+Cl+S]$ index > 0.5) for a dust period (left) and a low-dust period (right)

*index value: ratio of the atomic element content of the particular element to all elements found in the particle with $Z > 8$

Origin and characteristics of fine particulate matter and its exceedance in Berlin (Germany)

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Long-term sampling with full chemical analysis of PM₁₀ is very spare in literature. In many cities urban pollution is focussed on PM and the discussion is ongoing what the local contribution versus transportation is for establishing city control measures. Under this aspect we have carried out a one-year measurements in Berlin (6 stations including one tower station) and surrounding (2 sites). Main ionic species, many metals, OC and EC have been analysed for daily samples. The stations design did allow characterizing the background and different urban pollution levels. Between the rural and urban background only a PM difference of about 2 µg m⁻³ (or 10% of PM) and between urban background an heavy traffic street a PM difference of about 12 µg m⁻³ (or 50% of PM) have been found. This difference remains constant independent from air masses, season and meteorological conditions. 90% of the street contribution is by resuspension, thus not to be influenced by air pollution control measures. Periods of exceeded PM are almost all connected with long-range transportation from SE direction where. Relative chemical composition of PM in pollution episodes is similar to the rural background (ammonium, sulphate and nitrate) showing that only transport characteristics are responsible for up-concentration of PM due to chemical processing and missing deposition. At all, urban control is very limited to direct emitted soot only.

Modeling spatial and temporal variations of tropospheric data in Lake Como area (Italy) during the period 1992-2007 using principal component analysis and multi-way analysis

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It is well established nowadays that there exists a significant human impact on the environment. In particular, the troposphere is the region of the Earth's atmosphere in which we live and into which chemical compounds are generally emitted as a result of human activities. The study and the monitoring of its composition are major scientific issues in today's atmospheric research.

The development of observational data sets is very important as they provide the background present knowledge of an investigated area, but they also will form the basic source of information for the future. However, the usability of the information hidden in the data could be limited as these data sets are often huge. Suitable methods of data treatment should be used to rationalize the information.

In this work, multivariate data analysis methods were employed in the modeling of NO, NO₂, NO_x, SO₂ e O₃ data in the troposphere of Lake Como district (Lombardy, northern Italy) from 1992 to 2007. Three sampling station were considered, two of them located in industrialized areas and the third located in a rural area.

In particular, Principal Component Analysis and multi-way methods such as PARAFAC and Tucker3 were employed with the aim of modeling the spatial and temporal variations of the investigated analytes in the considered area.

Pro et contra of the use of multidimensional data treatment methods againts classical bidimensional ones will be discussed, and the results of the modeling will be shown.

Intercomparison of elementary carbon from source samples of carbonaceous aerosols using the BGI 505-44, the VDI 2465 and the NIOSH 5040 methods

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In this intercomparison, source samples of carbonaceous aerosols were analyzed with three different methods. BGI 505-44 and NIOSH 5040 are used for occupational exposure of diesel exhaust particulates. VDI 2465 and also NIOSH 5040 are used for ambient environmental measurements. For some samples measurements with a Micro Soot Sensor was also performed. The objective was to compare measurements of elementary carbon (EC) and organic carbon (OC). Filters were divided in four quarters to ensure identical sample conditions.

Samples of different particle sizes were produced from a test aerosol generator (Combustion Aerosol Standard, CAST). The content of EC is lower for the smaller sizes, but rises with increasing particle size. Pyrolysis of carbon could be observed in the 20 and 33 nm CAST samples with the NIOSH method, but not for larger sizes, 80 113 and 120 nm.

Standard diesel engine exhaust shows a good match of EC for all methods. For non-road engines operating with diesel/5% biodiesel, EC was higher with the BGI method compared to the NIOSH method. Samples from engines using oils and fats from vegetable and animal sources, as well natural gas, showed very little EC. The highest values were for the BGI method, lower for VDI and lowest for the NIOSH method, but the total content of carbon correlated well between the methods. This is because some OC chars and new, pyrolytically formed EC (PC) is created for in the analysis. The VDI-method corrects for this to some extent using an additional extraction step before thermal desorption, and the NIOSH method corrects for PC optically.

When marine diesel exhaust (containing 2% sulphur) was analyzed, the VDI method showed less EC compared to the BGI method. If the automatic split procedure of the NIOSH method was applied for the marine diesel samples, the results show even less EC than compared to the VDI method. These EC-results are also in accordance with simultaneous results obtained by the AVL Smoke Meter 415.

However, if the split between OC and EC is changed to match an unusually sharp drop early in the thermogram of the samples, the NIOSH results compare more to the BGI method. One possible explanation for this sharp drop is that deposited sulphuric acid (from the fuel) on the filters increase the charring of OC early in the desorption step of the NIOSH method and consequently give a negative bias of the EC-values. Another possibility could be that the filters were high in moisture, because water changes the light transmission of the filter but quickly evaporates in the analysis as the temperature rises.

Xenoestrogenic compounds in the atmosphere of Thessaloniki, northern Greece

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The aim of this study was to investigate the occurrence of endocrine disrupting compounds in atmosphere in the area of Thessaloniki, Northern Greece. Target compounds are alkylphenols and phthalate esters. These compounds have widespread use in industrial processes and commercial products and enter atmosphere through emissions during their production, volatilization from the products, emissions from wastewaters, from combustion sources and uncontrolled burning of wastes and water-air exchange [1-6].

The study was conducted at two sites in the major area of Thessaloniki, an urban-traffic site (AS) and an urban-industrial site (EK). 24-h PM10 samples were collected for two months using low-volume air samplers. The target compounds were recovered from particulate matter by extraction with dichloromethane in ultrasonic bath. Extracts were further clean up through a silica gel column. Alkylphenols, after derivatization, and phthalates were determined by employing GC-MS.

The alkylphenols NP, tOP, NP1EO and the phthalates DEHP, DBP, BBP were detected in particulate matter (Fig. 1). DEHP and NP were the predominant compounds. The occurrence of alkylphenols in wastewater, surface water and seawater has been previously reported in the study area [6]. Similar concentrations of NP determined at both sites, whereas higher concentrations of DEHP were found in the urban-traffic site. Generally, the studied compounds are within the ranges reported in literature [1-5]. Possible relationships of target compounds with other parameters such as total and water soluble organic fraction, ions, toxic elements and wind direction are discussed.

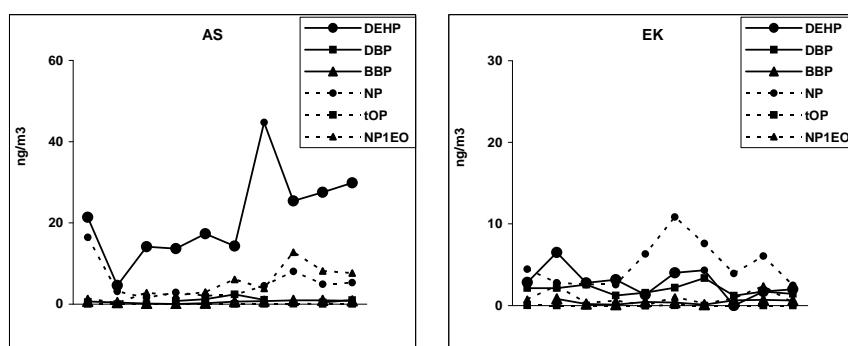


Fig. 1. Concentrations of xenoestrogens in PM10.

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Studies of wet and dust-fall deposition fluxes in Pune region, India

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Wet and dust-fall deposition samples were collected in the Pune (city) region at four locations, representing different surroundings, namely, Swargate (Traffic Junction), Bhosari (Industrial), Pashan (Semi-urban) and Sinhagad (High Altitude-rural) during the period from June 2006 to May 2007. It is found that rainwater at all the locations was alkaline with a volume-weighted mean pH of 6.73, 6.24, 5.90, and 5.83 respectively. Surprisingly the rain water was more alkaline at traffic junction and at industrial sites than those at semi-urban and high altitude sites. Sulphate ion was the main acidic constituent at Bhosari, whereas NO_3^- was dominant at Swargate. Neutralization to these acidic components at both the locations was mainly from Ca^{2+} . Chemical constituents measured in rain water at Sinhagad showed comparatively low concentrations. At Sinhagad also, the major neutralizing component was Ca^{2+} and it was not as effective in neutralizing the acidic components as at the other three locations, due to its comparatively low concentration. Source apportionment for different chemical constituents is carried out using principal component analytical technique.

The wet and dust-fall deposition fluxes ($\text{g/m}^2/\text{y}$) were estimated for all the major ionic components. It is observed that the wet deposition fluxes of all the ionic components were higher than the dust-fall deposition fluxes at two locations i.e., Pashan and Sinhagad. Whereas, at Bhosari, the dust-fall deposition fluxes of all the ionic components, except sea salt (Cl and Na) and NH_4 were higher compared to wet deposition fluxes. At Swargate, a traffic junction, the dust-fall deposition fluxes of NO_3 , Ca and K were higher than those of wet deposition fluxes. This indicates that the air pollution levels are higher at industrial and traffic locations.

Treatment of non-ideality in the air parcel model SPACCIM

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A cloud is a multiphase system comprising a gaseous phase, a particulate phase, and an aqueous phase. The interaction between aerosols and water vapor plays a large role in determining their effect on the environment. To assess the role of cloud chemistry at a local scale, interactions between gases, cloud droplets and aerosol particles have to be taken into account in numerical cloud chemistry models [1,2]. The detailed dynamic modeling of multi-component aerosol particles is complex by a variety of factors, together with a complex set of ionic and non-ionic species produced in the system, complex thermodynamics, and simultaneous phase as well as reaction equilibria. In multi-component systems phase transfer processes take place, which can influence the particle and droplet formation as well as particle growth. In the modeling of such multiphase processes it is necessary to consider non-ideal conditions for deliquescent particles. For a physically correct analysis (and prediction) of the effect of fine, dispersed phase drops or particles on the mass transfer rate in multiphase systems, it was demonstrated, heterogeneous mass transfer models should be used.

Furthermore, the phase interactions strongly depend on the phase surface area. Therefore, a highly resolved drop spectrum should be considered for an appropriate description. For this purpose the air parcel model SPACCIM (Spectral Aerosol Cloud Chemistry Interaction Model) will be used for the description of cloud processes which combines a complex multiphase chemistry with detailed microphysics [3]. The extension, accounts for dissolution, diffusion, and chemical reactions in multi-component aerosol particles, to provide a parameterization for the heterogeneous uptake under non-ideal conditions. The non-ideal behaviour can be described by activity coefficients. The influence of activity coefficients on multi phase chemistry will be calculated using the activity coefficient models (LIFAC, UNIFAC, and Pitzer model) to investigate the deviations from ideality. For the determination of activity coefficients, an extended version of UNIFAC [4, 5] coupled with the Pitzer method [6] is implemented in SPACCIM. For the model studies, a complex multiphase reaction scheme extracted from CAPRAM (Chemical Aqueous Phase RADical Mechanism) [7] is applied. The results of the effects of non-ideality on multiphase chemistry considering deliquescent particles will be shown for a test scenario with cloud cycles, to compare the in cloud chemistry with the chemistry of cloud droplets

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Micro-Raman imaging of nitrate formation on mineral dust

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Mineral dust is known to act as a reactive surface in the global atmosphere [1]. Mineral dust is typically composed of various oxides and carbonates that can react with gaseous species to form complex aerosols [2]. Such reactive uptakes on the surface of mineral dust during their atmospheric residence time can significantly alter their optical properties and affect their ability to act as cloud condensation nuclei. In situ observation of the atmospheric processing of mineral dust can be performed by confocal Raman microspectrometry. The technique is a powerful tool to determine the distribution of molecular species within individual micrometer-sized particles [3]. Raman mappings of particles can be obtained using computer-controlled XY scanning and Z focusing of the laser probe to automatically acquire hundreds of Raman spectra. The combined use of automated mapping with relevant data treatment (Multivariate Curve Resolution) allows resolving spectra of mixtures into pure compound spectra in order to obtain reconstructed molecular images [4].

In this study, laboratory experiments were conducted to simulate heterogeneous reaction on mineral particles by atmospheric processing. In particular, we investigated surface reactions of nitrogen species and mineral particles under controlled humidity by using Raman imaging. Pure compounds (calcite, quartz, gypsum, alkali feldspar) and certified dust samples (AC Fine Test Dust) were exposed to NO₂ trace gas (~140 ppm) with varying relative humidity (10-60% RH). Synthetic mineral dust was found exhibiting core-shell structures after 10 min exposure to NO₂. Formation of nitrate salts on the surface of mineral dust was clearly evidenced. For instance, local nitrate formation onto Na-feldspar particles was observed. As Raman spectroscopy is suitable to probe liquid or solid particles, unique information about the physical state as well as the mixing state of mineral particles could be obtained.

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Inorganic Environmental Chemistry

Poster abstracts

Ino P1-P42

Strategy for treatment of historic sulphidic mine waste – experiences from the Ljusnarsberg Mine Field, Sweden

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Bergslagen in south central Sweden is an old mining area, covering some 60,000 km². Altered felsic metavolcanic rocks, often associated with crystalline carbonate, host metallic mineral deposits that are about 1.9 Ga in age. Mining for copper in this region started already in the 13th century and for iron in the 14th century. Remains from the historic mine operations are some 500 deposits, and traces from early rational mining can be seen at more than 3000 places. Copper-zinc-lead and iron deposits predominate in the northern part of the region, and zinc-lead sedimentary deposits, with less copper and iron, in the south

Oxidation of sulphidic ore residues and mine waste creates an acidic metal-laden leachate water (acid mine drainage, AMD), and the large amounts of waste in the region have the potential to result in leachate generation over long periods of time. The oxidation is driven by the oxygen from the air in open deposits but also, in the absence of air, by ferric iron present as hydroxides/oxides deposited on site. Thus, oxidative weathering will continue in deposits containing historic sulphidic ore residues even under unaerobic conditions – a cover that prevents air intrusion is not sufficient.

A strategy for reduction or prevention of the release and spreading of metals (Cu, Zn, Cd and Pb; occasionally As) is suggested and tested in pilot-scale at the Ljusnarsberg mine field. Mining was in operation on this site from the early 17th century until late 19th century. The field tests include studies of

(1) Reactive additives - infiltration systems for control of the weathering of sulphides; injection or infiltration of materials that buffer pH to levels above 10 and the redox potential to low levels

(2) Geologic barriers - reactive mineral components in sequence; increase of pH and precipitation of iron, lowering of the redox potential and addition of metal scavenging materials that adsorb remaining metals in the leachates

Alkaline waste materials are used as reactive additives and as components in the barrier systems: Lime mud (LM) as well as green liquor dregs (GLD) from pulp and paper industry, lime kiln dust (LKD) from liming industry, fly-ash from incineration plants, residues from the Linz-Donawitz process (LD-stone) from the industry; brick and granulated illitic clay (Leca), granulated peat etc. Tests that have been running for 1-2 years (cubic meter scale) indicate substantial reductions in weathering rates in the infiltration systems, as well as in metal mobilities through the reactive barriers. Preliminary performance assessments based on the results from the pilot tests indicate that long-term control of metal releases from historic sulphidic mine waste is feasible.

Leaching of metals from contaminated soil with polyhydroxicarboxylic acids of natural origin

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The effect of addition of complexing agents, generated from natural products, on the release and redistribution of metals from contaminated soil has been studied. Water soluble humic substances (fulvic acids, FA) generated by leaching of high-molecular weight humic matter (peat) at high pH, and isosaccharinic acid (ISA), generated by degradation of wood (saw-dust) at high pH was used and compared with some synthetic complexing agents representing naturally occurring products: Citric acid (CA), ethylenediamine disuccinic acid (EDDS) and methylglycine diacetic acid (MGDA).

Four contaminated soils with elevated levels of particularly As, Cr, Cu, Ni and Pb at maximum levels of 1.5, 1.2, 1.7, 0.14 and 3.8 g/kg, respectively (two from shooting-ranges, one from a steel-works site and one from a wood impregnation site) were leached with alkaline solutions (pH 12) containing peat degradation products (1.2 g/l TOC; some 90 % FAs) and wood degradation products (0.7 g/l TOC, some 50-60 % ISA), as well as solutions of CA, EDDS and MGDA (0.25 mM, pH 6-8). Metal releases were analysed after various leaching times: 24 h, 1 week, 5 weeks. Results are related to the total content of metals in the soil (XRF-analysis), total leachable fractions (sequential leaching according to Tessier) and leaching with nitric acid (pH 3).

A release of some 10 % of the lead inventory and up to 50 % of the copper in one of the soils could be achieved in the FA and ISA leaching systems, while the synthesised agents EDDS and MGDA led to releases of some 60-90 %. The effects of FA and ISA were generally significantly lower than those of the other complexing agents for As, Cr, and Ni, but significantly higher for V (present at the level 40 mg/kg). Thus, a significant enhancement of the release of particularly copper and lead from the contaminated soils by leaching with alkaline (pH 12) leachates of wood and/or peat appears to be feasible.

Remediation of soils and sludges containing organic contaminants as well as metals – soil-wash procedures combining biodegradation, chemical complexation and mechanical separation of particulate matter

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Soil contamination is an urgent issue world wide. More than 83,000 contaminated sites have been identified in Sweden alone, of which approximately some 4,000 require treatment in the near future. Most of the sites carry a mixture of contaminants, metals as well as persistent organics. Most soil remediation efforts are made *ex situ*, which means that the soil or sludge is dug up and transported to a facility for treatment, or simply for deposition. The aim of the present project is to design a strategy for *ex situ* treatment of soils with mixed contaminants. A variety of soils and sludges from different sites (around 10), essentially all with organic as well as inorganic (metallic) contaminants, have been selected for experimental studies in laboratory and pilot scale: Military sites (metals, explosives), wood preservation sites (PAHs, As, metals), industrial sites (metals, hydrocarbons, mercury, dioxins and others). Of particular importance in the present study are:

Metals – Pb, Cu, Zn, Cr, Hg, as well as As
Organics – PAHs, nitro aromatics, dioxins

A number of processes are selected and applied:

- Biodegradation - use of commercially available cultures, as well as bacteria cultivated from the contaminated site itself
- Mobilisation of organics - use of surface active agents
- Mobilisation of metals - use of (1) complexing microbial metabolites produced in the soil (by fungii in particular), (2) complexing agents generated by degradation of natural organic products (polyhydroxy carboxylic acids), and (3) artificial complexing agents (polyamino carboxylic acids).

Biodegradation is performed in batches (anaerobic in most cases), while release and mobilisation of contaminants from soil aggregates are achieved during soil-wash performed in a dynamic system where wash solution is forced through the soil under high pressure (the WTC-process). The efficiency of biodegradation and subsequent soil-wash under various conditions is evaluated from chemical analysis, but also by several ecotoxicological tests. Some results are given that illustrates suitable strategies for treatment of mixed contaminated soil from real sites (soil) as well as for treatment of residues from industrial production (sludges etc).

Mobilisation of mercury from polluted soil by leaching

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Leaching tests were performed on mercury contaminated soils from two different chlor-alkali industry sites (80 and 180 mg/kg, respectively) using nitric acid (pH 1-4) with additions of mercury complexing anions: Chloride (0.01 – 1 M) or iodide (0.01 – 1 M). Less than 1% of the mercury inventory could be extracted at pH 1 after one week in nitric acid alone. Leaching with chloride enhanced the release to some 20% of the inventory, while iodide (0.1 M I⁻, pH 1) led to a release of up to 90%.

A parallel extraction procedure for characterisation of the chemical state of the mercury in the contaminated soils was designed with the following arbitrary defined species:

- Volatile: Heating, 70 °C for 5 days and recovery of gases in 0.5 M HNO₃
- Exchangeable: Extraction with 1 M NaClO₄
- Secondary precipitates: Extraction with 0.1 M HNO₃
- Organic associations: Extraction with 0.05 M HNO₃ and 15 % H₂O₂
- Humic complexes: Extraction with 0.1 M NaOH
- Sulphides and consolidated organics: Digestion in Aqua Regia

Extracts from each step was analysed with respect to TOC, total mercury (CVAAS), macro elements (ICP-AES), and organomercurials (GC-AED).

The speciation scheme was compared with a standard sequential extraction procedures (Tessier). The mercury was highly immobile in both soils and largely associated with organic matter of low solubility (at least 60 %) or existed as HgS of low solubility. The leaching results, as well as the response to the parallel extraction fractionation, reflect the chemical behaviour of mercury that differs from other heavy metals in many respects. The enhanced release in the presence of iodide is due to a combined redox and complexation process. Leaching at low pH and with addition of iodide can be the basis for a full-scale remediation process.

Evaluation of heavy metals pollution loadings in the sediments of the Ave river basin (Portugal)

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Heavy metal concentrations in the particulate form are several orders of magnitude higher than in the dissolved form. Because of their large adsorption capabilities, fine-grained sediments represent a major repository for heavy metals and record the temporal changes in contamination of the overlaying water column. Heavy metals accumulated in this way may be subsequently released to the overlaying water column as a result of physico-chemical disturbance, and the sediments may persist as a source of pollutants after the cessation of direct discharges.

The Ave river basin is located in the North of Portugal in a very populated region of the country. River water is intensively used for agricultural and industrial purposes.

The main aims of this study were: (i) to determine the total contents of heavy metals in surface sediments, (ii) to evaluate the distribution of heavy metals binding phases in the sediments where high metal pollution loadings were verified and (iii) to explore the physicochemical factors that govern metal speciation in these sediments, using multivariate analysis, in order to predict if metal remobilisation would be expected.

Sediment samples were collected and Cr, Cu, Fe, Mn, Pb and Zn total concentrations were determined in the fractions <63µm. Metal speciation was also applied to sediments, where high metal pollution loadings were verified, using the original BCR (Community Bureau of Reference) protocol. Some physico-chemical parameters were also quantified in water samples collected in the water column just above the sediments.

Metal contamination factors (CF) determined in the sediments evidenced a moderate contamination by Cr (CF between 3 and 11). For Zn, a slightly pollution was observed, with CF values not higher than 4. For Cu and Pb, sediments analysed did not show such enrichment in the whole studied region.

The pattern that emerged from distribution of Cr binding phases in the sediments evidenced that association of Cr decreased in the following order: residual > organics/sulphides > reducible oxides > exchangeable, acid water soluble. In addition, significant amounts of Cr were associated with strongly (oxidable and residual) bound fractions (> 85%). These results suggest that changes in physical or chemical properties (e.g. pH, Eh) of the river water should not be accompanied by a significative Cr remobilisation from the sediments.

The relationships between Cr speciation fractions, physico-chemical parameters of the sediments and water samples were studied by Principal Component Analysis, and allowed to reduce the dimensionality of the data matrix from 14 to 3 significant components accounting for 89% of the variance. It was found that hydrous Fe/Mn oxides and organic matter were the “carriers” of Cr associated to fractions exchangeable and oxidable.

Synthesis and characterization of mesoporous SnO₂/SiO₂/c-graphite composite

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Mesoporous materials have shown high potential for applications in areas related to catalysis, sorption and separation processes. In recent years there has been an increase interest in the mesostructured material field, where the control and reproducibility of the synthesis methods are very important. Pechini method has been widely used in the synthesis of oxides for several applications [1,2]. This procedure consists of the preparation of a polymeric resin by reacting ethylene glycol with citric acid, in which the metal ions are dissolved. Among the advantages obtained are the uniform distribution and low grain size of the particles. In this work, the synthesis, characterization and potential application of SnO₂/SiO₂/C-graphite composite are presented. The XRD pattern of the composite, Fig. 1, implies the crystallization of SnO₂, the major peak at about 26.6° is due to cassiterite structure, but the intensity also indicates the contribution of graphite crystalline phase. SnO₂/SiO₂/C-graphite is composed of 27 % of SnO₂ (determined by X-ray fluorescence spectrometry), 19 % of carbon (by elemental analysis) and 61 % of SiO₂ (by the difference). The BET-specific surface area of the composite was 222 m²g⁻¹ and a mean pore diameter of 10.6 nm.

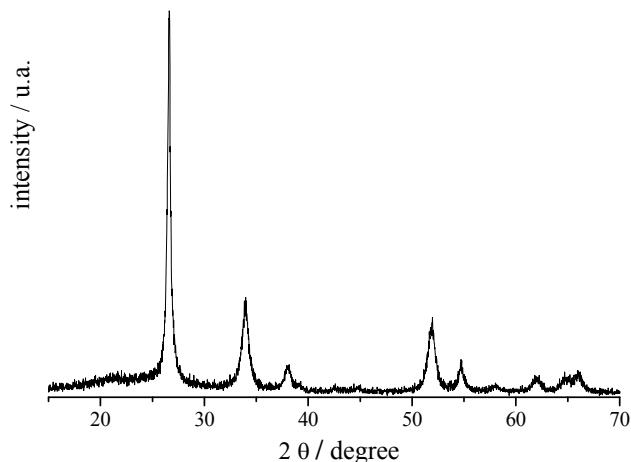


Fig.1. XRD patterns of synthesized SnO₂/SiO₂/C-graphite composite

EDS analysis reveals that Sn and Si follow the same distribution profile indicating an uniform dispersion on the surface of the composite. Electrochemical measurements are performed by using finely divided powder of SiO₂/SnO₂/C-graphite pressed in a format disk as working electrode. The surface of the electrode (5 mm in diameter) was successfully employed to adsorbed electroactive ferrocenecarboxylic acid.

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Possible artefacts in determining the metal speciation in sediment pore waters using a thermodynamic equilibrium model: the role of organic matter

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The role of sediments as a potential sink or source of metallic and organic contaminants is not yet fully understood. It is however well known that dissolved organic matter plays a key role in the speciation and partition of trace metals in aquatic environments, in this way influencing the mobility and the biodisponibility of these contaminants. Indeed, dissolved organic matter, mainly fulvic and humic acids, presents a wide range of chemical functions (hydroxyl, carboxylic or phenolic acids groups...) which may complex efficiently trace metals. The modelling of trace metals – organic matter interactions is difficult because the heterogeneity of humic substances and the competition for binding sites between trace metals and other ions have to be taken into account.

Several models can be applied for the modelling of organic matter in thermodynamic speciation calculations. The Visual Minteq software (version 2.40b) includes the NICA-Donnan model and the Stockholm Humic Model (SHM). The SHM employs a discrete-site approach while the NICA-Donnan model supposes a bimodal and continuous distribution of organic matter binding sites.

This study is part of the European research project INTERREG III – STARDUST which aims at elucidating the fate of sedimentary metallic contaminants in transborder rivers of France and Belgium. Three sediment cores were collected in the Spiere, Lys and Scheldt canals, which drain a highly populated and industrialized area. Pore waters were analysed for the determination of dissolved trace metals (cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc), anions, cations, sulphides and dissolved organic carbon concentrations.

First, association of trace metals to the carboxylic or phenolic groups of the dissolved organic matter appeared to be strongly influenced by the pH, as a result of their respective values of equilibrium constant (pK_a close to 4 and 10).

Second, we have investigated the influence of the organic matter modelling on the speciation of trace metals between the free, inorganic and organic species. NICA-Donnan and SHM models predicted similar species distributions for manganese but significant differences were noticed in the case of iron and zinc. Indeed, the fraction of iron bound to fulvic and humic acids was more important in the case of the NICA-Donnan model. At the opposite, the complexation to organic ligands for zinc and, to a lower extent for cadmium, cobalt and nickel, was larger when using the SHM. No differences could be noticed for copper, lead and manganese. Overall, a reasonably good agreement was reached between the SHM and NICA-Donnan models, except for iron and to a lower extent for zinc.

In conclusion, there is a need for an experimental determination of speciation in sediment porewaters and for a better characterization of natural organic matter, especially of its complexing capacity and its evolution with depth.

Two flotation methods for preconcentration of manganese from fresh and surface waters before AAS determination

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A methods for manganese determination in natural waters by two new flotation procedures performed by cobalt(III) heptyldithiocarbamate, $\text{Co}(\text{HpDTC})_3$, and chromium(III) pentamethylenedithiocarbamate, $\text{Cr}(\text{PMDTC})_3$, are presented. The optimization of the most important experimental parameters for both methods is given. Zeeman electrothermal atomic absorption spectrometry (ZETAAS) is used as an instrumental technique for manganese measurement. Natural fresh water samples, as well as surface water samples, were collected and analyzed by the proposed method. Flame atomic absorption spectrometry was applied for some of the river water samples. The proposed flotation procedures were verified by the standard addition method. ZETAAS limit of detection for manganese using $\text{Co}(\text{HpDTC})_3$ as collector is 0.05 µg/L, while by $\text{Cr}(\text{PMDTC})_3$ is 0.10 µg/L.

Sol-gel synthesis of Au/TiO₂ nanoparticale photocatalysts toward visible photodegradation for water and wastewater treatment

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Environmental pollution is the area of concern and there is need to pay more attention on it. It is estimated that 1–15% of the dye is lost during dyeing processes and is released in wastewaters [1]. AR27 is one of the most widely used dyes in textile industries. Among the heterogenous photocatalysis by using semiconductors, TiO₂ because of its high photocatalytic efficiency, non-toxic properties and more stability in UV light and water is being widely used as a relatively new technique of pollution abatement; however, the need of an ultraviolet excitation source restricts its technological utility for limited applications. For extending applications toward the industrial usage, it should be activated with visible radiation or solar light. TiO₂ absorbs only 3-5% energy of the solar spectrum [2]. In this sense, doping with noble metals could make a double effect: Firstly, it could reduce the band gap energy, thus shifting the absorption band to visible region. Secondly, metals could provoke a decrease in electron-hole recombination rate, acting as electron traps.

Tetraisopropyl orthotitanate (Ti(OC₃H₇)₄) and Tetrachloroauric (III) acid (HAuCl₄.3H₂O) were used as a source of TiO₂ and gold, respectively. A certain amount of Ti-isopropoxide was taken and added to an appropriate amount of methanol and refluxed at 70 °C for 3 h, while refluxing an exact molar ratio of bi-distilled water added to this solution drop wisely [3]. Two different methods were applied for reducing gold solution; 1) Photodeposition method: The known concentration of gold solution was directly added to the recent solution. Afterwards, this mixture was irradiated under UV-C (30 W) for 2 h. 2) Chemical reduction by NaBH₄ solution: The NaBH₄ solution was drop wisely added to the same concentration of gold [4] that applied for first method. Reduced solution was mixed with TiO₂ sol follow by. Both of the two prepared sols were dried at 70 °C and calcined in 550 °C for 10 h. All of photocatalysts were characterized by XRD, FTIR, SEM-EDS and UV-Vis spectrophotometer.

The XRD analysis results confirmed that Au doped TiO₂ which is reduced by NaBH₄ solution has a little difference with pure TiO₂ in peaks width at 2θ=25.2° (anatase region) which indicated that Au did not interfere in TiO₂ structure and keeps it in anatase phase. Crystal's diameters in anatase form obtained from Scherrer's equation and XRD patterns were 14 nm for both of Au/TiO₂ (reduced by NaBH₄) and pure TiO₂, and 12 nm for Au/TiO₂ that was reduced by photodeposition method. According to the FTIR results, wide and broad absorption peaks at about 576 cm⁻¹ and 3323 cm⁻¹ correspond to Ti-O-Ti and O-H surface vibration bands, respectively. Another absorption peak at about 1623 cm⁻¹ related to H-O-H stretching vibration bands. Results show that Au doped TiO₂ is more efficient than pure TiO₂ at photocatalytic degradation of AR27 in the presence of UV and visible light irradiations. Au content has a desired value of 1.82 and 2.12 wt% for achieving high photocatalytic activity by chemical reduction and photodeposition method respectively.

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Recent progress in structure determination of metal hydrides

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During the last years hydrogen has become a more and more popular candidate as fuel for motor vehicles because of its harmless combustion product, water, in comparison to fossil fuels e.g. natural gas and petroleum. Unfortunately the ways of storing hydrogen are limited. Today's storing methods are basically limited to high pressure tanks and liquid storage, both encountering significant drawbacks. In the case of high pressure hydrogen, the containers have to be made of a high durability material; hence these containers will be very heavy and high pressure combustible gas always involves a risk e.g. at a collision. Liquid hydrogen on the other hand has the advantage of higher energy density, but with its boiling point 20.3 K it is unreasonably expensive to store it, as well as there will be a loss over time, hence a new method is desired.

Metal hydrides have been known since 1808 when Humphry Davy discovered that elemental hydrogen was absorbed by sodium to form a new compound. Since then much research has been conducted in the field of metal hydrides and the ability of transition metals to absorb large amounts of hydrogen was reported by Graham in 1866, using palladium. The advantage of storing hydrogen as hydride is the high energy density, this arises from that the H₂-molecule is split and chemically bonded to a metal alloy or –ion. The challenge is to find a hydride which absorbs hydrogen at elevated H₂ pressure and releases hydrogen when the pressure is decreased. The hydrides tend to adopt a number of different very interesting structures; ionic, covalent, interstitial and as intermetallic hydrido complexes.

As a line in my research I am investigating these different structure types and evaluating trends in the formation of these arrangements. This poster will present some of the cutting edge research at Stockholm University; example of the structure types, structures found as well as the techniques and work behind the elucidation of these structures.

Lichens as bio-indicators of atmospheric heavy metal pollution in South Africa

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I prefer an **oral** presentation

There are numerous anthropogenic sources of heavy metal pollutants in South Africa, including those related to the mining, chemical and transport industries. A portion of the emitted metals is usually associated with dust particles, and may therefore have impacts on air quality as well as on human health in affected areas.

The potential use of available lichens in the city of Pretoria was therefore investigated as a cost effective means of evaluating relative ambient concentrations of heavy metals, particularly manganese and lead arising from vehicular emissions.

Lichen samples were collected from trees in the central business district as well as at three sites to the east of Pretoria, namely the CSIR campus, the National Botanical Gardens, and in the suburb of Lynnwood. Samples were analysed by atomic absorption spectroscopy after microwave assisted acid digestion.

There was no significant difference between the Mn content of lichens from all the sampling sites (overall average of $97.1 \pm 39.1 \mu\text{g.g}^{-1}$, $n = 28$). This was probably due to the current dominance of natural sources of Mn in the soils of the region to atmospheric levels, thus contributions from vehicular emissions (arising from manganese anti-knock fuel additives) were not evident.

The Pb concentrations in lichens growing in the CBD were higher than the corresponding Mn concentrations and the Pb levels were also significantly higher (95 % confidence limits) than those growing outside of the CBD ($181.1 \pm 98.0 \mu\text{g.g}^{-1}$, $n = 10$ as compared to $41.5 \pm 36.4 \mu\text{g.g}^{-1}$, $n = 18$). Of the non-CBD sites, higher Pb levels were recorded at sampling sites nearer busy roads. Historical impacts as a result of leaded fuel usage were therefore evident.

Continuous-flow copper biosorption in regenerable *Ascophyllum nodosum* seaweed

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The conventional methods for treatment of industrial effluents containing toxic metals have found their application limited due to the high operation costs. The biosorption process offers lower operating costs and in addition to high efficiency in treatment of diluted effluents. These advantages serve as primary incentives for developing full-scale biosorption processes to cleanup metal-loaded waters and wastewaters. The practical application of metal biosorption is carried out in packed column operation mainly for economical reasons.

Regeneration of the sorbent material is of crucial importance for the economic sustainability of the process. The desorption process must be effective, without causing much damage to the biosorbent, making it reusable in several sorption/desorption cycles.

The brown algae represent an especially efficient and resilient class of biosorbents when compared with other biomass types. The order Laminariales and Fucales of the brown algae (division Phaeophyta) are the most important groups of algae for biosorption because of the abundance of alginate and fucoidan in their cell wall matrix.

The objective of this research was to study the biosorption of copper from aqueous solutions by *Ascophyllum nodosum* in a continuous packed bed column. The behaviour of alga in four consecutive sorption/desorption/washing cycles has also been investigated.

Experimental work was performed at pH 5.0 and 20 °C using a 50 mg/L inlet concentration of copper. The loaded biomass was regenerated using 0.1 mol/L HCl solution. The column was operated down-flow at a flow rate of 9.2 mL/min.

In the beginning of the biosorption cycles, it was observed the simultaneous release of H⁺ with the uptake of copper. As the saturation of the bed progressed, pH gradually increased. This might suggest that ion exchange is one of the main biosorption mechanisms.

The total organic carbon leached into the solution was used as a coarse way of monitoring the loss of biomass organic content during regeneration cycles. The acidic washing leached smaller organic molecules and ions.

The breakthrough curves were analyzed using the Yoon-Nelson, Thomas and Yan's models, being the latter the best model. The breakthrough time (when the copper concentration in the effluent was 1.0 mg/L) decreased from 140 min (first cycle) to 120 min (second cycle) and was kept constant in the following cycles (30 min). According to Yan's model the biosorption capacity decreased along with the cycles: 82 ± 1 (cycle 1), 53 ± 1 (cycle 2), 39.7 ± 0.7 (cycle 3) and 39.1 ± 0.7 (cycle 4).

The application of biosorption of copper ions by *Ascophyllum nodosum* in a packed bed column is potentially well suited for the detoxification of metal-bearing industrial effluents in large-scale columns.

Development of alginate hydrogel beads; potential delivery systems for nitrification and urease inhibitors to soils and slurry

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A problem to the environment is the loss of soil nitrogen as gases or to groundwater via leaching as nitrates. The application of urease and nitrification inhibitors which act on microbes in the soil and slurry has the potential to prevent these losses. One drawback to these inhibitors is that they must be regularly applied to the soil or slurry tank.

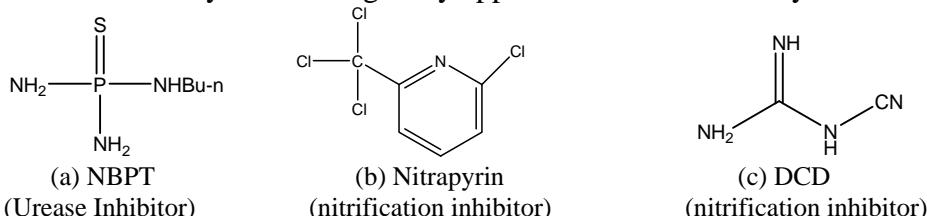


Figure 1: Example of Inhibitors

Hydrogels are three dimensional hydrophilic polymer networks capable of absorbing large amounts of fluid. The ability of molecules of different size to diffuse into and out of hydrogels, permits the use of hydrogels as delivery systems. Alginate (a naturally occurring polysaccharide) was chosen to form the hydrogels used here as it is both biocompatible and biodegradable. The alginate hydrogel was formed as beads using calcium or barium ions as the cross-linker with diameters in the range of 710-850 µm. Microscopy studies on the beads showed that the surfaces of the beads were quite smooth and contained no large pores. The swelling characteristics of the alginate hydrogels were determined by immersing dried test samples in distilled water and sodium chloride solutions. Swelling was significantly slower in distilled water than in sodium chloride solution (Fig. 2) due to the ion exchange mechanism available with NaCl solution. As there is a wide variety of monovalent cations present in soils and slurry, these will aid the hydrogels to swell and release the encapsulated inhibitors. The beads can take in approximately 10 times their original weight of water. The release of the urease inhibitor NBPT from the beads was monitored using UV/vis spectroscopy. Figure 3 shows a typical set of experimental data in which the solution surrounding the beads was monitored. It can be seen that the marker band (λ_{\max} 212 nm) for NBPT increased as a function of time. Factors that are important in controlling the rate of release from the beads such as the calcium ion content of the hydrogel and the sodium ion content of the solution into which the NBPT is released will be described.

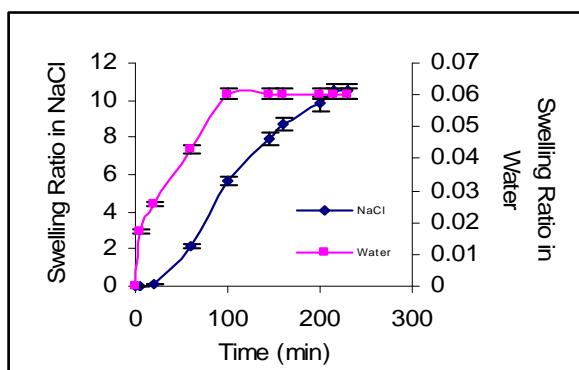


Fig 2: Swelling behaviour of beads in NaCl and water

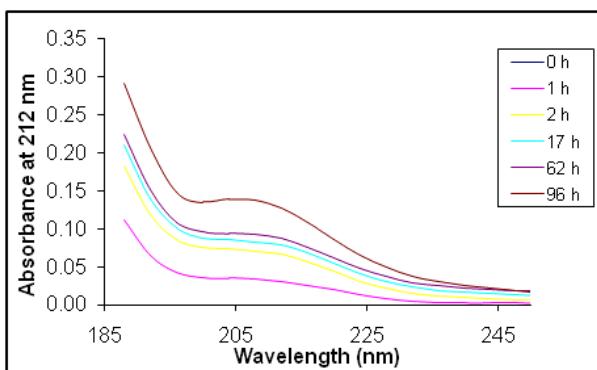


Fig 3: NBPT release into distilled water

Assessment of potential reutilization of recovered alkaline baths for aluminium extrusion dies cleaning

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The aluminium extrusion industry has a significant economic importance all over Europe. Aluminium extruded products have a high value in end-use applications and an increasing demand in sectors such as building and construction, transportation and engineered manufactured goods. The process is carried out employing extrusion dies, steel disks with an opening cut through them, with the size and shape of the intended cross-section of the final extruded product. An aluminium billet pre-heated at a temperature of 500 °C is forced to flow through the die in order to get the required profile. At the end of the cycle, it is necessary to remove all the remaining metal inside the cavities of the die to reuse them in production of new pieces.

The ordinary cleaning method consists in loading the dies into a tank filled with boiling NaOH for at least four hours followed by a water soak. The main problems related to this operation are high consumption of sodium hydroxide (6 kg/die) and water, loss of aluminium in the spent bath dissolved as aluminate (600 - 1000 kg/die) and the volume of exhausted caustic solution sent to treatment (4500 L/day).

The aim of this work was to assess the performance of the reutilization of a spent alkaline bath, treated with CaO to remove the aluminate salts, in the extrusion dies cleaning process.

Representative samples of spent cleaning baths from an aluminium extrusion company (Total NaOH: 297.50 g/L and dissolved aluminium: 71.50 g/L) have been treated with hot solutions ($T = 60$ °C) of different quantities of CaO in order to remove at least 90 % of dissolved aluminate salts. Experimental design has been set to study the optimal conditions of this treatment. Recovered samples were filtered and used with and without corrections in NaOH concentration to simulate the extrusion dies cleaning at bench scale. The optimal conditions for the rest of main process parameters, temperature (°C) and time of permanence of the die (minutes), were set by the predictions of a regression model for maximum dissolved aluminium built in the region of desirable operational conditions. Aluminium content was determined by a volumetric method.

Preliminary results show that a recovered bath with an addition of NaOH to get the usual range of concentrations in the extrusion companies (15%) is applicable to get at least 70 % of the maximum concentration of aluminium dissolved in an unrecovered bath operated in the same experimental conditions. This performance could be enough to guarantee the dies cleaning.

Reutilization of recovered spent baths would offer a wide range of environmental advantages for aluminium extrusion industry such as NaOH and water consumption savings, increase useful life of cleaning baths, reductions of hazardous waste production and treatment costs.

Multicorrelation models for the estimation of bioavailable metal concentration in soil fertilized with cattle manure

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Soil is defined as the top layer of the earth's crust, formed by mineral particles, organic matter, water, air and living organisms. It is in fact an extremely complex, variable and living medium which performs many vital functions. The soil compartment is continuously receiving a significant amount of pollutants from different sources and, therefore, it acts as a sink of a wide variety of emissions, including heavy metals. To prevent this contamination and protect soils across the EU, the European Commission has adopted a Soil Thematic Strategy (COM(2006) 231) and a proposal for a Soil Framework Directive (COM(2006) 232).

Sources of heavy metals include aerial deposition of particles emitted by different industrial activities, vehicle exhaust, etc. (Fernández et al., 2002). In addition, if the soil is dedicated to agricultural activities, other emission sources have to be considered, like the application of commercial fertilisers, sewage sludge, cattle manure or pesticides, which usually may contain heavy metals as impurities. Once in soil, heavy metals can be readily transferred to soil solution, depending mainly on soil properties. From soil solution, leaching of heavy metals to groundwater and biotransfer to vegetation, livestock and finally to humans, can occur.

In Galicia (NW Spain) the application of organic wastes to agricultural land is a common practice, which may increase total and bioavailable metal contents in the soil. Arable layer of pastureland in a specific area was monitored for total and assimilable content of heavy metals. On this basis, multicorrelation models were obtained for the estimation of bioavailable metal concentration in soil (extracted with DTPA and Mehlich-3) in relation to total metal concentration and soil properties. Metals analysed were Mn, Fe, Zn, Cu, Cr, Co, Ni, Cd and Pb. Acceptable R² values were obtained in all cases, ranging from 0.48 for Cr to 0.90 for Cu.

Acknowledgements

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Genetic engineering of tobacco for mercury phytoremediation

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Mercury is still one of the most important environmental pollutants at global level. The effect of mercury on the ecosystem and human health are growing concerns. To prevent the environmental mercury poisoning incidents, an effective technology for treating mercury-polluted environments is becoming increasingly urgent. Recently, attempts are being made to utilize bacterial *merA*-mediated reduction and volatilization of mercurials for the environmental remediation of mercury pollution. However, in an open system, mercury vapor (Hg^0) released in this way will become part of the local mercury cycle and repollute the environment again. To help solve this environmental problem, a new mercury scavenging mechanism that could be expressed in living cells and accumulates mercury from contaminated site without releasing mercury vapor into the ambient air, is necessitated instead of the mercury reduction mechanism.

In the present study, to explore the potential of plants to sequester mercury, we engineered the bacterial polyphosphate kinase gene *ppk* and mercury transport gene *merT* under control of a plant promoter for expression in genetically engineered tobacco plants. We found that transgenic expression of mercury transporter resulted in accelerated and enhanced mercury uptake into tobacco. In addition, tobacco expressing polyphosphate and mercury transporter accumulated significantly more mercury than its wild-type progenitors from mercury-containing medium and simulated soils without taxing the tobacco plants. The combination of accelerated mercury uptake and enhanced mercury accumulation represents one way for shortening the purification complete time, and for improving the tobacco plants to be more suitable for phytoremediation of low levels of mercury contamination.

Based on the results obtained in the present study, the expression of polyphosphate and mercury transporter in transgenic tobacco plants may provide an ecologically compatible approach for phytoremediation of mercury pollution.

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Kinetics of nickel leaching from spent catalysts in acidic solutions

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Recently, relatively great attention has been paid to the research connected with the recovery of nickel from secondary resources. Recycling of spent catalysts became an unavoidable task not only for lowering the catalyst cost but also for reducing the catalyst waste to prevent the environmental pollution [1].

The kinetics of spent nickel oxide catalyst ($\text{NiO}/\text{Al}_2\text{O}_3$) leaching in sulfuric acid and hydrochloric acid solutions was investigated. The effects of spent catalyst particle size, acid concentration and reaction temperature on Ni extraction rate were determined. The results obtained show that extraction of about 96% is achieved using 200 mesh spent catalyst particle size at a reaction temperature of 100 °C for 360 min reaction time with 60% sulfuric acid concentration. Also extraction of about 87-88 % is achieved using 200 mesh spent catalyst particle size at a reaction temperature of 100 °C for 360 min reaction time with 37% hydrochloric acid concentration. The solid/liquid ratio was maintained constant at 1:5 g/ml. The leaching kinetics indicates that chemical reaction at the surface of the particles and shrinking sphere is the rate-controlling process during the reaction for H_2SO_4 and HCl , respectively. The activation energy was determined as about 33.65 kJ/mol and 24.038 kJ/mol, respectively.

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Sedimentation and chemical processes on the Mkuze floodplain: Implications for wetland structure and function

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The Mkuze Wetland System, situated in northern KwaZulu-Natal, is South Africa's largest freshwater wetland area. The system plays a vital role in the functioning of the local landscape and has been identified as an important site for the retention of a number of solutes. The mechanisms through which this retention occurs were investigated through analysis of sediment, groundwater and porewater samples collected from the lower floodplain. Sample analysis was achieved through the use of several techniques, including Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), X-ray Diffraction (XRD), X-ray Fluorescence (XRF), electron microscopy and sequential extraction.

Data collected indicate that evapotranspiration is the primary mechanism controlling the retention of chemicals. Groundwater, introduced by flow from the Mkuze River, becomes increasingly concentrated under the effects of evapotranspiration, resulting in the precipitation of less soluble minerals, such as calcium carbonate and silica-bearing phases. Evapotranspiration also indirectly influences the sediment redox status, which exerts control on the formation of Fe/Mn oxyhydroxides and sulphides. Clay mineralogy is dominated by Fe-rich smectite, which is suspected to be predominantly neogenetic in origin. Seasonal drying and flooding of floodplain sediments, as well as the build up of silicon in solution under evapotranspiration, results in the *in situ* formation of smectite. Under the influence of evapotranspiration, chemical precipitation is identified as the main factor responsible for the removal of significant quantities of dissolved solutes from solution.

Aggradation of the floodplain thus appears to be a combination of both clastic and chemical sedimentation. Calculated sedimentation rates, derived from ²¹⁰Pb and ¹³⁷Cs dating, estimate that clastic accumulation rates are approximately 0.30 cm/yr, with most of this accretion expected to be associated with seasonal flooding events. It is suggested that chemical sedimentation is an important contributor to long-term floodplain evolution, as it has the potential to modify the chemical and physical characteristics of wetland sediment. When viewed over long timescales, chemical sedimentation will affect the local landscape by altering hydrological flowpaths, vegetation distribution and topography. Under climatic conditions where potential evaporation exceeds rainfall during some part of the year, similar processes are likely to be occurring in other wetland systems. Wetlands from southern Africa therefore appear to function very differently from their more well-studied counterparts in cool, temperate settings.

Geochemistry of Fe, Mn, U and Ni in the water column of a former uranium open pit mine using size fractionation

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Natural geochemical dissolution, weathering and microbial leaching are responsible for the release of metals in a soluble form and account for the natural concentrations of metals in freshwater systems. Mine wastes are a major source of metal load on a numerous water systems in Sweden. Increased knowledge regarding the size distribution of organic material and metals will add to the understanding of the metal cycling in water systems with elevated concentrations of both toxic and essential metals. The aim of this investigation is to study the distribution of metals in size fractionated samples from an artificial lake at a former mining site and to compare the metal distribution and the organic matter concentration in the water column.

The artificial lake (Lake Tranebärssjön) at the former uranium mining site in Ranstad (Sweden) was used as study site and is situated in an area of carbonate rich bedrock. The sampling of the lake water was performed at stratified conditions from the surface water, the thermocline and near the oxygen depleted bottom. A small ultra centrifugal device with 10 kDa, 3 kDa and 1 kDa cut-off filters were used to fractionate the water. Unfiltered and 0.45 µm pore size filtered samples were also investigated. The concentrations of Fe, Mn, U and Ni were determined with ICP-OES and dissolved organic carbon (DOC) was also analyzed.

We found that the size distribution of organic carbon varied by depth. About 50% of the total amount of organic carbon in the surface and thermocline water is present as compounds <1 kDa. In the bottom water this fraction is even higher, 60 - 80%. The total concentration of the metals investigated increased significantly by depth. Most of the metals, except for Fe, make up the fraction <1 kDa. The majority of the Fe (~95%) in the surface and thermocline water is found in the fractions >10kDa. In the bottom water these fractions make up ~50% of the total Fe. In the anoxic bottom water 35% of the Fe is found in the fraction <1 kDa. For Mn the distribution is different, at all depths 80% of the Mn is found in the <1 kDa fraction. No Ni could be detected in the surface and thermocline water and the Ni found at the bottom is mainly present (~70%) in the <1 kDa fraction. About 50% of the detected U occurs in the <1 kDa fraction regardless of depth. We conclude that most of the organic carbon in the water is in dissolved form, which is also true for the investigated metals. 40% of the Fe is found in a particulate form, except for in the anoxic bottom water where this fraction is < 5%. For the other metals none or only a few percent is found in the unfiltered fraction. Predominance diagrams indicate that Mn, Ni and U occur as dissolved ions in this system. Since there is no particulate organic matter in the surface water the metals in the unfiltered fraction may be associated with iron precipitations and could thereby be transported down streams, especially during turnover. Some of the Fe in the oxygenated surface water is found in a dissolved form (<1 kDa), even though the pH is almost 8. At this pH Fe normally precipitates, which indicates that the dissolved Fe is probably in a complex with small ligands. To strengthen this hypothesis the <1kDa fraction will be further studied for the presence of biogenic ligands like siderophores and small organic acids that could form very strong complexes with metals.

Speciation and removal of chromium from aqueous solution by white, yellow and red UAE sand

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Removal of the heavy metal contaminants Cr(III) and Cr(VI) from aqueous solutions by different types of sand as a low-cost abundant adsorbent was investigated. White, yellow and red sands from the United Arab Emirates (UAE) were employed at various adsorbent/metal ion ratios. The effect of contact time, pH, temperature, metal concentration and sand dosage was studied. The optimal pH for adsorption was *ca.* 5.0 for Cr(III) and 2.0 for Cr(VI). The optimal adsorption time for both ions was *ca.* 3 hours. Even at the optimal pH, adsorption of Cr(VI) on all sand forms was very low (removal \leq 10%) and could not be fitted to any of the common isotherms. While at pH 5.0 Cr(VI) was not adsorbed at all, Cr(III) was totally removed. Adsorption of Cr(III) by the three sand forms obeyed Langmuir first order kinetics. The rate constants at 25.0 °C were 3.95×10^{-4} , 2.28×10^{-5} and $7.75 \times 10^{-6} \text{ s}^{-1}$ for white, yellow and red sand, respectively. For Cr(III), the Langmuir isotherm gave the best fit for adsorption. At 25.0 °C, the maximum mass of Cr(III) removed per gram of sand (Q_{max}) was 62.5, 9.80 and 2.38 (mg/g) for white, yellow and red sand, respectively. ΔH° was 14.5, 51.2 and 45.8 kJ mol⁻¹ and ΔS° was 24.0, 136 and 111 J K⁻¹ mol⁻¹ for adsorption on white, yellow and red sand, respectively. The results are discussed in terms of the chromium species present in solution and the effect of sand particle distribution and metal composition on adsorption efficiency.

Factors affecting the recovery of nickel from refinery spent NiO/Al₂O₃ catalysts

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The increasing demand for metals in the world has required intensive studies for the extraction of metals from secondary resources. After periodical use of the catalysts, due to poisoning effect of foreign material and impurities, which deposit on the surface of the catalyst, they will become inactive. In such cases, fresh catalysts have to be substituted and the spent catalyst will be discarded as waste material. Disposal of such catalyst materials, which contains appreciable amounts of heavy metals, is environmentally hazardous. Therefore, a suitable and economically viable method is required for recovery of metals at the same time method should not pose the risk of environmental hazards [1-3].

This study investigates the possibility of recovering nickel from the spent catalyst (NiO/Al₂O₃) resulting from the steam reforming in Tabriz refinery (Iran). According to environmental considerations it is very useful to reuse the solid waste to produce a salable product such as nickel sulfates which can be used in electroplating. The leaching stage were investigated, so the optimum leaching parameters determined. In the extraction process, nickel is recovered using sulfuric acid, nitric acid, hydrochloric acid and aqua regia as a media reaction. The considered parameters affecting nickel recovery were acid concentration, temperature and time of reaction, solid:liquid ratio, particle size and stirring rate, then experimental was performed and the optimum condition determined. The results obtained show that recovery percent were 96%, 87.41%, 93%, 81% for H₂SO₄, HCl, HNO₃ and aqua regia, respectively.

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Trace metals in airborne particulate matter from a roadside area of Daejeon city, Korea

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In this study, using instrumental neutron activation analysis we undertook the measurements of about 29 metal elements in airborne PM_{2.5/10} samples that were collected from a roadside sampling station at a moderately polluted urban area of Daejeon city in the southwestern region of Korea. An inspection of our metal measurement data indicated that the concentrations of several metals (such as Al, Fe, K, Na, Cl, and Mg originating as crustal aerosols) are much higher than that of any other metal. The mean concentrations of toxic metals within the coarse fraction, that is, As, Mn, Se, V, and Zn were 1.26 ± 0.93 ng/m³, 16.2 ± 7.68 ng/m³, 0.82 ± 0.77 ng/m³, 1.45 ± 0.78 ng/m³, and 47.9 ± 47.1 ng/m³, respectively. Those of toxic metals within the fine fraction, that is, As, Mn, Se, V, and Zn were 1.22 ± 0.70 ng/m³, 6.7 ± 3.13 ng/m³, 0.97 ± 0.73 ng/m³, 1.08 ± 0.62 ng/m³, and 32.9 ± 13.3 ng/m³, respectively. The range of distribution is clearly distinguished between metals with their concentrations ranging over several orders of magnitude. Expanded uncertainties of measurements were also calculated by applying both GUM approximations and Monte-Carlo technique. The estimate of As concentration on a specific day by the Monte-Carlo technique differed from those of GUM approximation method 1 and 2 by 6 and 2%, respectively. These differences may be increased with additional non-linearities such as counting efficiency and geometry. The sensitivity test of the measurement uncertainties showed that neutron flux(38%), efficiency(28%), counting error(14%), and decay factor(10%) are the major factors of uncertainty variations. Based on concentration data and measurement uncertainties of analyzed trace elements, we conducted a probabilistic assessment of their distributions. The distributions of concentrations and measurement uncertainties were significantly different from each other. This result means that the concentrations and measurement uncertainties have no exact correlations with each other because of many factors contributing to the measurement uncertainties. Thus, we need to evaluate measurement uncertainty of every concentration point to obtain a reliable data set.

Column studies for aluminium elimination from wastewaters using beach cast seaweed as biosorbent

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In this work it is studied the application of a nuisance material (beach cast seaweed) as biosorbent for aluminium elimination from synthetic and real wastewaters. There is little work based on aluminium adsorption, probably due to the fact that it is not considered as a major pollutant. Nevertheless, it is involved in acid water pollution and could pose a serious threat to human health as it is considered a neurotoxic, normally linked to several skeletal and neurological disorders like Alzheimer's disease.

We try to find viable alternatives to traditional depuration techniques, such as precipitation and ion exchange that generate large quantities of toxic sludge or may be ineffective or extremely expensive. Biosorption, the passive sequestration of pollutants by non-metabolizing, non-living biomass, may be an attractive option^[1, 2].

The experiments were carried out in fixed bed columns filled with different quantities of biomass. The breakthrough curves were obtained for 550 mg·L⁻¹ aluminium concentration of synthetic solutions at 20 mL·min⁻¹ flow rate; moreover, real wastewaters from a company that manufactured aluminium panels were also tested using beach cast seaweed in column during three adsorption-desorption cycles. The obtained results demonstrated that this biomaterial could compete with conventional techniques for the removal of aluminium from wastewaters in fixed bed columns.

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Fern biomass as a useful adsorbent for mercury decontamination

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Mercury toxic effects, transmission through the food chain and its persistence in the environment render this metal as one of the most harmful heavy metals for human health or aquatic life. For this reason, finding an economical and effective decontamination technique is important in order to reduce the levels of this metal in wastewaters ^[1, 2]. In this work, biosorption efficiency in mercury removal has been tested using bracken fern (*Pteridium aquilinum*) as low cost biosorbent.

Adsorption isotherms were fitted to Langmuir model obtaining maximum uptake values around 60 mg·g⁻¹, which are similar to the obtained with other low cost materials ^[3]. Ionic strength variation showed no effect on the mercury adsorption indicating the presence of neutral mercury species in solution such as HgCl₂, HgOHCl and HgOH₂. Mercury adsorption capacity was also tested in presence of other metals in solution such as cadmium, lead, copper, magnesium or calcium, but it is remarkable that mercury removal is not affected even at high concentration of these competitive metals. Kinetic studies showed high removal capacities at very low times, so this material was also used for the development of adsorption columns in order to obtain breakthrough curves.

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Geochemistry of anthropogenic sedimentary metals (Cd, Cu, Pb and Zn) in Deûle river (in northern France)

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(in northern France) was investigated. For that purpose, sediment cores were sampled in an area that, in the past, suffered a major impact from smelting industries; they were sectioned under nitrogen and centrifuged to recover interstitial waters. Total and available metals (Fe, Mn, Cd, Co, Cu, Cr, Pb, Sr, Zn) in solid phases and total dissolved metals, oxygen, nitrates, sulfates and sulfides in the pore waters were analysed. It was found that peak contents in total metals of the sediment were obtained for Zn, Cd and Pb at specific depths in the core as a result of more important industrial discharges in the past. Rapid and near-simultaneous depletions of the following oxidants: O_2 , NO_3^- and SO_4^{2-} (that were consumed by microorganisms for the mineralisation of organic matter), were observed with depth; and as a consequence, natural potential decreased significantly with depth to reach negative values below -330mV versus the Ag/AgCl reference electrode, thus indicating that strong anoxic conditions did prevail all along the sediment core. Under these geochemical conditions, the reductive dissolution of Mn (IV) and Fe (III) oxides/hydroxides occurred easily in the medium and generated Mn (II) and Fe (II) ions in pore waters; and during this microbial reduction process, some trace elements were liberated as well. The detailed examination of the dissolved trace-metal profiles versus depth further revealed that Cu, Pb, Zn and Cd could be liberated from organic matter through microbial decompositions observed inside a thin sediment layer of about 3cm below the sediment/water boundary. Over the entire length of the sediment core, pH was in the range of 6.5-6.8 and bicarbonate alkalinity and sulfide anions were generated within the pore waters (many of these solutes resulted from the bacterial SO_4^{2-} reduction). However, the increases in HCO_3^- and HS^- were less than those calculated from the balances of the various sedimentary processes [i.e., respiration, O_2 ; denitrification, NO_3^- ; reductions SO_4^{2-} , Mn (IV) and Fe (III)], suggesting that metal-carbonate and metal-sulfide precipitations should be expected to take place in the sediment. To sustain this hypothesis, the partitioning among four operationally-defined solid fractions (i.e., exchangeable-carbonate, reducible, oxidizable and residual) was measured under strictly anoxic conditions for Fe, Mn, Sr, Co, Cu, Cd, Ni, Zn and Pb at 2 cm intervals from the sediment-water interface to a depth of up to 34 cm. Overall, our investigations showed that: (i) some metals (Cd, Co, Cu, Pb and Zn) were inferred to occur more abundantly in association with organic matter and/or sulfides; and (ii) other metals (Mn, Sr) seemed rather to be bound to carbonates via formation of pure metal-carbonate phase and/or sorption into calcite (this latter was identified to be present in Deûle sediments by X-Ray diffraction). Geochemical model simulations were used to raise thermodynamically the possibility of (co) precipitations of metal solutes with HCO_3^- and HS^- ions and to predict formation of some specific anthropogenic minerals.

Determination of Ni in soil and Tl in marine sediments by AAS: Capabilities and limits of deuterium-, Zeemann and of High- Resolution Continuum Source AAS (HR-CS AAS) background correction techniques

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Measurement of Nickel seems to be a standard application for Atomic Absorption Spectroscopy in environmental samples. However, high iron contents of soil samples may cause interferences with the Nickel-signal, pretending too high Ni concentrations.

Less common is the measurement of highly toxic ultra trace element Thallium in marine sediments. Even if electro-thermal Atomic Absorption technique, especially with direct solid sampling, is by far sensitive enough for analysis of Thallium in this matrix, method development becomes difficult with conventional AAS-Systems due to interferences of Sulfate.

This work compares and evaluates results for above mentioned measurements, received by AAS with three different background correction techniques. The reasons for deviations of these results will be explained by means of the spectra. It can be shown, how -in spite of spectral interferences and direct line overlapping- correct results were achieved with HR-CS AAS.

Removal and selective recovery of copper, nickel and zinc from real electroplating effluents

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Electroplating processes produce large amounts of effluents per year, which includes variable amounts of harmful metals; these effluents should be treated before being discharged into the aquatic systems. Usually, hydroxide precipitation is the standard method for removing harmful metals from the effluents. This treatment process is based on phase transference of metals from the liquid phase (effluents to be treated) to a solid phase (formation of sludges). Thus, new residues (sludges) are generated, which are classified as hazardous residues and should be deposited properly.

In order to overcome this problem, a multi-stage process, which combines biosorption and chemical methodologies, was implemented to remove and recover selectively the metals.

For this purpose, a real effluent was collected from a Portuguese electroplating industry. Firstly, concentrations of the major metals (Cu, Ni and Zn concentrations were 19.6, 21.5 and 24.9 mg/L, respectively), inorganic ligands (chloride, carbonate, sulphates and phosphates concentrations were 114, 4.5, 350 and 33 mg/L, respectively) and total organic carbon (7.4 mg/L) were determined in order to perform the chemical characterization of the effluent.

Then, in the biosorption step, effluent was efficiently treated by using inactivated flocculent cells of *Saccharomyces cerevisiae* (an inexpensive by-product from fermentative industry) at pH 6.0. This step allowed to reduce metals concentrations in the treated effluent to values (final Cu, Ni and Zn concentrations were < 0.15, 1.6 and 0.9 mg/L, respectively) below to the legal discharge limits. Then, biomass containing metals was incinerated, which reduced 99% the amount of residue produced in the bioremediation stage. Later, ashes were totally acid digested and a reduced volume of an acid solution containing high concentration of metals was obtained: 3.5 g/l of Cu, 2.8 g/l of Ni and 4.3 g/l of Zn. From this solution, the electro deposition of Cu, at a controlled potential, followed by the alkalinisation of the solution (to pH 15), allowed the selective recovery of the three metals with high yield and purity: (i) metallic copper (recovery: 99.9%; purity: 99.7%) (ii) nickel as nickel hydroxide (recovery: 99.98%; purity: 80.6%) and (iii) zinc as tetrahydroxozincate (recovery: 95.7%; purity: 99.98%).

In conclusion, a clean (without residues) and low cost process was developed for removing metals from real electroplating effluents followed by a selective recovery of copper, nickel and zinc.

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Surface modification of tubular silicalite membrane with using hydrophobic materials for concentrating bio-ethanol

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Silicalite as one of zeolites is expected as a material of ethanol-selective membranes because of its high hydrophobicity, and we reported the silicalite membranes on the porous stainless steel support tube [1]. Sano *et al.* have succeeded in the improvement of hydrophobicity on the membrane surface by modification with silane coupling reagents, and the improvement of the separation performance [2]. In this study, we investigated the effect of surface modification of the tubular silicalite membranes using silylation reagents on the separation performance. Tubular silicalite membranes were prepared by hydrothermal synthesis with EPD as a seeding technique [1]. Four kinds of silylation reagents were examined for the hydrophobicity on the membrane surface. The tubular silicalite membrane surface was treated with the silylation reagent and the pervaporation performance of the obtained membranes was measured. Ethanol aqueous solution of 5 % (v/v) was used as the feed of pervaporation. As a result, the surface of silicalite membrane modified with trimethylchlorosilane (TMCS) shows the largest contact angle, and the separation factor has improved only on the membrane modified with TMCS as shown in Table 1.

Table 1 Effect of surface modification using silylation reagent

Silylation reagent	None	Trimethylchlorosilane	Methyltrichlorosilane	Propyltrichlorosilane	3,3,3-Trifluoro-propyltrichlorosilane
30°C	Flux / kg m ⁻² h ⁻¹	0.32	0.31	0.34	0.31
	α	105	115	86	90
Image					
Contact angle	20°	130°	85°	62°	25°

This work has been carried out as a research project by New Energy and Industrial Technology Development Organization (NEDO)

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Distribution and speciation of metals in a contaminated estuarine system

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The Isipingo estuarine system located in Durban, South Africa has undergone a number of radical changes over the past twenty years. This region is characterised by a mixture of industrial and residential areas. Changes have been implemented to prevent the Isipingo River flooding into the industrialised section. These changes include reclamation of the wetland area to facilitate the construction of a number of large industries e.g. airports and oil refineries, reduction of inflow into the area controlled by sluice gates, diversion of the main river and canalisation to control the water inflow into the industrial sector¹. All the storm-water runoff and a number of industrial waste streams drain into the estuary. The changes made to the river system have resulted in inadequate inflow into the estuary. In addition, the canalisation has also restricted the natural flow of water into the system from the surrounding wetland, creating conditions under which the estuary is unable to function naturally. A survey of the estuaries along the KwaZulu-Natal coast identified the Isipingo estuary as contaminated with heavy metals². The complexity of this system poses both challenges and opportunities for the determination of the source and fate of such pollutants.

Sediment and water samples have been collected over a two year period and the heavy metal content analysed. A number of metal contaminants have been identified in the system, most notably zinc, which is present at levels higher than 9000 mg/kg at some areas of the system. The distribution of Zn in the canals is not uniform and it is not evident that the Zn present is due to a point source or if the Zn is being mobilised within the water column and redistributed. Sediment core data has been analysed to show the deposition cycle of zinc into the canal and estuary system.

Selective extraction and metal partitioning of the soil have shown that the zinc is predominantly bioavailable for uptake by plants and animals in the ecosystem. The stability of metal species is variable and depends on the pH and redox potential of the system. The variability of these parameters is dynamic due to the influx of seawater and the discharge of industrial waste into the canals.

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Enhanced EPS production by an *Arthrobacter viscosus* biofilm supported on zeolite for biosorption purposes

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The pollution caused by heavy metals, specially by hexavalent chromium, deserves special attention because their deposition in aquatic systems is very detrimental for animals and for the human being. The search for new technologies for the treatment of chromium polluted solutions leads to methods using sorbents of biological origin.

Several factors influence the bacterial production of exopolysaccharides, EPS, and consequently the biosorption process, and those include solution pH, temperature, ionic strength, biosorbent dosage, biosorbent particles size, initial solute concentration, work volume and agitation rate.

The use of a biosorption system consisting of a biofilm supported on a specific zeolite carbon allows to combine and even to enhance the ability of both, bacteria and zeolite, to remove chromium and consequently to increase the maximum removal of each one.

The objective of this work was to optimize the EPS production of an *Arthrobacter viscosus* biofilm supported on a 13X zeolite aiming the application of this system to the biosorption of Cr(VI). The parameters optimized were agitation rate, work volume, pH and glucose concentration. After the EPS production optimization, the biofilm was used in the biosorption of hexavalent Cr from liquid solutions. Differences between the use of dead or active biomass and between zeolites in powder or in pellets were also studied.

An optimized method to increase the EPS production by *Arthrobacter viscosus* was found and the application to the biosorption of Cr(VI) was tested. A maximum quantity of EPS (5 g/L) was obtained with an agitation rate of 175 rpm, 20 % of work volume, pH 7 and 20 g/L of glucose in the culture medium. Total Cr removal ranged from 96.4 % to 89.2 % at initial Cr(VI) concentration of 20–60 mg/L, for the active biomass and optimal conditions of EPS production, from 95.8 % to 86.2 %, for the dry biomass and optimal conditions of EPS production and from 100 % to 80.2 %, for autoclaved biomass and optimal conditions of EPS production. For assays using active biomass, the removal percentages were 88% and 65%, respectively, for optimal conditions of EPS production and poor conditions of EPS production, for an initial Cr(VI) concentration of 20 mg/L. The optimal conditions of EPS production allow to obtain a maximum accumulation of 7.88 mg/g_{sorbent}, for an initial concentration of 60 mg/L. The poor conditions of EPS production represent a decrease of 10% on the removal percentage of chromium and the use of pelleted zeolites represent a decrease of 46.5% on the removal percentage of the same metal. The use of active biomass allows to remove chromium faster than the inactive one.

Speciation of some heavy metals in bottom sediments exemplified by the Bobrza River (Świętokrzyskie district)

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The Bobrza River is a right-bank tributary of the Czarna Nida River and flows through the central part of the commune from the north to the south. It is a land located in northern part of the Świętokrzyskie Mountains mesoregion in the range of Chęcińskie Heights formed of Middle Devonian limestones and dolomites. A lowering between Bolechowicki Ridge and Zgórskie Range (Chęciny subregion) is occupied by deposits formed by Pleistocene fluvioglacial accumulation. The Bobrza River flows through lands diversified with regard to development which at the same time are representative for the Świętokrzyskie Mountains region as far as geological origin is concerned. In headspring area there is no direct anthropogenic impact whereas in other areas business activity is carried out influencing both acidification and alkalization of the environment. Lime industry is a significant source of dust emission which results in increasing pH of the environment and alkalization including surface waters. Additional problem and threat to water is posed by soil contamination by heavy metals emitted by means of transportation and industry or by uncontrolled waste disposal.

The study presents the results of analysing the bottom deposits of the Bobrza River for aluminium, cadmium, nickel, lead and zinc. Samples taken at the three survey points: headspring area, acidification environment and alkalization environment. The sediment samples were analysed for pH and grain size distribution. The grain size fraction $< 2 \mu\text{m}$ was used for chemical analysis: total element content (Al, Cd, Ni, Pb, Zn), total inorganic and organic C, and bonding form fractionation with a five-step sequential extraction by Tessier *et al.* procedure supported by microwave radiation [1]. Each of the chemical fractions is operationally defined as follows: (1) exchangeable; (2) bound to carbonates or specifically adsorbed; (3) bound to Fe-Mn-oxides; (4) bound to organic matter and sulphides; and (5) residual [2]. Residues after sequential extraction were mineralised in concentrated nitric acid in order to check if applied sequential extraction procedures allowed to extract total amount of metals from bottom deposits. Metal contents were determined with F-AAS technique in particular extracts.

Bottom deposits of tested the Bobrza River are characterized by high diversity of occurrence and content of individual fractions of analysed heavy metals. Among others it is a result of different land development, plants and possibility for inflow of pollutants from flow down. Moreover diversified surface features and lithology of catchment significantly contributes to permeability of surface deposits and water quality. The multielement measurements gave useful information to assist in the interpretation of the possible geochemical forms and sources of the trace elements in sediments of the environment of the Bobrza River.

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An investigation on biodegradable hydrogels as potential delivery systems for nitrification and urease inhibitors

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It is well documented that agriculture can be a significant polluter of the environment when nitrogen applied to the soil as fertilizer is lost as gases or to groundwater via leaching as nitrates. Currently in Ireland there is much interest in employing chemicals (Figure 1) which are known to be nitrification and urease inhibitors¹ and reduce the activity of soil microorganisms as a medium-term strategy to reduce nitrogen losses.

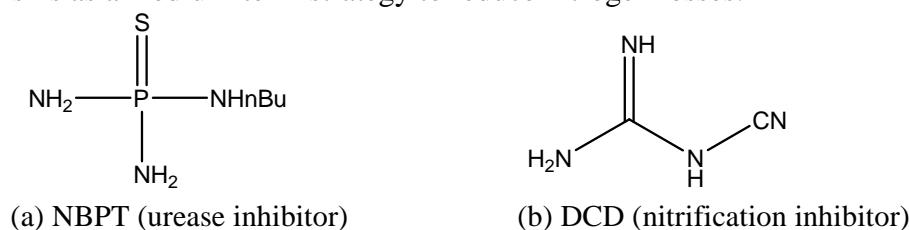


Figure 1 Structure of Inhibitors

However, these inhibitors need to be regularly applied to the soil and the slurry, thus in order to increase their viability as an environmental technology it is necessary to develop a means of delivering them in a controlled and sustained manner. The hydrogels chitosan and alginate were chosen as materials to fabricate the delivery system. Hydrogels have been extensively investigated as drug delivery systems² as upon absorbing water they swell and molecules encapsulated within them can diffuse out. In both cases the hydrogels were formed as spherical beads; experimental procedures were established so that the beads were formed with a uniform shape and a reproducible size distribution (1.18-1.40 mm chitosan and 0.71-0.85 mm alginate). The swelling characteristics of the hydrogels were determined by immersing dried test samples in distilled water and (in order to mimic real soil conditions) in solutions containing different concentrations of monovalent cations. It was found that the nature of the surrounding aqueous medium had a significant influence on the swelling behaviour of the alginate beads and this behaviour will be correlated to the ability of the beads to release the inhibitor. Our results showed that the alginate beads can trap NBPT, while the chitosan beads successfully trapped DCD. The release of DCD and NBPT from the beads was monitored using UV/vis spectroscopy. Systematic studies on the chitosan beads showed that it was possible to manipulate the release rate of the DCD by altering the molecular weight of chitosan, percentage of cross-linker used and curing time and release times for DCD over a period of about 1 week have been achieved.

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Heavy metals as technogenic pollutants: forms of presence

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At present, the problem of environmental pollution by heavy metals worries us greatly. First of all, industrial objects are main pollutants. In present report, the area of the Dzhida tungsten-molybdenum mining-concentrating complex, located in the vicinity of Zakamensk town in Buryatia Republic (Russia), is considered. Molybdenite and sulfide-hubnerite ore concentrating wastes up to 40 mln. tons in total have been accumulated in this place.

For estimate of landscape pollution for purposes of nature protection and those of hygiene and sanitation, the information not on total contents of heavy metals in soils, water, air, etc., but their species, percentage of mobile forms that are accessible for vegetation, conditions of mobile forms element migration is most important.

For diagnosis of heavy metal species, the procedure of sequential extract is widespread in practice of geochemical and geoecological researches. For comparison two most commonly used procedures of sequential extract have been chosen: technique reported by A. Tessier et al. [1] and modified BCR three-step procedure [2]. The relative standard deviations of results obtained by these techniques are $\leq 10\%$.

The considered methods equally describe the nature of metal distribution by fractions. In technogenic sand (wastes of the Dzhida tungsten-molybdenum complex), copper mainly concentrates in sulphide fraction, zinc – in sulphide and sedimentary fractions, and lead – in iron and manganese oxide fraction. Degree of ore mineral oxidation in technogenic sand is approximately estimated ($Pb > Zn > Cu > Mo$) by results of element content comparison in geochemical fractions.

Dependence of heavy metals mobile form concentration on acid-alkaline characteristics of technogenic sand is considered. It is necessary to note that mobile forms of Cu and Zn 10 times exceed maximum allowable concentration for soils [3]. The questions about neutralising ability of the waste depository, expected quantities of heavy metal mobile forms and their influence on vegetation of nearby territories need further studies.

The work is supported by integration project of Siberian Division Russian Academy of Science 122 and project RFBR 08-05-98042-r_sibir_a.

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Synthesis and characterization of novel perovskite related metaloxides as electrode materials in solid oxide fuel cells

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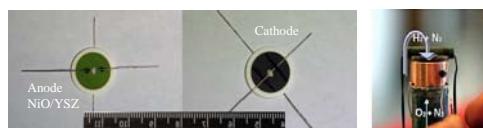
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The global warming of the earth during the last century due to large emissions of greenhouse gases such as CO₂ and NO_x makes it necessary to produce energy without the use of fossil fuels and coal. One contribution to this is the development of fuel cells and batteries. The research conducted in this project aims on the development of new electrode and electrolyte materials for the Solid Oxide Fuel Cell (SOFC).

The SOFC is based on a ceramic electrolyte typically Y₂O₃(8-15%)/ZrO₂ (YSZ) designed in a platelike or a tubelike manner with a working temperature of 800-1000°C to achieve acceptable ionic conductivity (~10⁻² S/cm) through the electrolyte and enough catalytic activity in the electrode materials to produce electrical energy directly from H₂, CO and CH₄ by reaction with O₂ (from air). However, the high operating temperatures introduce problems like cracks due to different thermal expansions of the materials and unwanted reactions between the electrode-electrolyte materials. This lowers the efficiency, the life time and increases the costs of the fuel cell. Typically the electrode materials are made out of different metal oxides, usually for the anode a “cermet (ceramic-metal)” made of a Ni/YSZ composite is used in which the Ni⁰ particles serves as the catalyst for the oxidation of the fuel and to conduct the electrons. For the cathode electronically and oxide ion conducting metal oxides are used e.g.; La_{1-x}Sr_xMnO_{3-d} or La_{1-x}Sr_xCoO_{3-d}, La_{1-x}Sr_xCo_{1-x}Fe_xO_{3-d}.

The materials that are of aim to be synthesized for cathode and anode electrodes will have perovskite related structures, mainly because the perovskite structure is very flexible. It is stable even with a large amount of vacancies and the properties can be tuned by simply doping the material with different cations. Syntheses are carried out by sol-gel chemistry e.g. citrate route to obtain homogeneous powders with small particle size and high surface areas.

The characterized materials are then tested and evaluated in a small scale model of SOFC as illustrated below.



The project can be divided into three major stages i) synthesis and characterization of novel electrode materials ii) synthesis of powders with high-surface area for deposition on electrolyte by screen-printing technique and deposition of electrode materials on electrolyte membranes iii) determination of electrochemical characteristics of model SOFC with novel materials.

The presentation will discuss some new materials being possible candidates as electrodes materials which we are studying at present.

Arsenic removal using synthetic adsorbents: Kinetics, equilibrium and column study

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Arsenic contaminations are seldom of anthropogenic origin (mining, wood preservatives,...) being generally caused by the natural dissolution of minerals in surface or underground waters. In natural waters, arsenic is present either as As(III) or As(V). Both ions are toxic and carcinogenic. High concentrations of arsenic in the groundwater (>1000 µg/L) of natural origin have been found in some areas in countries like Bangladesh, West Bengala, India, Mexico and some areas in Argentina, Chile and U.S.A.

The technologies commonly used are oxidation, coagulation-precipitation, ion-exchange and adsorption onto activated alumina, activated carbon and ferric hydroxides either in granular form or as coating material. Membrane technologies, namely reverse osmosis and nanofiltration, are also effective but they are not feasible for economic depressed areas. In the last decade the research has been focused on the development of cheap and easy-to-handle removal technologies especially for decentralized use in developing countries.

The main objective of this research is to establish a comparison between the performance of different sorbents for the removal of As(V): (i) a reference sorbent commercially known as ARM-300 (BASF Corporation) and two synthetic sorbents prepared at the laboratory, (ii) the hydrous ferric oxide (HFO) in suspension and (iii) loaded onto granular activated carbon (GAC). The research focused in the kinetics and chemical equilibrium using batch scale testing for the three systems. The results were adjusted to non-linear models and a statistic treatment was performed. Models were compared using the Fisher's test.

In general a pseudo-second order kinetics was followed. For the synthetic materials, most of the sorption occurred in the first minutes, indicating that they might be applied in batch treatment using short contact times, around 10 min. The kinetics of the reference material is slower.

The equilibrium isotherm of the HFO suspension was best described by Langmuir model; for the other two systems Langmuir and Freundlich models were statistically equivalent. The reference material exhibits the highest monolayer sorption capacity, 49 ± 9 mg/g, followed by the HFO suspension, 38 ± 2 mg/g, and by the HFO loaded onto GAC, 5.5 ± 0.5 mg/g. This last sorbent was also tested using a downward continuous flow through a packed column operating at a constant rate of 8.0 mL/min; Yan's model exhibits the best fit to the experimental results and a loading capacity of 3.6 ± 0.3 mg/g was obtained for an outlet concentration of 50% (after 500 min operation).

It can be concluded that both synthetic materials are promising for arsenic removal; however, when HFO is used in suspension, it should be followed by sedimentation and filtration (using e.g. sand/anthracite) in order to produce treated water without turbidity.

ICP-MS detection of trace elements in oil for ecological monitoring and geochemistry

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Determination of trace elements in oil and oil products is very difficult analytical task. Information about concentration of trace elements in oil plays a very important role for saving some actual problems of ecological monitoring and geochemistry.

Most of metals are presented in crude oil as organically bound metals (porphyrines and piridines). Also metals could be found as other metal-organic compounds, salts of organic acids, solutions or absorbed matter. Since some metals in oil, so-called “catalyst poisons”, deactivate catalysts (such as V, W), a method based on representative volumes of analysed oil could govern the choice of catalyst for cracking/pyrolysis. A precise method for the determination of prohibited diesel/fuel dopes could be also helpful in ecological monitoring. A possibility of isolation and concentration of rare-earth elements from crude oil allows some geochemical investigations [1].

Nowadays methods of metals determination in oil and oil products (ASTM D, IP, EN ISO, UOP) could be characterized by complex sample preparation with possible loss of volatile compounds; insufficient detection limits (DL) and confined number of measured elements. Prevalent instrumental technique in oil elemental analysis is atomic adsorption flame spectroscopy.

In the meantime ICP-MS was found to be the most suitable technique for the determination of trace and REE elements in oil (after the step of pretreatment). ICP-MS detection usually combines with these pretreatment methods: acid digestion, direct dilution and autoclave decomposition [2]. All these methods can not allow the pre-concentration effect of elements and not to get low value of DL. We suggest isolation of inorganic impurities via counter-current chromatography (CCC). An oil sample is continuously pumped through the CCC column of special construction as the mobile phase whereas an aqueous acidic solution is retained as the liquid stationary phase. Two phases are kept well mixed and agitated but there is no emulsion on the interface surface. Special features of CCC give an opportunity to vary the volume of oil sample from 10 mL to 1 L or more. Trace metals are concentrated into 10 mL of the stationary aqueous phase and than can be easily determined by ICP-MS. It should be mentioned that CCC pre-concentration step enables to minimize bleeds of the volatile compounds. Such combination (CCC pre-concentration with ICP-MS detection) gives possibility to develop a new method of quantitative trace metals analysis in oil.

Suggested method was tested on Tengizskaya (light Kazakhstanian) oil and diesel oil. Optimal conditions for pre-concentration of elements from oil by CCC have been found. CCC pre-concentration with ICP-MS detection allow us to measure elements concentration till ppt level.

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Distribution of some elements in surface soil over the Kavadarci region, Republic of Macedonia

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The results of a first systematic study of spatial distribution of different elements in surface soil over of the Kavadarci region, Republic of Macedonia, known for its nickel industrial activity in the nearest past are reported. The complete investigated region (360 km^2) is covered by a sampling grid of $2 \times 2 \text{ km}^2$; in the urban zone and around the ferronickel smelter plant (117 km^2) the sampling grid is denser, $1 \times 1 \text{ km}^2$. All together, in 172 locations 344 soil samples were collected. At each sampling point were collected soil samples at two depths, topsoil (0–5 cm) and bottom (20–30 cm) soil. Inductively coupled plasma – mass spectrometric (ICP-MS) determinations of 36 elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mn, Na, Mg, Mo, Ni, P, Pb, S, Sb, Sc, Se, Sr, Th, Tl, Ti, U, V, W and Zn) was performed. Data analysis and production of maps were performed on a PC using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software.

Four geogenic and three anthropogenic geochemical associations were established on the basis of: visually indicated similarity of geographic distribution of elemental patterns in topsoil and subsoil, comparisons of the averages of particular chemical elements according to basic lithological units, the correlation coefficient matrix, the results of factor analyses and comparisons of the enrichment ratios. Within the research, natural and anthropogenic enrichment with heavy metals was determined. Principally, the natural enrichment is related especially to Ni. Pollution with As, Cd, Co, Cr, Cu, Hg, Mo, Pb and Zn is basically insignificant. Areas with critically high concentrations of Cr and Ni cover about 5.5 km^2 of topsoil (0–5 cm) and 5.4 km^2 of subsoil (20–30 cm).

Application of synchrotron based X-ray spectroscopy for the speciation of metals in ash from combustion of biomass and waste

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In the process of creating a sustainable system for production of heat and power a number of biomass fuels and waste derived fuels will be introduced. Thus, the occurrence and chemistry in ash of metals that are potentially harmful in the environment is in focus for research.

Zinc is one of the metals that are of concern when the possible environmental impact and toxicity of combustion residues are discussed. On one hand, zinc is a valuable nutrient in wood ash that is recycled to forest soil. On the other hand it is considered eco-toxic in high doses in certain chemical forms. This paper presents an investigation of the presence and speciation of zinc in the ash fractions formed from fluidised bed combustion of forestry residues with and without an addition of either kaolin or sulphur to reduce ash sintering and corrosion problems. In addition, the speciation of Zn was investigated for ashes from combustion of municipal solid waste in three combustion units, one fluidised bed boiler and two stoker fired boilers.

Direct identification of trace metal compounds in solid materials is difficult to achieve due to the detection limits of conventional analytical methods. Extended X-ray Absorption Fine Structure spectroscopy (EXAFS) measurements using synchrotron based X-rays to identify zinc compounds in ash samples was used in this work. The spectroscopic measurements were carried out at the beam line I811 in the Swedish national synchrotron facility Maxlab at Lund University. The aim of the investigation was to test the applicability of the EXAFS method for identification of trace metal compounds in ash.

The results showed that the lowest concentration of Zn in ash for which it is possible to get any information about the nearest neighbour atoms around zinc is about 500 mg Zn per kg dry ash. If the concentration is higher than 1000 mg/ kg it is possible to obtain information, not only about the nearest neighbour, but also about more distant atoms surrounding the central zinc atom. The most common zinc species found in wood ashes were silicate, aluminate and to a lesser extent hydroxide. It cannot be ruled out that zinc can be bound as ZnO but this form is not dominant.

For the MSW ashes a combination of silicate and hydroxide or oxide is the most probable speciation in FBC bottom ash and cyclone ash, i.e. the most silicate rich ashes. The filter ash, i.e. the ash flow containing the smallest mineral particles, contains the same zinc species as the bottom and cyclone ashes with the addition of chloride or sulphide. For the fly ashes from the two stoker fired MSW combustors the results were somewhat different. For one of the ashes the data was very well described by a model based on Zn_2SiO_4 and a small amount of $ZnCl_2$. It cannot be ruled out that some of the Zn may be bound as ZnO as well. However, the modelling of the data for the other fly ash indicated that Zn had substituted for other metal ions in oxide minerals, such as oxides, hydroxides, silicates or mixed spinels. The data for that ash also showed the presence of a hydrated zinc chloride.

Porous carbon from unburned carbon in fly ash

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This paper describes the separation and activation of unburned carbon in fly ash and its utilisation for environmental applications. It was found that the unburned carbon present in large amounts in bagasse fly ash can be easily separated. The separated carbon had a reasonable surface area ($\sim 200 \text{ m}^2/\text{g}$), amorphous nature and retained the morphology of the parent bagasse¹. Activation of this carbon led to increase in surface area. Activation in a laboratory muffle furnace could produce activated carbon with surface area up to $450 \text{ m}^2/\text{g}$. However, activation in a rotary kiln pilot plant produced activated carbon with higher surface area (Figure 1) ($\sim 700 \text{ m}^2/\text{g}$). The unburned carbon and the activated carbon had mostly micropores (5-10 Å and 10-12 Å). The activated carbon could be used as a catalyst support. Loading of iron from red mud using wet impregnation method led to reduction in surface area of 20-25%. It is anticipated that these could be used for emissions reduction such as CO and VOC oxidation. The unburned carbon was also coated on ceramic fly ash membranes using different binders. Of the binders used, carboxy methyl cellulose gave best results. It is anticipated that such carbon membranes can be used for water / wastewater treatment, gas separation etc. Thus, the unburned carbon in bagasse fly ash shows a lot of promise for use as a porous adsorbent, catalyst support or for carbon membranes.

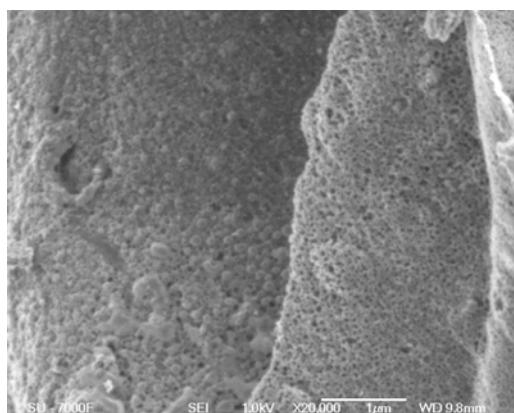


Figure 1 Image of activated carbon showing fine pores on the carbon surface

¹ Batra, V.S., Urbonaite, S., Svensson, G., 2008. Characterization of unburned carbon in bagasse fly ash. Fuel 87, 2972-2976.

Monitoring of Particles PM₁₀ and PM_{2.5} in the Mitrovica Urban Atmosphere - Kosovo

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The city of Mitrovica, approximately 40 km north of Prishtina, was the site of one the largest lead smelters in Europe. The present environmental situation in Mitrovica, put as in front of the responsibility to act more rationally towards nature and to be more responsible towards the protection of the environment for future generations. The protection lack of the environment during the last ten years, as well as the conflict in Kosova is the origin of huge problems regarding present environmental situation in Mitrovica (Kosova). Mitrovica has its air divided in two kinds, speaking in quality terms: Air above rural and mountainous zones, which is clean. Air above the city centre urban and nearby different plants, which is more polluted. Urban air contains dust particles and gases, added on it is as results of normal activity of the city and industries in them. Mitrovica can be cited as one of the capitals of Europe with worst air pollution. Exposure to airborne particulates PM₁₀ and PM_{2.5} containing low concentrations of heavy metals, such as Pb, Cd and Zn, may have serious health effects. However, little is known about the specification and particle size of these airborne metals. Fine and PM₁₀ particles size with heavy metals in aerosol samples from the Mitrovica urban area were examined in detail to investigate metal concentrations and speciation. The crystal structures of the particles containing Pb, Cd and Zn were determined from their electron diffraction patterns by XRF methods.

Sampling of suspended particulate matter, PM10 and PM2.5 started in July April 2003 and are still in progress at three sites in the very urban area of Mitrovica: roof of the FXM building MIP, roof of the elementary school “Bedri Gjina” at about 4m height; 40m far from heavy-traffic streets; on the platforms above entrance stairs to the faculty of Mining at the height above 3m from the ground. Suspended particles were collected on Pure Teflon filters, Whatman (37 mm diameter, 2µm pore size) and Pure Quartz, Whatman (37 mm diameter) filter paper, using the low volume air sampler Mini-Vol Airmetrics Co, Inc. (5 l min⁻¹ flow rate). The duration of each sampling period was 24 hours.

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Adsorption of binary metal ions on surface modified activated carbon from Eucalyptus wood

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Activated carbon prepared from Eucalyptus wood by chemical activation with H₃PO₄ was oxidized with HNO₃ to introduce oxygen surface groups and then used to study the equilibrium adsorption of five binary metal ions in solutions including Pb²⁺ / Cu²⁺, Pb²⁺ / Zn²⁺, Zn²⁺ / Cu²⁺, Pb²⁺/Ca²⁺ and Cu²⁺ / Ca²⁺. Competitive adsorption in all binary systems decreased the amount of each ions adsorbed with the maximum adsorbed amount followed the order Pb²⁺ > Zn²⁺ = Cu²⁺ > Ca²⁺. Ratio of the amount adsorbed for each pair of metal ions was approximately equal to that of single ion adsorption, suggesting that the basic adsorption mechanism of ion exchange was unchanged and partly depended on how fast the ion could transport to the surface active sites. The presence of Ca²⁺ in any binary system gave virtually no consequence on the adsorption of the other ion. All adsorption isotherms were fairly well fitted by the extended Langmuir adsorption model.

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Removal of residual dye from dyeing effluent using activated carbons with different porous texture

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In this research work, coconut shell- and wood-based activated carbons with different porous texture were used to remove residual dye from silk dyeing effluent. Spent water from dyeing process using natural dye (*Ceasalpinia Sappan* Linn.) with alum as mordant, contains mostly cationic dye complex of $[Al(brazilein)_2]^+$ (1). Two coconut shell-based activated carbons were prepared by both physical and chemical activation method and wood-based activated carbons were prepared using different chemical ratios by chemical with H_3PO_4 and these adsorbents were then used for the assessment of dye complex adsorption. Results from N_2 adsorption isotherm data at -196°C revealed that the coconut shell-based activated carbon from chemical activation had higher proportion of mesopore than that derived from physical activation. For wood-based carbon, the much greater proportion of mesoporosity compared to coconut shell-based carbons could be achieved by using the higher chemical ratio of H_3PO_4 : wood (2:1). Those activated carbons having higher proportion of mesopores showed correspondingly higher dye removal capacity. Activated carbon with mainly microporosity displayed a typical Type I isotherm whereas mesoporous carbon gave the isotherm resembling the initial part of Type III isotherm. All isotherms were well described by Langmuir model equation. This finding illustrated that the relative proportion of micropore and mesopore volume obtained from different biomass could influence significantly the adsorption of relatively large dye molecules.

Acknowledgements. The authors acknowledge support for this work from Suranaree University of Technology and Nakhon Ratchasima Rajabhat University.

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Organic Environmental Chemistry

Poster abstracts

Org P1-P80

Bioavailability of pharmaceutical residues in fish exposed to sewage effluents subjected to modern treatment technologies

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Knowledge of the uptake of pharmaceutical residues in fish is of vital importance for the risk assessment of environmental exposure to this inhomogeneous group of substances. Rainbow trout was exposed to several sewage effluents containing pharmaceutical residues for two weeks on-line to study bioconcentration. Sewage influent was treated in parallel with seven different technologies and/or add-on treatments including for example a membrane bioreactor, sand-filter and ozonation in a semi-large pilot plant at Henriksdal, Stockholm. Pharmaceutical residues in the effluents were determined by SPE/UPLC/QTOF-MS. A novel equilibrium passive sampler made of absorptive material was used to assess the bioaccumulation potential of pharmaceuticals in fish, and the bioavailable fraction was estimated by analysis of the pharmaceuticals in blood plasma and bile.

Uptake pattern and maternal transfer of polybrominated dioxins and furans in zebra fish (*Danio rerio*)

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Polybrominated dioxins (PBDD) have recently been found in mussels and fish from the Baltic with high levels in especially mussel [1, 2]. The consistency of the substitution pattern of major PBDDs through the food web suggests a natural origin of these compounds. The findings have raised concern for possible hazardous effects of these compounds on marine life and spurred a series of studies on uptake and biological effects of PBDDs.

In the current study, zebra fish was fed PBDD contaminated feed at NOEL levels (approx. 1ng of each congener per g feed) and the assimilation and possible maternal transfer to roe of different PBDD-congeners (mono- to tetra-substituted) were investigated. Zebra fish was chosen as it is a key test species in several test protocols (OECD, ISO etc.) to evaluate aquatic toxicity. The assimilation of PBDDs was followed for 12 weeks, and the depuration for 6 weeks. Eggs were collected during and after exposure and analyzed for PBDDs to investigate maternal transfer.

Analysis of whole fish except the GI-tract showed that bioaccumulation is strongly dependent on the PBDD substitution pattern. Tri- and tetrabrominated dioxins were found preferably substituted in lateral positions. Lower brominated PBDDs seem to be rapidly metabolized, albeit substantial levels of these compounds are found in biota. This may imply heavy dietary exposure for these compounds, or exposure through a different route, e.g. via the gills. To assess the metabolic influence on the uptake pattern screening for first phase metabolites was performed. Transfer of assimilated compounds to roe was shown for tetrabrominated compounds.

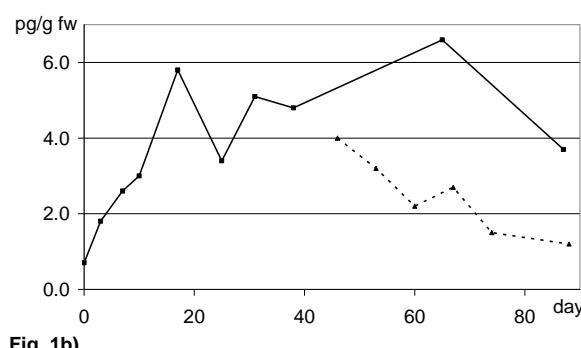
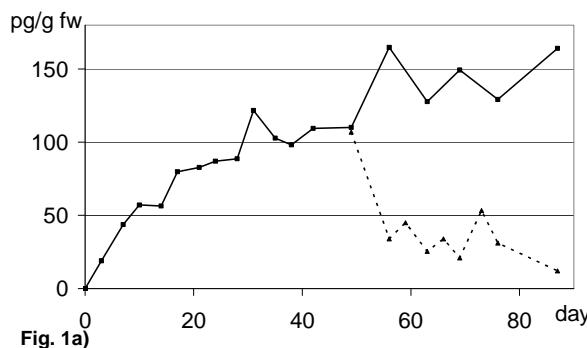


Fig 1a) Assimilation of 2,3,7,8-TeBDD in zebrafish; solid line uptake day 0-87, dashed line elimination day 49-87. b) Maternal transfer of 2,3,7,8-TeBDD to roe; solid line uptake phase day 0-87, dashed line elimination phase day 46-87.

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Tracing past and present inputs of legacy and emerging contaminants in the Oslo harbour

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Urban harbours are continuously exposed to diverse pathways in which organic contaminants can enter from atmospheric, coastal and terrestrial sources, either as freely-dissolved compounds or in the particle-bound phase. Because of these diverse multi-phase inputs, and the ever increasing list of organic compounds of concern, it is becoming increasingly difficult to conduct comprehensive risk assessments. As we shall present, we employed two strategies in the harbour of Oslo, Norway to assess how legacy and emerging contaminants enter the harbour, and distribute within it. The first strategy involved the analysis of sediment cores throughout the harbour, followed by core characterization and analysis of a diverse set of compounds (chlorinated paraffins, brominated flame retardants, perfluorinated compounds, disinfectants, PAHs and PCBs). The second strategy involved the placement of polyoxymethylene (POM) equilibrium passive samplers throughout the harbour in the sediment, water and air phases. The sediment cores provided information on temporal trends of particle-bound contaminant inputs, whereas the POM samples provided information on the contemporary distribution of freely-dissolved contaminants.

Some of the general observations to come are as follows. The input of particle-bound PAHs and PCBs is decreasing. For PAHs, this is explainable by an increase in the use of alternative energy sources from fossil fuels (particularly hydropower). For PCBs the observed decrease is explainable by the 1980 ban in Norway. However, POM measurements indicate ongoing input into the harbour of certain freely-dissolved PAHs, such as fluoranthene and pyrene, which are attributable to diesel emissions and other combustion processes. This is evident by a strong flux of these PAHs from the atmospheric to the water phase. Though PCB levels are decreasing, they are still an issue due to re-suspension and volatilization from legacy sources. For emerging contaminants, generalisations can also be made. For most brominated flame retardants, chlorinated paraffins and the disinfectant triclosane, the particle-bound inputs seems to have peaked and are now decreasing, likely due to increasing regulations on these chemicals. However, particle-bound concentrations of certain compounds are expected to increase, such as decabromodiphenyl ether and medium-chain chlorinated paraffins, as these compounds are not as tightly regulated. For these and other large apolar emerging contaminants, the highest concentrations appear from river outlets, due to their strong affinity for particles and likely upstream industrial sources for these compounds. Polar emerging contaminants, such as perfluorinated surfactants, are more widespread in distribution, similar to PAHs and PCBs. This is expected, as polar compounds, like PAHs and PCBs, are readily enter the freely-dissolved phase, where they are more rapidly transported.

POPs in Swedish and imported crayfish

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Within a project regarding environmental monitoring, crayfish from thirteen different Swedish lakes have been analysed for a number of substances including persistent organic pollutants (POPs) like PCB, chlorinated pesticides, brominated flame retardants and perfluorinated compounds.¹ Swedish crayfish are regarded as a delicacy but most of the crayfish consumed in Sweden are imported. Six samples of crayfish imported from China, Spain and Turkey were analysed for some of the POPs in order to compare the levels with the results for Swedish crayfish. The organs analysed were the abdominal muscle (muscle meat), the midgut gland hepatopancreas, and in some cases also the roe. The results for some of the compounds analysed are presented as median levels and range (min-max) in the table below.

	Swedish crayfish (N=13) µg/kg fresh weight			Imported crayfish (N=6) µg/kg fresh weight		
	<i>Muscle mea</i>	<i>Hepato-pancreas</i>	<i>Roe</i>	<i>Muscle meat</i>	<i>Hepato-pancreas</i>	<i>Roe</i>
ΣPCB(6)	0.53 (0.17-2.3)	57 (2.4-180)	19 (2.3-54)	<0.03 (<0.03-0.19)	2.1 (0.94-9.9)	0.58 (0.35-2.6)
PCB153	0.28 (0.08-1.0)	30 (1.2-93)	11 (1.0-29)	<0.005 (<0.005-0.04)	0.59 (0.25-1.9)	0.14 (0.06-0.54)
HCB	0.02 (0.003-0.68)	0.51 (<0.02-200)	0.66 (0.12-4.0)	0.10 (0.01-0.16)	5.9 (0.67-18)	2.0 (0.10-2.9)
p,p'-DDE	0.09 (0.04-0.39)	10 (0.30-66)	5.3 (0.39-7.8)	2.0 (0.91-2.4)	150 (90-270)	59 (15-120)
ΣBDE(5)	0.06 (<0.06-0.10)	1.4 (0.38-5.3)	-	<0.06 (<0.06)	0.76 (0.30-1.3)	-
HBCD	<0.02 (<0.02-0.17)	0.36 (<0.11-5.3)	-	<0.02 (<0.02-0.05)	0.19 (<0.10-5.4)	-
PFOA	-	2.1 (0.84-5.5)	-	-	-	-
PFOS	-	15 (1.3-71)	-	-	-	-

ΣPCB(6) is the sum of PCB28, 52, 101, 138, 153 and 180. ΣBDE(5) is the sum of BDE47, 99, 100, 153 and 154. Concentrations below LOQ have been set to LOQ.

Generally, the highest levels were found in the hepatopancreas followed by the roe, while the lowest levels were quantified in the muscle meat. The levels of PCB were higher in the Swedish samples than in the imported crayfish. However, the levels of chlorinated pesticides (HCB and *p,p'*-DDE) were higher in the imported crayfish, except for one Swedish sample with elevated level of HCB. The levels of brominated flame retardants (ΣBDE(5) and HBCD) are somewhat higher in the Swedish than imported samples. Only hepatopancreas from the Swedish crayfish were analysed for perfluorinated compounds (PFOA and PFOS).

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Seasonal variability in atmospheric concentrations of polyfluorinated chemicals (PFCs) at 2 sites in the UK

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Weekly and fortnightly air samples were collected between Jan 2006 and Jan 2007 at two sites in the Northwest of England: Hazelrigg (54.05N, 2.80W), a semi-rural field station belonging to Lancaster University, and Manchester (53.50N, 2.22W), a large urban centre. Air samples were collected with hi-volume samplers, and chemicals were trapped using a glass fibre filter (GFF) for particle phase chemicals, and a polyurethane foam (PUF)/XAD-2 resin/PUF sandwich for gas phase chemicals. Mass-labelled internal standards were added to samples prior to extraction to obtain recovery efficiency information and monitor matrix effects. PUF/XAD sandwiches were extracted using ethyl acetate, and extracts were cleaned using Envi-Carb, prior to the analysis of neutral PFAS by GC-MS. GFFs were cut in half, with one half sonicated in ethyl acetate and analysed for neutral PFAS by GC-MS, and the other half sonicated in methanol and analysed for ionic PFCs by LC-MS. Field and lab blanks were also analysed. Preliminary results show that a wide range of neutral PFAS, including 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 12:2 FTOH, 8:2 FT acrylate, 10:2 FT olefin, 12:2 FTolefin, NMeFBSE, NMeFOSE and NEtFOSE were frequently detected in the gas phase. A much smaller range of neutral PFCs were sporadically detected in the particle phase, and always at much lower concentrations than in the gas phase, in support of earlier data from these sites. Finalised analyte air concentrations and gas/particle partition coefficients, and their relationship with temperature and air mass back trajectory, will be presented and discussed. Compound profiles and levels at the urban and rural sites will be compared to enable conclusions to be made about sources of PFCs to the atmosphere. Levels will be compared with those published previously from Europe, North America and Japan.

Perfluorinated acid isomer profiling in ocean water by large volume injection-HPLC-MS/MS

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While the majority of perfluorochemicals produced by electrochemical fluorination (ECF, mixture of branched and linear isomers) were phased out in 2002, the production of others was continued by a telomerization process that yields exclusively the linear isomer. Environmental models predict that historic releases of ECF perfluorinated acids (PFAs), and their subsequent slow transport in oceans, are the dominant source of global PFA transport, however little empirical evidence exists. To validate these model predictions, we examined the PFA isomer patterns in water from the Atlantic Ocean, Arctic Ocean, and coastal Asia (Figure 1) and calculated the contribution of ECF perfluorooctanoic acid (PFOA, C₇F₁₅COOH) to total PFOA concentrations (Figure 2).

In Atlantic and coastal Asian water samples, perfluorooctane sulfonate (PFOS, C₈F₁₇SO₃⁻) and PFOA isomer profiles in all samples were fairly consistent with 3M ECF standards. Exceptions to this were PFOA isomer profiles in Tokyo Bay and 4 Atlantic samples, which showed significant contributions from a linear (presumably telomer) source.

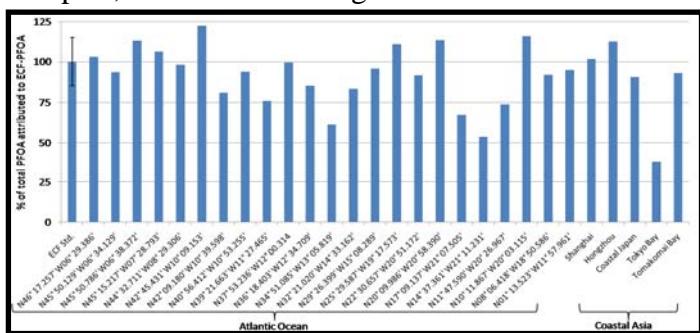


Figure 2. % of total PFOA attributed to ECF PFOA in Atlantic and Coastal Asian Ocean water.

Tokyo Bay. In Atlantic samples, long chain carboxylate (C₉, C₁₀, C₁₁, C₁₂, C₁₄) in coastal Asia, a single branched isomer for each chain length was detected in Tokyo Bay. In Atlantic samples, long chain carboxylate profiles were predominantly linear, with only C₉ and C₁₀ branched isomers detected intermittently. While the ECF fingerprint found in most ocean water samples is consistent with global models, in some cases (e.g. Tokyo Bay, some Atlantic locations) contributions from telomer-derived PFOA cannot be explained by current knowledge. Further isomer-specific monitoring is needed, particularly in the Arctic Ocean, to gain a better understanding of global sources.

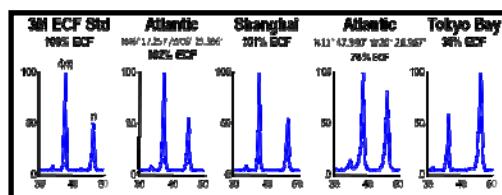


Figure 1. PFOA isomer profile (m/z 413/369) showing differences in 4m-PFOA to n-PFOA ratio depending on location.

Of these, only Tokyo Bay samples were found to have contributions of telomer-derived PFOA of over 50%. A single Atlantic sample showed significant apparent enrichment of branched PFOA isomers relative to the 3M ECF PFOA standard we were using. For long chain carboxylates (C₉, C₁₀, C₁₁, C₁₂, C₁₄) in coastal Asia, a single branched isomer for each chain length was detected in Tokyo Bay. In Atlantic samples, long chain carboxylate profiles were predominantly linear, with only C₉ and C₁₀ branched isomers detected intermittently. While the ECF fingerprint found in most ocean water samples is consistent with global models, in some cases (e.g. Tokyo Bay, some Atlantic locations) contributions from telomer-derived PFOA cannot be explained by current knowledge. Further isomer-specific monitoring is needed, particularly in the Arctic Ocean, to gain a better understanding of global sources.

Screening of “new” chemicals in the Swedish environment

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The occurrence and the environmental risk of chemicals are prioritized issues in several internationally legislative acts (e.g. EUs, Water framework directive, REACH, Stockholm Convention on POPs and the Convention on long-range trans-boundary air pollution – LRTAP) and there is a focus on “new or emerging” chemicals in different research and monitoring programs. In order to investigate the presence of chemicals in the Swedish environment screening studies have been carried out for more than 10 years (initiated and founded by the Swedish Environmental Protection Agency). Screening in this context means that environmental samples from various matrices in different geographical locations are analysed for certain selected chemicals.

The overall objective of a screening study is to investigate the occurrence and concentration levels of selected chemicals in a variety of environmental media. Additional aims are to identify possible emission pathways, highlight important transport pathways in the environment and to investigate accumulation in the ecosystem and human exposure.

In a screening a sampling strategy is worked out, based on identified possible emission sources and use as well as on the behavior of the chemicals in the environment. The measurement program may include urban and background areas, and sites close to potential point sources. Measurements of diffuse pathways from the society include samples from sewage treatment plants systems. Examples of chemicals which have been included in screening studies are such as surfactants, pharmaceuticals, flame retardance, chemicals included in personal care products and polar pesticides.

However, there are limitation and uncertainties in screening studies, e.g. measurements of a chemical are carried out in several media but only a few samples at each site are analysed which gives a ”snap shot” of the situation. There may also be limited information of sources, pathways and concentration levels of the selected chemical and no available sampling and analytical methods are available.

In this presentation the screening concept will be discussed based on the results of previous screening studies (carried out by IVL). The use of the results from the screening will be illustrated, e.g. how could the results be applied in research project or in monitoring program.

6-2 Fluorotelomer alcohol biotransformation in aerobic soils

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The widespread detection of perfluorinated acids such as perfluorooctane sulfonate and perfluorooctanoate in the environment has led to numerous investigations about their potential origins including both direct and indirect sources. 8-2 Fluorotelomer alcohol (8-2 FTOH, $C_8F_{17}CH_2CH_2OH$) is a raw material used in the manufacture of fluorotelomer-based products and its transformation has been extensively studied in activated sludge, soils, sediments and landfills. A shorter chain analog, 6-2 FTOH ($C_6F_{13}CH_2CH_2OH$), is also an important raw material used to manufacture fluorotelomer-based products.

This paper will present research to determine in closed and flow-through aerobic soil systems 6-2 FTOH biodegradation pathways, metabolites, metabolite yields and kinetics. In the closed system, 6-2 FTOH was fractionally transformed into four fluorinated acids. Perfluoropentanoate ($C_4F_9CO_2^-$, 34% yield) was the most abundant metabolite, indicating that biotransformation of both the first perfluorinated carbon (- CF_2 -) and the two non-fluorinated carbons (- CH_2CH_2 -) in 6-2 FTOH takes place in aerobic soil. In stark contrast, 8-2 FTOH aerobic biodegradation leads to 25% conversion to perfluorooctanoate as a result of the two non-fluorinated carbons degrading. This result suggests different biodegradation pathways are available and preferred in aerobic soil for 6-2 FTOH versus 8-2 FTOH. To confirm these observations, additional biodegradation studies with radiolabeled 6-2 FTOH [$C_6F_{13}^{14}CH_2^{14}CH_2OH$] were carried out in a flow-through aerobic soil test system. Use of ^{14}C -labeled 6-2 FTOH enabled mass balance determination. 6-2 FTOH showed much faster transformation kinetics than 8-2 FTOH. For both 6-2 and 8-2 FTOH, $> 25\%$ of ^{14}C is irreversibly bound and not extractable from FTOH aerobic soil transformation. The combination of relatively rapid biotransformation and irreversible binding to soil greatly decreased the fraction of 6-2 FTOH present in the headspace air in the flow-through test system.

The artificial sweetener acesulfame as marker of domestic wastewater in groundwater

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To assess sources and magnitude of possible groundwater contamination, chemical markers have proved to be useful. A chemical that is used in everyday life, the artificial sweetener acesulfame, may be ideally suited for detection of traces of domestic wastewater in natural waters. The compound was found ubiquitously in wastewater, surface waters, and groundwater from Switzerland. Acesulfame was not eliminated in wastewater treatment plants (WWTPs), and was quite persistent in lakes, where concentrations increased with population in the catchment area and decreased with water throughflow (Fig. 1). Highest concentrations in groundwater were observed in areas with significant infiltration of river water (Fig. 2), where the infiltrating water received considerable discharges from WWTPs. Given the currently achieved detection limit of $\approx 0.01 \mu\text{g/L}$, presence of $\geq 0.05\%$ wastewater can be traced in groundwater.

Fig. 1. Concentrations in lakes are proportional to the ratio population in the catchment area per throughflow of water. P/Q is a measure for the actual anthropogenic burden of a lake by domestic wastewater. The upper abscissa indicates the estimated wastewater burden, derived from the mean per-capita wastewater discharge of $0.5 \text{ m}^3/\text{d}$.

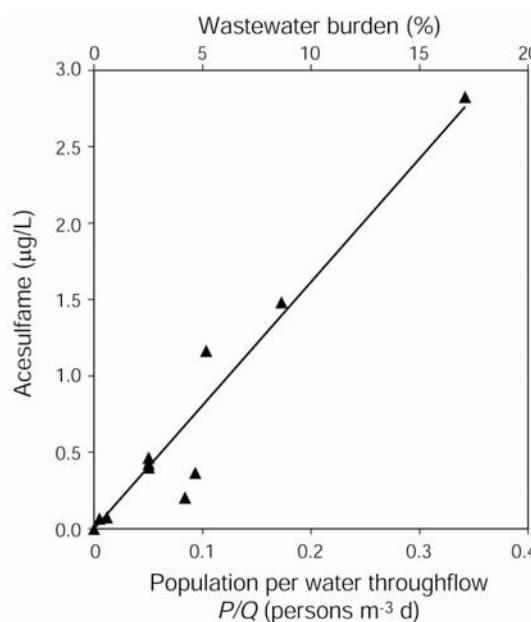
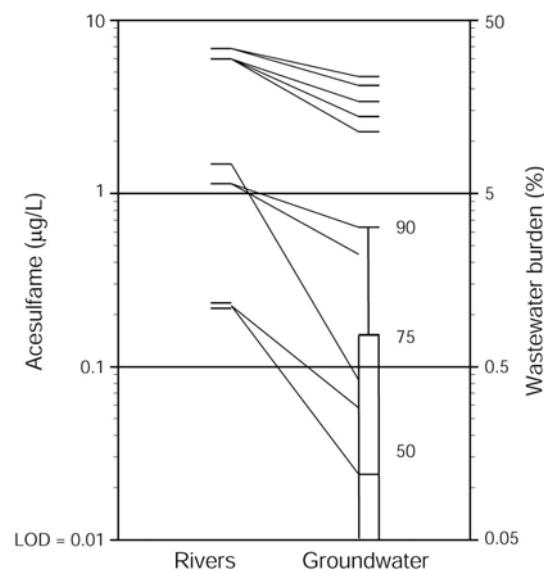


Fig. 2. Acesulfame in rivers and groundwater. Detectable in 65 of 100 groundwater samples; the numbers indicate percentile values. Some groundwater samples are linked to the infiltrating river sample upstream of the pumping stations. The second ordinate indicates the approximate wastewater burden, derived from a mean acesulfame concentration of $\approx 20 \mu\text{g/L}$ in wastewater.



From 3D-pharmacophore models to synthetic route towards anti-HIV agents

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Human Immunodeficiency Virus (HIV) infection is one of the leading causes of death in the world. Although a great deal of research has been focused on the development of efficient anti-AIDS therapeutic strategies, at present neither a vaccine nor an effective drug able to solve definitively this problem is available. Thus, there is a pressing need for new and broadly effective therapeutics to combat HIV.

An essential step in the retroviral life cycle is the integration of the proviral DNA into the cellular genome of the host cell. Integration is mediated by the viral integrase (IN) enzyme and results in a provirus that remains present as long as the cell survives. Before integration, the viral cDNA is associated with a number of viral and cellular proteins to form a large nucleoprotein assembly called preintegration complex. Human cellular LEDGF/p75 (lens epithelium-derived growth factor) is one such protein. LEDGF binds HIV-1 IN via a small IN-binding domain (IBD) which is both necessary and sufficient for the interaction with the enzyme.

The present research is addressed toward the rational design and synthesis of new small molecules as IN and IN-LEDGF/p75 interaction inhibitors.(1-3)

Ligand- and structure-based pharmacophore models have been developed and used for the design of new scaffolds of potential anti-HIV agents. By functionalizing the different designated scaffolds, a number of structurally diverse molecules has been prepared for properly exploring a large chemical space.

The most innovative eco-friendly methods and technologies have been used for the synthesis of the new compounds. In particular the application of microwave-assisted organic synthesis was adopted in the steps requiring heating in order to shorten reaction times and to increase the yields. With the aim to obtain small library of the designed derivatives, solution-phase parallel synthesis has been also planned. The developed synthetic protocols were highly efficient and the obtained compounds represent interesting analogues useful for their application in medicinal chemistry having showed potent inhibitory effects on IN enzyme and its interaction with co-factor LEDGF/p75.

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Identification and quantification of products formed via photolysis of decabromodiphenyl ether

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Background: Decabromodiphenyl ether (DecaBDE) is used as an additive flame retardant in polymers. It has become a ubiquitous environmental contaminant, particularly abundant in abiotic media, such as sediments [1], air [2,3] and dust [4-9], and also present in wildlife [10-13] and in humans [9]. The perbromination of BDE-209 makes it vulnerable to a range of chemical reactions, such as substitution, reduction and photolysis [14-17]. The latter two reaction pathways are leading to, among other products being formed, lower brominated diphenyl ether congeners [14,16,18,19]. Anaerobic reductive debromination of decaBDE has been shown in sediment [20], sewage sludge [21] and by anaerobic bacteria [22]. This work is aimed at identifying and assessing the relative amounts of products formed after UV irradiation of BDE-209.

Materials and methods: The experimental procedure is based on the work previously described by Eriksson et al. 2004 [15,23]. BDE-209, dissolved in tetrahydrofuran (THF), methanol or combinations of methanol:water, was exposed to UV-light for 100 or 200 minutes. Samples were analyzed by gas chromatography / mass spectrometry (electron ionization) for polybrominated diphenyl ethers (PBDEs), dibenzofurans (PBDFs), methoxylated PBDEs and phenolic PBDE products.

Results: The products formed were hexaBDEs to nonaBDEs, monoBDFs to pentaBDFs and methoxylated tetraBDFs to pentaBDFs. The products found in the fraction containing halogenated phenols were assigned to be pentabromophenol, dihydroxytetrabromobenzene, dihydroxydibromodibenzofuran, dihydroxytribromodibenzofuran and dihydroxytetrabromodibenzofuran. The PBDEs accounted for approximately 90% of the total amount of substances in each sample and the PBDFs for about 10%.

Conclusions: Photolysis of decaBDE yields a wide span of products, from nonaBDEs to hydroxylated bromobenzenes. It is evident that irradiation of decaBDE in water and methanol yields OH-PBDFs and MeO-PBDFs, respectively. BDE-202 (2,2',3,3',5,5',6,6'-octabromodiphenyl ether) is identified as a marker of BDE-209 photolysis. BDE-209, is primarily forming debrominated diphenyl ethers with higher persistence which are more bioaccumulative than the starting material when subjected to UV light. Hence, DecaBDE should be considered as a source of these PBDE congeners in the environment.

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Laboratory leaching study of Polycyclic Aromatic Hydrocarbons through soil columns

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Polycyclic Aromatic Hydrocarbons (PAHs) are among the most widely distributed pollutants in the environment posing great threats to human health since some PAH species have been identified as carcinogenic, mutagenic and teratogenic. Soil contamination by PAHs is a worldwide environmental problem. Soil acts as a filter for seepage water and thus plays an outstanding role for the environmental fate of PAHs. Their input to soils is governed by two major pathways: (a) wet/dry deposition of combustion products following atmospheric transport and (b) disposal and spills of PAH-enriched products at industrial sites. Therefore, understanding the transport and fate of PAHs in soil is a useful tool for developing remediation strategies for contaminated areas. Laboratory leaching procedures can be used for source term determination as a basis for risk assessment for soil-groundwater pathways on contaminated sites.

The purpose of this study was to investigate the leaching potential of PAHs and their residues in six unattached Greek soils with varying physical and chemical properties. The leaching study was performed under controlled laboratory conditions (OECD, 312; Gupta, 2004). Briefly, glass columns were packed with 100 g of soil, saturated with artificial rain and equilibrated for 24 h. After draining, the surface of each soil column was treated with a mixture of 18 PAHs. Artificial rain (3000 mL in total) was continuously applied to soil columns and several fractions of soil leachates were sequentially collected. Columns were run over a range of L/S ratios varying from 1 to 30 mL/g (dm). At the end of leaching experiments, each soil column was horizontally sectioned into two equal segments. Soil segments and leachates were analysed for PAHs by GC/MS.

Results were interpreted on the basis of the liquid to solid ratios (L/S), which play an important role in the assessment of leaching behaviour. In all soil types, only low- and medium-molecular weight PAHs were detectable in leachates exhibiting different leaching patterns. Even after a continuous rainfall of approximately 78 cm (equivalent to 3000 mL of leachate), the major mass (55-98%) of PAHs remained in the upper half soil segment.

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New synthetic routes for N-terminal valine adducts of isocyanates to be used as references for biomonitoring using LC/MS/MS

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Isocyanates have a wide range of uses as chemicals in industry to produce pesticides, flexible and rigid foams, elastomers, coatings and textiles. It is claimed that isocyanates are one of the main causes of occupational asthma. Analysis of adducts to hemoglobin (Hb) is a method to monitor exposure to isocyanates. Particularly useful is the measurement of carbamoylation of N-terminal valines in Hb, after detachment as hydantions. The synthesis of references from the reactive isocyanates, especially diisocyanates, has been problematic due to by-reactions and polymerisation of the isocyanate starting material. A simpler, safer and more general method for the synthesis of valine adducts of isocyanates with much higher yields has been developed using N-[(4-nitrophenyl)carbamate]valin methylamide (NPCVMA) as the key precursor to adducts of various mono- and di-isocyanates of interest. By reacting NPCVMA with a wide range of primary amines, carbamoylation urea products are formed without the use of toxic isocyanates. These ureas can be used as standards for identification and quantification of isocyanate adducts. This new synthetic pathway for the hydantions of the carbamoylated N-terminal valine with isocyanates is useful in the preparation of a wide range of reference compounds derived from mono- and diisocyanates where polymerisation has been a difficulty. The urea products form hydantions after acid hydrolysis are used as references for measuring isocyanate exposure. The new quantification method has been performed using LC/MS/MS in biological samples showing the occurrence of background levels of valine hydantion (VH) and phenyl hydantion (PVH).

Perfluorinated substances in the Arctic marine system

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Perfluoroalkyl compounds (PFCs) were determined in ~2 L samples collected in the Canadian Arctic onboard the Canadian ice-breaker CCGS ‘Amundsen’ in conjunction with the Circumpolar Flaw-Lead System Study (CFL), during the International Polar Year (IPY). A total of 80 samples were collected from March to June 2008, when the ‘Amundsen’ was located in the eastern part of the Beaufort Sea near Banks Island. Whenever possible, an integrated sampling approach, combining air, snow, ice and seawater sampling at various CFL stations, was conducted to examine transfer between those compartments.

Results for sea-ice, snow and water are reported herein. Following the procedure described elsewhere (1), after filtration the dissolved phase was loaded on SPE Oasis WAX cartridges on board of the ship. Cartridges were then eluted in a clean laboratory (class 10 000) at GKSS in Germany. Finally the extracts were analyzed using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC–MS/MS).

Even though a recent work on PFCs distribution in superficial water of the Atlantic Ocean (1) together with previous investigations (2, 3) provide new insight into the global occurrence of these contaminants, oceanic measurements are still limited. Results presented here are the first data available for this region of the Arctic. So far PFCs have been measured in open-ocean water, while during this campaign water samples were also collected below the ice cover in the ocean. The objectives of this study are to assess inputs of PFCs to remote regions such as the Arctic and to contribute establishing the dominant transportation pathway involved in global occurrence and distribution of PFCs. It has not been established yet whether PFCs presence especially in remote environments is directly related to oceanic currents or to long-range atmospheric transport of precursor compounds.

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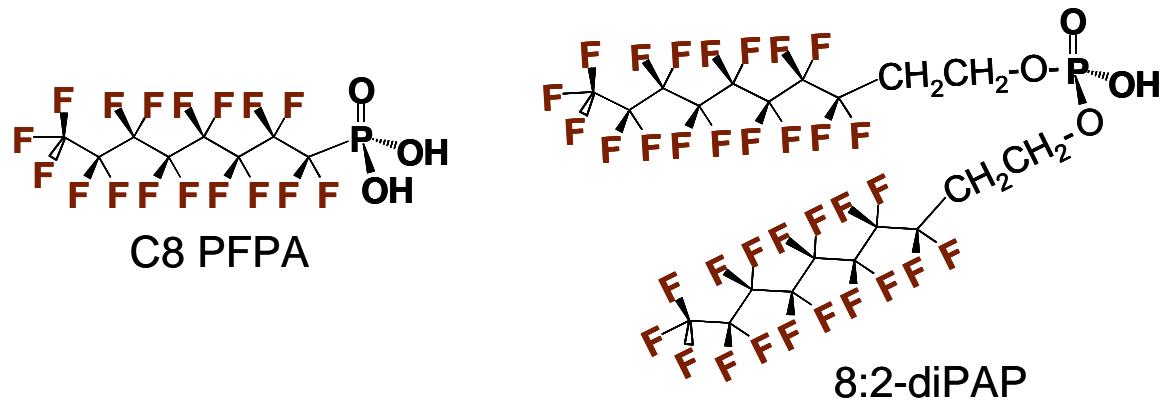
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Seasonal trends in perfluoroalkyl phosphonic acids and polyfluoroalkyl phosphoric acids in Canadian rivers

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Mono- and di-substituted polyfluoroalkyl phosphoric acid (mono- and di-PAPs) and perfluoroalkylphosphonic acids (PFPAs) are polyfluorinated chemicals that are used in to provide water and oil repellency in food-contact packaging, and as foam stabilizers in personal care products and pesticide formulations. Previous studies indicated PAPs undergo metabolism to produce perfluorocarboxylates (PFCAs) in rodents, suggesting PAPs may be a significant source of PFCA exposure in humans. The PFPAs are a high production volume chemical (>4000 kg/y 1998-2002). PFPAs are resistant to degradation and are recalcitrant similar to the highly persistent perfluorocarboxylates (PFCAs). In 2006, the USEPA prohibited the use of PAPs and PFPAs in pesticide formulations used for food crops, indicating concern over these chemicals in the environment. In order to gain an understanding of the distribution of these compounds in Canada, three major rivers were sampled monthly for this study: Fraser River in western Canada, Nelson River in central Canada, and the St. Lawrence River in eastern Canada. Analysis of PAPs and PFPAs was conducted in these samples to qualify spatial distribution and use of these compounds as well as the seasonal variability which may be linked to crop growing seasons. Solid-phase extraction was conducted on the samples using weak anion exchange cartridges. Analysis of di-PAPs ($(OH)(O)P(OCH_2CH_2(CF_2)_{x,y}F)_2$, where x and $y = 4,6,8,\text{or } 10$) and PFPAs ($(F(CF_2)_xP(O)(OH)_2$, where $x = 6, 8, \text{ or } 10$) was performed using liquid chromatography tandem mass spectrometry (LC-MS/MS) with quantification using authentic standards. Using measured flow rates at sampling stations permitted the calculation of mass flows of PFPAs and PAPs in these major rivers.



Polybrominated diphenyl ethers (PBDEs) in marine sediments of Thermaikos gulf, Greece

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Polybrominated diphenyl ethers (PBDEs) are organobromine compounds used as flame retardants in a wide array of products. This fact along with their structural similarities with persistent organic pollutants renders them as a group of substances causing additional worldwide pollution that reaches even remote areas (Rahman et al., 2001)

Thermaikos gulf is located in north Greece, on the rim of Thessaloniki city (population of 1-1.5 million) and is used for various activities of economic and social interest, like fish and mussel cultures, fishing, shipping and recreation.

Marine sediment samples from Thermaikos gulf were collected in a two year period seasonal sampling pattern and analyzed for PBDEs, according to Jensen et al., 2003, slightly modified to apply to sediments.

In all seven sampling stations PBDEs were detected, their average total concentration range (Σ PBDEs) from 0.29 to 4.98 ng/g d.w. (Table 1). The location of each sampling site, in relation with the concentrations observed, suggested pollution from industrial and urban activities. BDE-209 was the predominant congener in all samples.

In comparison to other worldwide studies, Thermaikos gulf is considered to be low-polluted, as the levels of PBDEs observed were in a lower order of magnitude.

SampL St.	bde28	bde47	bde99	bde100	bde153	bde154	bde183	bde190	bde209	Σ BDEs
S1	0.0047 (0.42%)	0.0527 (4.79%)	0.0182 (1.65%)	0.0042 (0.38%)	0.0019 (0.17%)	0.0012 (0.11%)	0.0015 (0.13%)	0.0007 (0.06%)	1.0150 (92.29%)	1.0998
S2	0.0050 (0.10%)	0.0653 (1.33%)	0.0299 (0.61%)	0.0153 (0.31%)	0.0066 (0.13%)	0.0115 (0.23%)	0.0127 (0.26%)	0.0003 (0.01%)	4.7703 (97.02%)	4.9168
S3	0.0033 (0.65%)	0.0343 (6.81%)	0.0103 (2.04%)	0.0038 (0.75%)	0.0012 (0.23%)	0.0009 (0.18%)	0.0007 (0.15%)	0.0003 (0.06%)	0.4486 (89.13%)	0.5033
S5	0.0076 (0.30%)	0.0700 (2.76%)	0.0609 (2.40%)	0.0094 (0.37%)	0.0030 (0.12%)	0.0028 (0.11%)	0.0028 (0.11%)	0.0006 (0.02%)	2.3760 (93.80%)	2.5331
S6	0.0044 (1.33%)	0.0651 (19.51%)	0.0330 (9.88%)	0.0084 (2.52%)	0.0014 (0.41%)	0.0016 (0.49%)	0.0013 (0.39%)	0.0006 (0.17%)	0.2180 (65.29%)	0.3339
S7	0.0043 (1.14%)	0.0503 (13.53%)	0.0175 (4.69%)	0.0045 (1.20%)	0.0044 (1.18%)	0.0023 (0.61%)	0.0725 (19.48%)	0.0015 (0.42%)	0.2149 (57.74%)	0.3721
S8	0.0064 (2.47%)	0.0739 (28.58%)	0.0175 (6.78%)	0.0047 (1.80%)	0.0017 (0.64%)	0.0012 (0.45%)	0.0012 (0.45%)	0.0003 (0.12%)	0.1518 (58.73%)	0.2585

Table 1: PBDE congener profile and mean concentration levels (ng/g d.w.) in sediments

References:

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Annual time series of air concentrations of polyfluorinated compounds

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Volatile and semi volatile polyfluorinated substances such as fluortelomer alcohols (FTOH), fluorotelomer acrylates (FTA), perfluorinated alkylated sulfonamides (FASA), or perfluoroalkylsulfonamido ethanols (FASE) are precursors of persistent perfluorinated compounds such as PFOS or PFOA and might contribute to the contamination of remote regions due to their transport over long distances. Studies describing the occurrence and distribution of PFC in ambient air only display a snapshot of PFC air concentrations; emission events, seasonality, or fluctuations in the highly dynamic atmospheric system are not accounted for. Therefore the aim of this study was to determine and characterize seasonal variations of PFC concentrations. Per- and polyfluorinated organic compounds (PFC) in air were determined in samples taken at two sites in the vicinity of Hamburg, Germany over a period of 14 months. PUF/XAD-2/PUF cartridges and glass fiber filters were applied for the collection of airborne PFC. A set of volatile, neutral PFC and ionic, non-volatile PFC like perfluorinated carboxylates (PFCA) and sulfonates (PFSA) were determined using GC-MS and HPLC-MS/MS. Backwards trajectory analysis was performed to elucidate the origin of the air mass parcels sampled. PFC were predominantly detected in the gas phase. Concentrations fluctuated in dependence on the air mass origin and potential PFC sources. Maximum individual PFC concentrations reached 600 pg m^{-3} (8:2 FTOH) in the gas phase and 13 pg m^{-3} (perfluorooctane sulfonate, PFOS) in the particle phase. The class of FTOH clearly dominated the gas-phase substance spectrum.

Polyfluorinated Compounds in the Atmosphere of the Atlantic and Southern Ocean: Evidence for a global Distribution

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Volatile and semi volatile polyfluorinated substances such as fluortelomer alcohols (FTOH), fluorotelomer acrylates (FTA), perfluorinated alkylated sulfonamides (FASA), or perfluoroalkylsulfonamido ethanols (FASE) are precursors of persistent perfluorinated compounds such as PFOS or PFOA and might contribute to the contamination of remote regions due to their transport over long distances. In order to investigate their large-scale distribution, air samples taken onboard several research vessels in the Atlantic Ocean, the Southern Ocean, and the Baltic Sea as well as at one land-based site close to Hamburg, Germany in 2007 and 2008 were analysed for per- and polyfluorinated organic compounds (PFC). A set of neutral, volatile PFC and ionic non-volatile PFC like perfluorinated carboxylates (PFCA) and sulfonates (PFSA) were collected on PUF/XAD-2/PUF cartridges and glass fiber filters and determined using GC-MS and HPLC-MS/MS. PFC were detected in all air samples, even in Antarctic regions and occurred predominantly in the gas phase. Total gas-phase concentrations of ship-based samples ranged from 4.5 pg m^{-3} in the Southern Ocean to 335 pg m^{-3} in European source regions. Concentrations of 8:2 FTOH, the analyte that was usually observed in highest concentrations, were between 1.8 and 130 pg m^{-3} . PFC concentration decreased from continental towards marine regions and from Central Europe towards the Arctic and the Antarctic. Southern hemispheric concentrations of individual PFC were significantly lower than those of the northern hemisphere. Based on this data set, marine background PFC concentrations and atmospheric residence times were calculated. This study gives further evidence that volatile PFC undergo atmospheric long range transport to remote regions and may contribute to their contamination of persistent PFCA and PFSA.

Recycling of dioxins and dioxin-like compounds in abiotic environmental compartments

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The decreasing levels of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in the environmental matrix have been observed in the last decade in many countries, due to the decreasing release from waste incineration and other known sources. Information on similar dioxin-like compounds containing in their structure sulfur instead of oxygen, i.e. polychlorinated thianthrenes (PCTAs) and dibenzothiophenes (PCDTs) are limited, but the occurrence of PCDTs has been confirmed in stack gases, sediments, biota, sludge and landfill leachates ^{1,2}, and similar tendencies might be expected. Thus, in spite of dioxin release, problems of mobilization and immobilization of dioxins already present in the environment are of equal importance.

Loads and recycling of PCDDs, PCDFs and PCDTs in the abiotic chain: waste – leachates – sewage treatment plant – sludge, was studied. PCDD/F/Ts levels were measured in the leachates from the biggest Polish landfill “Rokitno”. Approximately 44 m³ of leachate waters from the “Rokitno” drainage systems was collected daily (7 days per week) and transported to the municipal wastewater treatment plant (MWTP) in Lublin cit. PCDD/F/T concentrations were measured in the digested sludge. Analytical procedure was described elsewhere ².

Sum concentrations of 2,3,7,8-substituted PCDD/Fs in the leachates were within the range of 25.68 – 431.0 ng /dm³, which is equivalent to 7.8 – 36.40 ng TEQ/dm³. Concentrations of 2,3,7,8-PCDTs were within the range of 9 – 202 ng /dm³.

Based on the mean concentration of PCDD/F/Ts in wastes, amount of deposited wastes, and leachate volume we calculated than over 10% of PCDD/F/Ts is released from landfill and introduced into MWTP. According to previous studies on dioxin pathway in the MWTP, it should be stated that over 90% of PCDD/F/Ts entering MWTP goes to the sludge. PCDD/F concentrations in sludge were found to be within the range 635.5 – 10,500 ng/kg d.m., which is equivalent to 25 – 65 ng TEQ/kg d.m., while level of PCDTs was within the range of 55.9 – 119 ng/kg d.m.

Very low decrease of PCDD/Fs levels in the sludge in Lublin MWTP observed during last years may result from this recycling pathway ³. Further fate of contaminants depends on the sludge utilization method. Spilling of dioxins and dioxin-like compounds in the landfill leachates might have a long-time effect on the environment if leachates are treated together with municipal sewage. PCDD/F/Ts introduced into the environment are hardly degradable and may recycle together with waste recycling.

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Spatial distribution of perfluorinated compounds in herring liver along the Swedish coast

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Within the Swedish Environmental Monitoring Programme perfluorinated compounds (PFCs) have been analysed in herring liver from locations along the entire Swedish coast line starting from 2005. Up to now, results from three consecutive years (2005-2007) are available and show a consistent picture of concentrations, spatial distribution and trends over the three years. Results from 2007 for the most important PFCs are depicted in the figure.

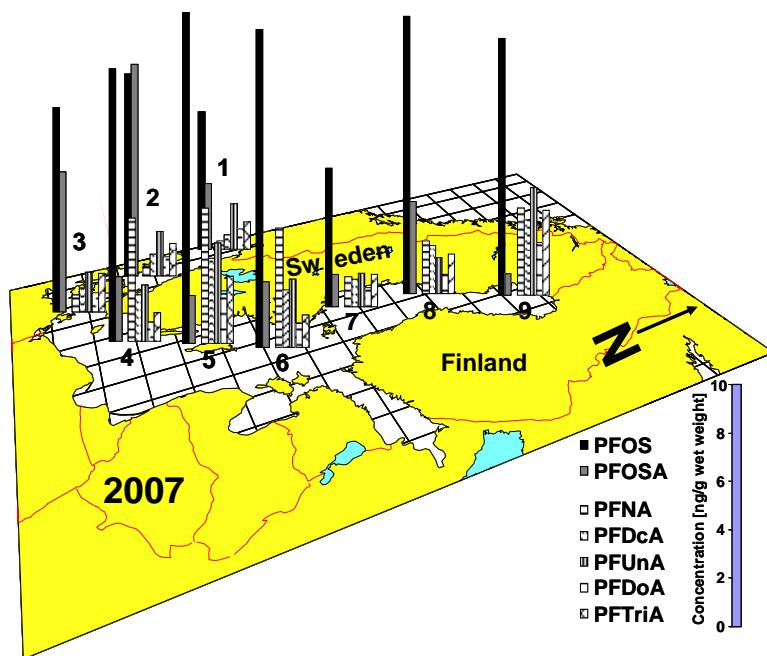


Figure. PFCs in herring liver sampled in 2007 along the Swedish coast. Mean values of two pools of 12 individuals per location are given.

In general, PFOS was the predominant PFC detected at levels around 10 ng/g wet weight followed by PFOSA (west coast, sampling points 1-3), PFNA (southern Sweden, Baltic Sea coast, 4-6) or the odd and long carbon chain length PFCAAs (northern Sweden, Baltic Sea coast, 7-9). These observations could tentatively be explained as follows:

- PFOS is quite evenly distributed throughout the whole study area. This is probably a result of its persistence and long history of use. Additionally, there do not seem to be any major current point sources of PFOS along the Swedish coast.
- The PFOSA/PFOS ratio is much higher along the west coast compared to the Baltic. This could indicate current sources of PFOSA (a PFOS precursor with limited environmental lifetime) in the vicinity of the Swedish west coast.
- The PFCA concentrations in general are lower along the west coast compared to the Baltic. This may be a result of dilution at the west coast, compared to the long residence time of the water in the almost enclosed Baltic Sea.
- PFNA is the dominant PFCA along the southern Baltic coast, possibly indicating current use in this relatively densely populated part of Sweden. PFDcA to PFTrIa are more evenly distributed and the levels may be ruled by long range transport scenarios.

Acknowledgments. Mats Hjelmborg, Henrik Dahlgren, Anne-Sofie Kärsrud and Merle Plassmann are thanked for help with sample preparation. The study was funded by the Swedish EPA.

Selective enantiomeric enrichment of hexabromocyclododecane in human breast milk samples from Spain

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The objective of this study was to determine HBCD diastereoisomer levels in human breast milk from Spain and to provide valuable information to evaluate the body burden of mothers and the exposure to this flame retardant in infants via breast feeding. Moreover, enantiomeric fractions (EFs) were calculated in order to investigate potential selective enantiomeric enrichment in human bodies.

Samples of human breast milk ($n=33$) from A Coruña (NW of Spain) collected between 2006 and 2007 were analyzed for HBCD diastereoisomers and enantiomers. HBCD was detected in 30 out 33 human milk samples, at concentration levels ranging between 3 and 188 ng/g lw, with a median value of 27 ng/g lw, showing higher levels than those published for other countries. Diastereoisomeric pattern shows the predominance of the γ -isomer, with low contribution of the α -isomer, and the β -isomer being below limit of quantification. However, in six samples, there is a dominance of the α -isomer versus the γ -isomer. Moreover and for the first time, HBCD enantiomeric analysis was carried out in human breast milk samples showing a selective enantiomeric enrichment in human body (Figure 1). As regards α -HBCD, an enrichment of (-)-enantiomer was observed. However, in the case of γ -HBCD, no clear preference for one or the other enantiomer was found. Finally, and based on the calculated HBCD concentrations in human breast milk from Spain, the daily ingestion rate of HBCD was estimated. The nursing infant dietary intake for HBCD was set at 175 ng/kg body weight per day.

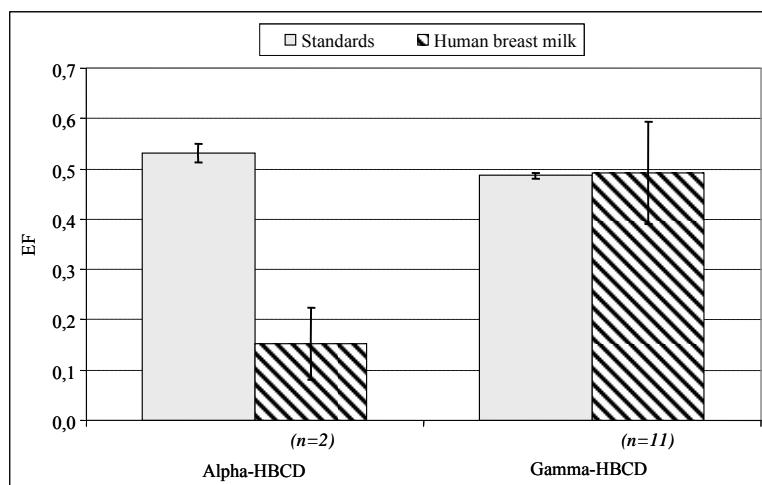


Figure 1. EF values (mean \pm sd) in standards and human breast milk samples analyzed.

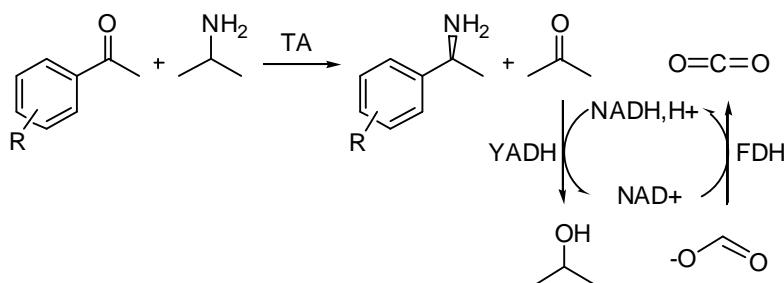
High yield transamination with isopropyl amine as donor, by employment of YADH and in situ cofactor regeneration

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Synthesis of chiral amines with transaminases has been shown to be feasible and effective¹. The reaction is performed with a ketone of choice, and an amine donor. Different techniques to improve the yield in this equilibrium reaction have been devised, e.g. by introducing secondary enzymes.^{2,3,4} Here we present a method for reducing the formed acetone, when using isopropyl amine as the amine donor, by employing *S. cerevisiae* alcohol dehydrogenase (YADH), which is specific for smaller alcohols and ketones. The cofactor is regenerated by Formate dehydrogenase (FDH).



Financial support from VINNOVA (The Swedish Governmental Agency for Innovation Systems) is gratefully acknowledged.

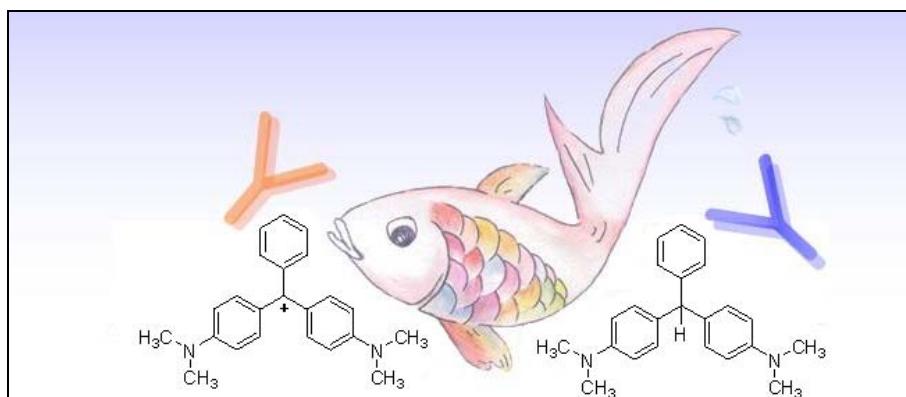
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Production of antibodies for selective detection of Malachite Green and Leucomalachite Green in fish and fishpond water

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This study provides a practical method for production of the antibodies against malachite green (MG) and its primary metabolite leucomalachite green (LMG). Two ELISA kits are constructed with the MG- and LMG-antibodies for detection of the residual MG and LMG in fish muscle and fishpond water. The detection limit is established at the level of 0.05 µg/L for both MG and LMG. Our ELISA kits show the advantages of good specificity, high sensitivity and convenience in rapid screening of MG and LMG residues. The sample of fishpond water, without extraction or prior preparation, is directly assayed by the ELISA kit. More than 80 fish samples can be simultaneously tested in a kit. The toxic crystal violet and its metabolite leucocrystal violet of illegal use in aquaculture are detected by our prepared MG- and LMG-antibodies, whereas the antibodies do not cross react with common antibiotics, sulfonamides and benzene derivatives.



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Two-dimensional isotope fractionation approach (TDIFA) for elucidating benzene and toluene biodegradation pathways

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The two-dimensional isotope fractionation approach (TDIFA) was applied in order to differentiate benzene and toluene biodegradation pathways under oxic and anoxic conditions. The carbon and hydrogen isotope fractionation associated to microbial benzene and toluene degradation was investigated in laboratory batch experiments with anaerobic and aerobic cultures.

Carbon as well as hydrogen enrichment factors (ε_C , ε_H) varied for the specific pathways and degradation conditions, respectively, so that from the individual enrichment factors only limited information could be obtained for the identification of biodegradation pathways. However, using the slope derived from hydrogen vs. carbon isotope discriminations or the ratio of hydrogen to carbon enrichment factors ($\Lambda = \Delta H / \Delta C \approx \varepsilon_H / \varepsilon_C$), degradation mechanisms could be distinguished.

Although experimentally determined Λ -values partially overlapped, specific ranges could be determined for different benzene biodegradation pathways (1). Λ -values were < 2 for dihydroxylation, between 7 and 9 for monohydroxylation and > 17 for anaerobic degradation. Moreover, variations in Λ -values suggest that more than one reaction mechanism exists for benzene monohydroxylation as well as for anaerobic benzene degradation (1).

For toluene biodegradation, the highest Λ -value was estimated for methyl monohydroxylation ($\Lambda = 53$). The lowest value was observed for ring dihydroxylation ($\Lambda < 2$). Λ -values for organisms attacking toluene under anoxic conditions by benzylsuccinate synthase were significantly different and ranged from $\Lambda = 4$ for a phototrophic strain, $\Lambda = 11 - 15$ for nitrate reducers to $\Lambda = 27 - 28$ for sulfate reducers (2).

Our results show that TDIFA has great potential to elucidate biodegradation pathways of pollutants in field and microcosm studies.

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Separation and NMR Characterisation of Hexabromocyclododecane (HBCDD)

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HBCDD is used commercially as a flame retardant, mainly in expanded and/or extruded polystyrene foam boards. The polystyrene foam boards are most often used as thermal insulators in buildings, but HBCDD is also used as a flame retardant for polymers used in other consumer products. Some examples include upholstery in textiles and plastic housings for electrical equipment.

Chemically HBCDD is classed as a halogenated cyclic aliphate which is manufactured by bromination of the π -bonds of *cis*-, *trans*-, *trans*-1-,5-,9-CycloDodecaTriene (CDT). In the bromination of CDT three major substitution isomers are formed, α -, β - and γ -HBCDD. The isomers enantiomeric pair of e.g. (+) α -HBCDD. This could be of importance to biota, which features many stereoselective systems indeed (-) α -HBCDD have been found to be more abundant in a population of fishermen's wives from the Swedish East coast.

In this study, samples of α -, β - and γ -HBCDD were isolated from technical grade HBCDD by separation with HPLC. Before the chromatographic separation the α - and β -HBCDD samples the relative concentration in each sample was altered in such a way that the concentrations of α - and β -HBCDD were enriched by thermal rearrangement and selective precipitation respectively.

Analysis of the enantiomeric pairs with NMR-spectroscopy was conducted to assign chemical shifts for the α -, β - and γ -HBCDD samples. This was successful when the experiments were conducted with THF-d₈ as solvent at 0°C, but not when DMSO-d₆ at 25°C was used. A significant line broadening was also observed at temperatures above -10°C for both solvents. Assignment of the DMSO-samples were complicated by not sufficiently resolved spectra, which made assignment of the NMR-signals hard. This is likely a temperature dependent effect since THF-samples run at higher temperatures also shows a significant line broadening.

Polychlorinated biphenyls and their metabolites in placenta samples from Spain

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Polychlorinated biphenyls (PCBs) are a group of ubiquitous pollutants that are usually present in environmental and biological samples as complex mixtures¹. It is well-known the toxic effects related to the presence of PCBs in animals and humans². However, it is still not clear that this toxicity is only due to PCB concentrations or is also due to the presence of PCB metabolites in the same individual. In a living organism, PCBs are initially metabolised by hepatic microsomal oxidases to their corresponding hydroxylated metabolites (OH-PCBs) which are eliminated mainly via the bile. However, some studies have also shown that OH-PCB metabolites can be bound to specific plasma proteins³. On the other hand, PCBs could be biotransformed through the mercapturic acid pathway to form the methyl sulfonyl PCB metabolites (MeSO₂-PCBs), which due to their lipophilic properties (similar to PCBs) and their resistant to further metabolic degradation tend to concentrate in lipid-containing tissues³.

PCB congeners and PCB metabolites show a different body distribution. So, it is important to investigate the accumulation patterns of PCBs and those of their metabolites in tissues not studied, such as human placenta, mainly when previous studies have demonstrated that PCBs are able to cross the placenta barrier reaching the foetus⁴. Placenta plays an important role as endocrine organ in the development of the foetus⁵ and, for this reason, the presence of endocrine disruptor compounds, such as, PCBs and their metabolites, in placenta samples is cause of concern.

The main objectives of the present work were to study the relationship between the concentrations of PCBs and their metabolites in placenta samples collected from the populations living in the Community of Madrid (Spain) and to report, for the first time, the concentration levels and accumulation profiles of PCB metabolites in placental samples from Spanish women.

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A QSPR method for the prediction of experimental half-lives of brominated flame retardants, their metabolites and chloro/bromophenols

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The higher the persistency is of a chemical the longer the compound will stay in the environment. Persistency is made up of the intrinsic properties of a compound, i.e. its physicochemical and chemical reactivity characteristics. The persistency is the abiotic parameter of a chemical that relate to the occurrence, partitioning and distribution of a chemical in each of the environmental compartments. Persistency is a key property for assessing the environmental fate of chemicals. The chemical reactivity of a compound is strongly influencing its bioaccumulative potential. The use of theoretical methods as alternative methods to estimate chemical characteristics has grown and become of importance for regulation, evaluation and risk assessment of chemicals. To evaluate the persistency of a chemical in the environment one should take into account the major degradation routes in different environmental compartments such as oxidation, radical reactions and UV degradation in air and water, reduction in soil and sediments. We have calculated a large suit of different physicochemical properties based on semi-empirical quantum calculations and using multiple regression methods to find correlations between physicochemical properties and experimentally derived oxidation half-lives ($t_{1/2}$). The training set consisted of 20 compounds: PBDEs 11, 28, 49, 66, 99, 153 and 6-OH-BDE17, 6-OH-BDE47, 6'-OH-BDE49, 2'-OH-BDE66, 6-OH-BDE85, 6-OH-BDE137 and 2-bromophenol, 2,4-dibromophenol, 2,6-dibromophenol, 2,4,6-tribromophenol, 2,3,4,6-tetrabromophenol, 2,3,4-trichlorophenol, bisphenol-A and trichlorobisphenol A. The prediction set consisted of 6 compounds: PBDEs 17, 47 and 4'-OH-BDE17, 6-OH-BDE90, 2,4,6-trichlorophenol and tetrabromobisphenol A. Using the training set and the use of multiple linear regression we constructed a linear mathematical model that related the oxidation half-lives to the calculated physicochemical properties. The results showed an excellent fit with a correlation coefficient R^2 of 0.91 and a goodness of prediction Q^2 of 0.87 and a Q^2_{ext} of 0.86 for the prediction set which is an excellent result. See the regression equation below:

$$\text{Log}(1/t_{1/2}) = 1.3871 - 24.4328 \times \mathbf{H}_{\text{charge}} + 0.2517 \times \Delta E + 1.9741 \times \mathbf{B} + 0.0221 \times \mathbf{pKa}$$

$$(n = 20, R^2 = 0.91, F = 36.5, p < 1.2E-7, S^2 = 0.49, Q^2_{ext} = 0.86)$$

Results show that the most reactive compounds is strongly correlated (with an correlation coefficient of $R^2=0.85$) to the hydrogen with the lowest positive charge (H_{charge}). The second most important variable is the energy difference between the E_{HOMO} of the substrate and E_{LUMO} of the oxidation agent (ΔE) or the potential for the substrate to have a nucleophilic reaction with the oxidation agent. Additional variables but with a decrease in importance is the hydrogen bonding basicity parameter (B) and pKa as compounds that are ionized at the experimentally utilized pH of 7.6 are more readily oxidized.

Analysis of PCDD/Fs in biota at the location of a former sawmill site

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Contaminated soils and sediments represent potential sources for food-chain accumulation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo-*p*-furans (PCDD/Fs). One of the tasks listed in the Dioxin Strategy of the Commission of the European Communities (2001) is to undertake a detailed survey of the locations of heavily contaminated soils and sediments. Old sawmill sites are often highly contaminated with PCDD/Fs, due to the widespread handling of chlorophenol (CP)-based wood preservatives. In particular, pentachlorophenol (PCPs) formulations contained high amounts of PCDD/F impurities. Sweden has approximately 400 CP and PCDD/F contaminated sawmills sites. The remediation of these sites would require enormous efforts and financial resources. As a consequence, many of these areas have therefore remained in their original condition and pose a potential risk to the surrounding terrestrial environment, and also to humans living in the vicinity. To be able to assess and quantify these risks, it is important to identify the PCDD/Fs transport routes from a contaminated site to biota and humans.

A former sawmill site, heavily contaminated, is Hillringssberg in Arvika, Sweden. The PCP-based preservative used at the former sawmill site was Dowicide G, which is known to be contaminated with PCDD/Fs during the manufacturing process. At a hot spot on the contaminated sawmill site, the TEQ PCDD/F level in soil was found to be 3450 times higher than the Swedish limiting value (200 ng TEQ/kg soil) of land for industrial use. This represents one of the highest measured PCDD/F levels in soil in Sweden.

The aim of the study was to provide a food web in order to investigate the transfer of PCDD/Fs from the current sawmill site to the biota. The food web provides field data on levels of PCDD/Fs by isomer specific analysis of soil, earthworms, farmed salmon, sheep grazing on the former sawmill site and milk from cows nearby the site. Chemical analysis was performed by HRGC/HRMS. In studying the levels as well as congener and isomer patterns of PCDD/Fs, information on whether the PCDD/Fs from the wood preservatives have reached the biota and food and consequently contribute to environmental and human health risks can be obtained.

The results from the food web study will be presented and shows that PCDD/Fs can pass from the soil to the food web. The result shows that the congener patterns of PCDD/Fs in the earthworms and sheep, grazing at the sawmill site, correlate well with the congener patterns in the soil from the contaminated sawmill site. The cow milk shows a similar congener pattern. The farmed salmon does not show the same pattern as it has been fed with commercial feed.

Perfluorinated surfactants in the Baltic Sea common guillemot – exposure, tissue distribution and maternal transfer

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Perfluorinated alkyl surfactants (PFAS) are ubiquitous contaminants in the environment. Previous studies have shown that eggs from the common guillemot (*Uria aalge*) in the Baltic Sea are highly contaminated with PFAS, with a low margin of safety from toxic effects. However, up to now, the exposure situation in the adult bird has not been investigated. In this study PFAS were investigated in tissues and organs of the common guillemot, and its main food source, the herring. Concentrations of 11 perfluorinated carboxylates, four perfluorinated sulfonates, and perfluorooctane sulfonamide were determined in egg, liver, kidney, and muscle of adult guillemot, as well as in liver from chicks, all sampled in 1989. Additionally, whole herring homogenates from 2005 were analyzed.

Quantifiable concentrations of PFAS were found in all samples. Perfluorooctane sulfonate (PFOS) was predominant, followed by perfluorotridecanoate (PFTriDA) and perfluoroundecanoate (PFUnDA). The median concentration of PFOS was highest in eggs followed by chick liver, kidney, adult liver, and muscle. Comparatively low levels of PFOS were found in herring, leaving a blurred picture of uptake routes. PFAS concentrations in livers of male and female guillemots did not differ significantly. The magnitude of transfer of different PFAS from the mother bird to the forming egg showed a pattern that resembled the pattern for bioaccumulation potential of PFAS homologues. The ratio of levels in egg/female liver, indicating mother-to-egg transfer capacity, increased with increasing PFAS chain length. PFOS showed a higher tendency for transfer than carboxylates of carbon chain lengths C9-C13. More toxicity data are needed to assess toxicological risks from the perfluorocarboxylates also found in guillemots.

Modelling the fate of petroleum type pollutant in the environment by simulated biodegradation

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The practical aim of simulated petroleum biodegradation, *in situ*, *ex situ* or in the laboratory is mainly to assess how much of this pollutant can be removed or decomposed by processes of microbial decomposition in different segments of the environment. However, bearing in mind that using these procedures the petroleum pollutant cannot decompose completely, simulated biodegradation can also be used to assess what is its fate in the environment, i.e., at what order and pace some compounds from oil decompose in the environment. The aim of this paper is to present the results of several experiments of simulated biodegradation of oil and petroleum pollutant.

First, microorganisms were analysed in a surface water sample from a canal (alluvial formation of the Danube, Oil Refinery Pančevo, Serbia), into which wastewater is released. The consortia of microorganisms were isolated from the water sample. The simulation laboratory experiments of biodegradation were conducted with the biomass suspension and crude oils (paraffinic and naphthenic types) within a three-month period.

Petroleum degradation by bacteria and fungi isolated from mud samples belonging to Pančevo also has been investigated. Total isolated microorganisms were divided into three parts. One part was added with actidione antifungicide so that only bacteria propagated in it. The second part was added with streptomycin antibiotic (fungi propagated in it). The third part contained consortium of fungi and bacteria. Paraffinic crude oil was a substrate in 30, 60 and 90 day's experiments.

Finally, the experiment of *ex situ* soil bioremediation was performed at the locality of Pančevo. Approximately a quantity of 150 m³ of polluted soil was collected. The experiments of biostimulation, bioventilation and reinoculation of autochthonous microbial consortium were carried out during the six-month period. The changes in the quantity and composition of the pollutant were monitored by analysis of the samples of the polluted soil taken in time spans of two weeks.

In all cases the contents of saturated hydrocarbons, aromatic hydrocarbons, alcohols and fatty acids in extracts was determined (the group composition). *n*-Alkanes, isoprenoid aliphatic alkanes and polycyclic alkanes in the aliphatic fractions were analysed using gas chromatography (GC) and gas chromatography mass spectrometry (GC-MS).

The experiments carried out show that the most susceptible to decomposition are *n*-alkanes (the most abundant compounds in the majority of oils). Polycyclic, especially aromatic hydrocarbons are resistant to microbial decomposition to a great extent. It has also been concluded that hardly soluble compounds transform under certain conditions to more active soluble fractions.

Levels of organochlorine compounds in *Mytilus galloprovincialis* from the Adriatic Sea in 2003 and 2008

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Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) belong to a group of persistent organic pollutants (POPs), and despite restricted and/or banned production and use, they are still found in all environmental compartments. Because of their high lipophilicity, they accumulate in the adipose tissue of animals and humans. The Mediterranean blue mussel (lat. *Mytilus galloprovincialis*) is a well known bioindicator of environmental pollution due to its great capacity to accumulate different contaminants, weak mobility, and wide geographical distribution.

In this study we investigated the levels of 17 PCB congeners and 7 OCPs in the edible tissue of mussels collected at two locations (L1-Martinska and L2-Ina-Vinil) on Croatian coast in 2003 and 2008. At L1 PCBs ranged between 0.09 and 12.77 ng g⁻¹ in 2003 and between 0.05 and 7.45 ng g⁻¹ dry wt in 2008. The respective ranges for L2 were 0.27-50.67 and 0.16-13.81 ng g⁻¹ dry wt. OCPs at L1 ranged between 0.11 and 4.34 ng g⁻¹ in 2003 and between 0.09 and 2.41 ng g⁻¹ dry wt in 2008. The respective ranges for L2 were 0.31-6.83 ng g⁻¹ in 2003 and 0.23-4.59 ng g⁻¹ dry wt in 2008. Analysed compounds showed similar profiles in all four analysed samples. From the OCP group, levels of α-HCH were the lowest in all analysed samples, followed by the DDD and HCB (similar levels found). Then followed β-HCH and γ-HCH with similar values, and finally DDT and DDE with the highest levels. PCBs also showed similar profiles on both locations in both years. The lowest levels were found for PCBs 114, 74, 157, and 189, while the highest levels were found for PCBs 52, 153, 101, 123, and 118.

At both locations, the levels of all analysed compounds had decreased over the five years at same or very similar rate (between 30 and 60 %). The exceptions were β-HCH and PCB-52 (with 75 % and 78 % decrease at both locations, respectively). The decrease was slower for PCB-28 (11 % at both locations) and α-HCH (18 % at L1 and 26 % at L2).

α-HCH/γ-HCH and DDE/DDT ratios are often used to see if there is a fresh input of γ-HCH or DDT in the environment. Ratios below 1 indicate fresh contamination. DDE/DDT ratio at L1 was 2.05 in 2003 and 1.62 in 2008 and at L2 1.05 and 0.83. The respective α-HCH/γ-HCH ratios were 0.05 and 0.09 at L1 and 0.08 and 0.15 at L2.

All the values obtained for mussels from the two locations on the Croatian coast are orders of magnitude below the Croatian maximum permissible levels (MLP) for PCBs and OCPs in mussels for human use (1, 2) and they do not pose any threat for human health.

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The equations for the determination of acidity of the dilute solutions of weak multibasic organic acids

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We suggest the new theoretical method for determination of acidity of the dilute solutions of weak multibasic organic acids which are widely used in medicine, pharmacology, food industry, organic synthesis and are often considered as pollutants and contaminants.

The general mass action equation suggested by us for the m dissociation step of weak multibasic organic acid H_nA with the close values of dissociation constants of various steps is written as follows:

$$K_m = \frac{[H^+](x_m - x_{m+1})}{x_{m-1} - x_m} F_m \quad (1)$$

where K_m is the dissociation constant for m step, $[H^+]$ is the total hydrogen ion concentration, x_m , x_{m-1} and x_{m+1} are the parts of $[H^+]$ value obtained at the corresponding dissociation steps, F_m is the quotient of the activity coefficients for the m step (the latters may be calculated with the aid of the Debye-Huckel equation). For the $[H^+]$ value we may write:

$$[H^+] = \sum_{m=1}^n x_m \quad (2)$$

With the aid of these equations the mass action expressions for weak dibasic acids (which represent the most numerous group of weak multibasic organic acids) may be obtained:

$$K_1 = \frac{x_1^2 - x_2^2}{c - x_1} F_1 \quad (3) \qquad K_2 = \frac{x_2(x_1 + x_2)}{x_1 - x_2} F_2 \quad (4)$$

where c is the total (analytical) concentration of acid. The x_1 and x_2 values (and then their sum – the $[H^+]$ value) can be calculated successively by iterative solution of two quadratic equations obtained from the equations (3) and (4):

$$x_1 = \frac{1}{2} \left[-\frac{K_1}{F_1} + \sqrt{\left(\frac{K_1}{F_1} \right)^2 + 4 \left(x_2^2 + \frac{K_1 c}{F_1} \right)} \right] \quad (5) \quad x_2 = \frac{1}{2} \left[-\left(\frac{K_2}{F_2} + x_1 \right) + \sqrt{\left(\frac{K_2}{F_2} + x_1 \right)^2 + \frac{4 K_2 x_1}{F_2}} \right] \quad (6)$$

We have also obtained the simple empirical equation for the fast approximate determination of the pH values of dilute (0.0001-0.01M) solutions of weak dibasic (and also tribasic with the low K_3 values) organic acids:

$$pH = -1.489 + 0.8pK_1 - (1.185 - 0.14pK_1)\lg c \quad (7)$$

Monitoring human levels of perfluorinated chemicals in Sweden

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Perfluorinated chemicals (PFCs) used in plastics, fire fighting foam, textile impregnation and many industrial applications, are detected in human blood worldwide. Since the late 1990ies regulatory and voluntarily efforts to reduce residual chemicals in products, emissions from manufacturing and to phase-out bioaccumulative PFCs have been conducted by many countries and companies. The work presented here are some results from monitoring PFCs in Sweden.

Analysis of perfluoroalkylated sulfonates and carboxylates in different matrices was performed by solid-phase extraction using Oasis Wax (Waters), and/or by clean-up using dispersive carbon ENVI-Carb (Supelco) followed by UPLC-MS/MS analysis (Waters).

Monitoring human blood levels in Sweden show a decrease for all sulfonates including PFOSA in 10 years between 1997-2000 and 2007-2008. Although levels of PFOA show the same but slightly weaker trend, other carboxylates like PFNA, PFDA, and PFUnDA seems to be increasing (*Figure 1*). Longer chain carboxylates >C11 are rarely detected in blood with current detection limits but are found in Swedes exposed to ski wax (*Figure 2*). Although not detected in Swedish human blood, the substitute for C8-based sulfonate chemistry, PFBuS, are now found in water resources¹ and have recently been detected in mink from Sweden².

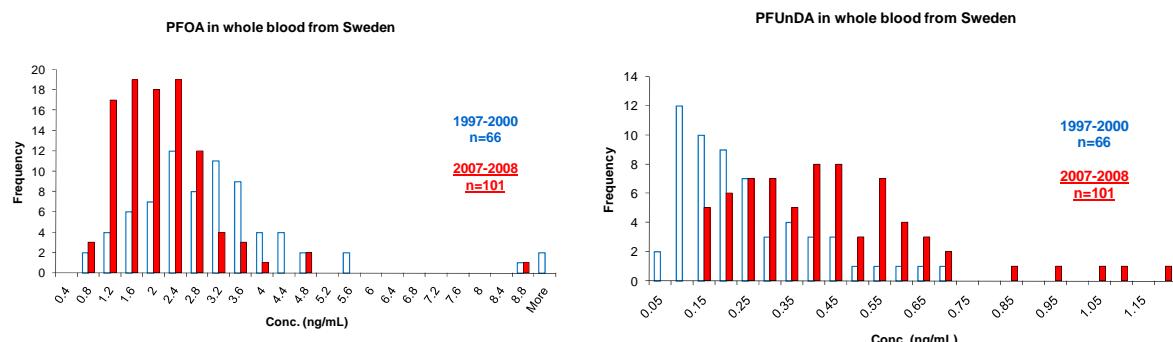


Figure 1. PFOA and PFUnDA (ng/ml) in Swedish whole blood from 1997-2000, and 2007-2008 (filled bar).

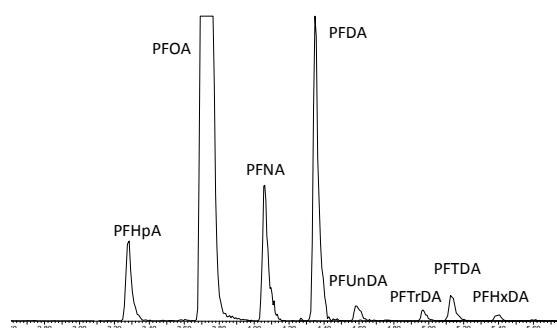


Figure 2. Profile of perfluorinated carboxylates in blood from a ski wax exposed Swedish man (2008).

References:

- Ericson Jogsten I, et.al. "Levels of perfluorinated chemicals in municipal drinking water from Catalonia, Spain: public health implications". Submitted.
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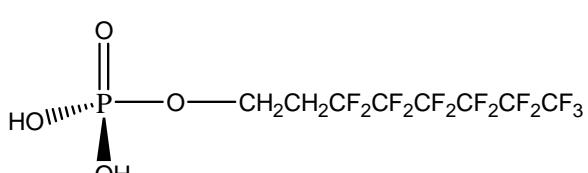
Biodegradation of fluorinated phosphate surfactants under environmental conditions

Holly Lee¹, Jessica D'eon¹, and Scott A. Mabury¹

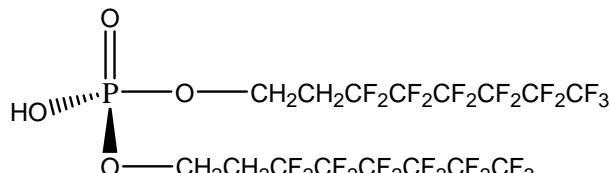
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Polyfluoroalkyl phosphate surfactants (PAPS) are commonly used as water/grease repellants in food packaging paper and as anti-foaming additives in pesticides. As fluorotelomer alcohol (FTOH) is a known source of the environmentally persistent perfluorinated carboxylic acids (PFCAs), there is concern for these FTOH-based PAPS to be potential PFCA precursors either by the presence of residual FTOHs in PAPS-based products or from the breakdown of PAPS. Our group has previously shown that the phosphate linkage in monoalkylated- and dialkylated phosphate surfactants (monoPAPS, diPAPS) are metabolically labile in rats and both congeners can biotransform into perfluorooctanoic acid (PFOA) and other 8:2 FTOH intermediates (1). What has not yet been addressed is the potential for PAPS to be microbially degraded under environmental conditions. After industrial and consumer use, PAPS-containing products may be released into wastewater treatment plants (WWTPs) and partition into the biosolids co-generated in these plants. Thus, these FTOH-based PAPS may act as a potential source of FTOH and ultimately, PFCAs, either through the presence of residuals or from biodegradation of the surfactant itself. We were particularly interested in the steric factors influencing the amenability of the phosphate linkage in PAPS to microbial cleavage. Two wastewater-mediated studies in activated sewage sludge from a local municipal WWTP were performed to address the following steric effects on the biodegradability of PAPS: (1) the length of the singly fluorinated tail in four different chain lengths of monoPAPS (4:2, 6:2, 8:2, 10:2); and (2) the number of fluorinated tails appended to the phosphate moiety in 6:2 monoPAPS and 6:2 diPAPS. Production of the suite of expected FTOHs, PFCAs, and intermediates was observed for the corresponding PAPS configuration, marking this study as the first confirmation of PAPS as a precursor to the PFCA load in the environment.

Due to the interaction between the bisphosphate moiety of monoPAPS and the stationary phase of reverse-phase liquid chromatography (LC) columns, chromatographic analyses of monoPAPS has always been complicated by severe peak tailing. Various methodologies involving pH modifications of the mobile phases and different stationary phases will be discussed. The new analytical method resulted in good peak shapes for monoPAPS with reasonably low limits of detection (LODs) in the range of 0.2-1.2 ug/L.



6:2 monoPAPS



6:2 diPAPS

(1) D'eon, J.C. *et al. Environ. Sci. Technol.* **2007**, *41*, 4799-4805.

The use of parent and alkylated phenanthrene ratios for PAH source apportionment in high-resolution biomonitoring

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Atmospheric PAH loads in Germany strongly depend on anthropogenic emissions. The main emission sources are traffic and domestic heating, but industrial processes, power plants, and municipal waste incineration contribute in variable proportions. Thus, in urban areas multi-sourced emission cocktails occur, which can hardly be differentiated. Ratios of parent PAHs (based on specific emission profiles) have frequently been employed in PAH source recognition, which still remains problematic due to shifts in PAH composition during transport and (re)deposition. Partitioning between air, water and solid matrices in particular depends on the different physico-chemical properties of PAH, commonly ranging from 2 to 6 benzene rings. We discuss the composition of closely related species of phenanthrene (P) and its mono- (MP) and di-alkylated (DMP) analogues collected on vegetation surfaces in the Greater Cologne Conurbation, NW-Germany, with respect to potential emission sources, distribution pathways and secondary degradation/alteration processes. In the densely populated and highly industrialized region of the Greater Cologne Conurbation 71 samples of *Pinus nigra* needles were taken covering an area of 3600 km². Solvent extraction followed by chromatographic separation, and GC-MS-analysis of the aromatic fraction was performed to analyze the pine needle PAH load.

Phenanthrene isomer ratio and absolute concentration maps, generated with a GIS spatial analyses tool, reveal different local hot spots in PAH load or isomer pattern. One feature is the dominance of P derived from power plant over traffic emission in the metropolitan area of Cologne. Furthermore, the 9-/(9+1)-MP isomer ratio highlights urban areas of variable size

and population/traffic density (Fig.1). Effects of secondary reactions with NO_x, ozone or reactive hydroxy radicals on the 9/1-MP ratio will be discussed. Compositional variation of DMP is preferentially attributed to evaporative loss (i.e. non-combustion) processes. The DMP variability thus depicts industrial activity in the region, which is dominated by refineries along the Rhine River in the Greater Cologne Conurbation.

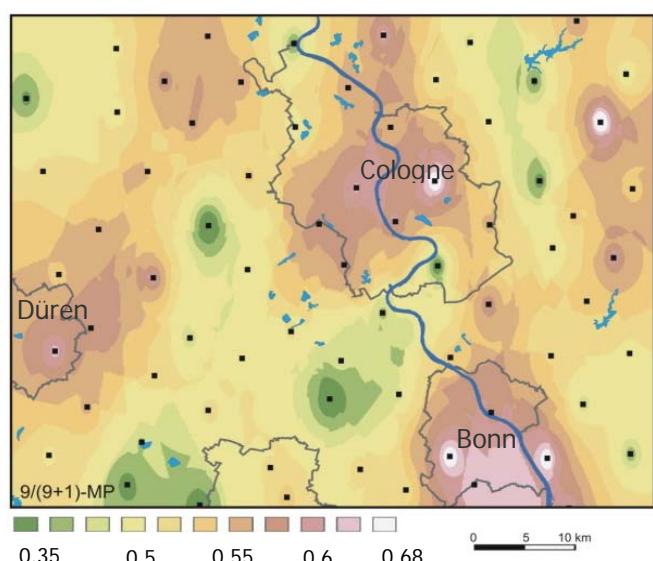


Fig.1: Ratio of 9/(9+1)-methylphenanthrene > 0.55 characterizes urban areas, which are outlined in grey.

Levels of organohalogen compounds in Guinea-Bissau - A time trend study

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Humans are exposed to a mixture of organic halogenated compounds (OHCs). There are many studies showing concentrations of OHCs in humans in the industrial countries as reviewed elsewhere^{1,2}. However, very little is known about levels and trends of these compounds in countries in transition. The objective of the present study was to determine the levels and trends of OHCs in humans living in Guinea-Bissau in western Africa. Serum samples were obtained from the Swedish institute for infectious disease control (SMI) from 33 HIV negative male police officers taken at 4-5 occasions between 1990 and 2007. Equal amount of serum from each person (0.25-0.5ml) were pooled to form 6 pooled samples with four or five time points for each pool. The samples were extracted and cleaned-up, with some modifications, according to Hovander et al 2000³.

The major OHCs found in all samples were 2,2-bis(4-chlorophenyl)-1,1-dichloroethene (DDE) and 2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane (DDT). Although the concentrations are relatively high, a decreasing trend was observed. A distinct decrease of the gamma isomer of hexachlorocyclohexane (γ -HCH) was observed whereas the decrease of β -HCH was slower. Polychlorinated biphenyls (PCBs) were found to decrease over time as well. Very low levels of the polybrominated diphenyl ethers (PBDEs) were found except for the deca brominated BDE209 and no time trend could be observed. Even though decreasing trends over time were seen for most of the OHCs studied, the use of old and damaged equipment that might contain hazardous chemicals combined with poor knowledge and small economical possibilities to take care of dangerous waste, might lead to an upcoming problem with POPs in the future. In conclusion, it is important to investigate the sources and to continue to monitor these chemicals in the environment.

Acknowledgement

Hans Norrgren from Lund University Hospital and Helen Linder from SMI are greatly acknowledged for supplying the samples. Ioannis Athanassiadis is acknowledged for the assistance with the mass spectrometry and the Swedish international development cooperation agency (SIDA) for the financial support (SWE-2006-376).

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The use of biological monitoring to determine children's exposure to pesticides living nearby banana plantations in Costa Rica

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Agricultural pesticide use is widespread in Central America, and one of the main environmental problems in rural areas. Central America is one of the leading banana exporting areas in the world. Banana cultivation heavily depends on the use of pesticides, with frequent aerial spraying of fungicide cocktails. These pesticides may pose a serious environmental health threat for many rural communities that are surrounded by plantations. Not only workers but also workers families may be exposed, especially children are a vulnerable group.

The fungicide Mancozeb is applied in vast quantities using aerial spraying. Ethylenethiourea (ETU) is one of the main metabolites of Mancozeb and can also be found environmentally as a degradation product. Mancozeb are generally considered to have a rather low-grade acute toxicity for mammals. ETU, on the other hand, is of major toxicological concern and has shown a large spectrum of adverse effects in experimental animals. The aim of this study was to evaluate children's pesticide exposure by analysis of ETU in urine. No studies of childrens exposure to ETU have previously been performed.

Urine was sampled from 165 children aged 6 to 9, for 40 children on more than one occasion and during 18 months. (N=550). In addition, urine was sampled on multiple occasions from 20 mothers and fathers (N=150). The samples were collected from three communities, a banana community surrounded by plantations, a plantain community with smallholders and a community that mainly produced organic plantain.

A novel LC/MS/MS method was used in the analysis of ETU in urine using a single step extractive derivatization using pentafluorobenzylbromide¹.

The urinary levels found in the children living nearby banana plantations were similar to ETU levels found in several studies of European occupationally exposed subjects. The ETU levels showed a correlation with aerial spraying activities. Although ETU have a short half-life in the body, the children seems to have a chronic exposure. It was estimated that a majority of the children exceed the Rfd set by the U.S. EPA.

¹Lindh CH, Littorin M, Johannesson G, Jönsson BA. Analysis of ethylenethiourea as a biomarker in human urine using liquid chromatography/triple quadrupole mass spectrometry. Rapid Commun Mass Spectrom. 2008 Aug;22(16):2573-9.

Reactivity scale of chloroaromatic POPs in S_EAr reactions

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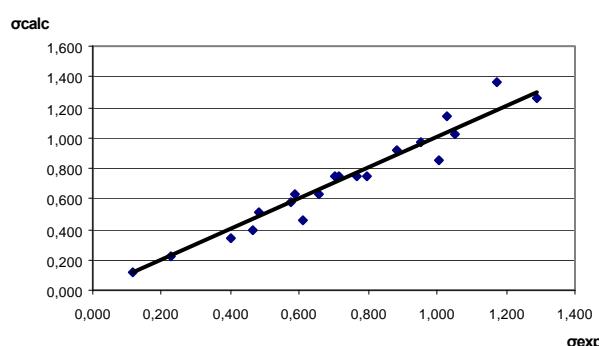
The influence of substituent on electrophilic aromatic substitution for polychlorinated benzenes, biphenyls, diphenyl ethers and naphthalenes was calculated using Hammett equation $\log k_{\text{rel}} = \rho \sigma_s^+$. σ_s^+ reflects overall influence of all Cl substituents and polycyclic system on the reactive center. Selected relative rate constants for model reaction - nitration are presented:

Benzenes		
Cl	σ_s^+	$-\log k_{\text{rel}}$
0	0,000	0,000
1,2(4)*	0,513	3,129
1,3(4)	0,343	2,250
1,2,3(4)	0,742	4,313
1,3,5	0,572	3,258
1,2,3,4	1,141	6,376
1,2,4,5	1,256	6,971
1,2,3,4,5	1,370	7,861
Naphthalenes		
Cl	σ_s^+	$-\log k_{\text{rel}}$
0(α)	-0,29	-1,448
1(4)	-0,18	-0,230
1,3(5)	0,00	0,778
1,3,5(8)	0,15	1,618
1,3,5,7(4)	0,38	2,605
1,2,4,5,7(8)	0,47	3,410
1,2,3,4,5,6,7	1,07	6,770
1,2,3,4,5,6,8	1,44	8,842

Biphenyls		
Cl	σ_s^+	$-\log k_{\text{rel}}$
0(4)	-0,179	-1,704
4(4')	-0,095	-1,270
4,4'(3)	0,366	1,115
3,4,4'(3')	0,394	1,261
3,3',4,4'(5)	0,793	3,324
3,3',4,5,5',6(4')	0,833	3,531
2,2',3,3',4,4'5(5')	0,964	4,206
2,2',3,3',4,5,5'6'(4')	1,496	6,956
Diphenyl ethers		
Cl	σ_s^+	$-\log k_{\text{rel}}$
0(4)	-0,500	-3,363
4(4')	-0,416	-2,929
4,4'(3)	0,515	1,882
3,4,4'(3')	0,548	2,056
3,3',4,4'(5)	0,947	4,119
3,3',4,5,5',6(4')	0,609	2,370
2,2',3,3',4,4'5(5')	1,128	5,056
2,2',3,3',4,5,5'6'(4')	1,176	5,302

* The most reactive positions are given in brackets. σ_s^+ and $\log k_{\text{rel}}$ are given for those positions.

Calculated reactivities for polychlorobenzenes are in good correlation with experimental values (σ_{exp}) [1]:



Acknowledgement: This work was supported by NorthPOP project (www.northpop.no)

[1] R. G. Coombes, D. H. G. Crout, J. G. Hoggett, R. B. Moodie, K. Schofield J. Chem. Soc. (B), 1970, 347.

Calculation of reaction rates for chloroaromatic POPs in model reaction with sodium methoxide and correlation with available experimental data for PBDEs

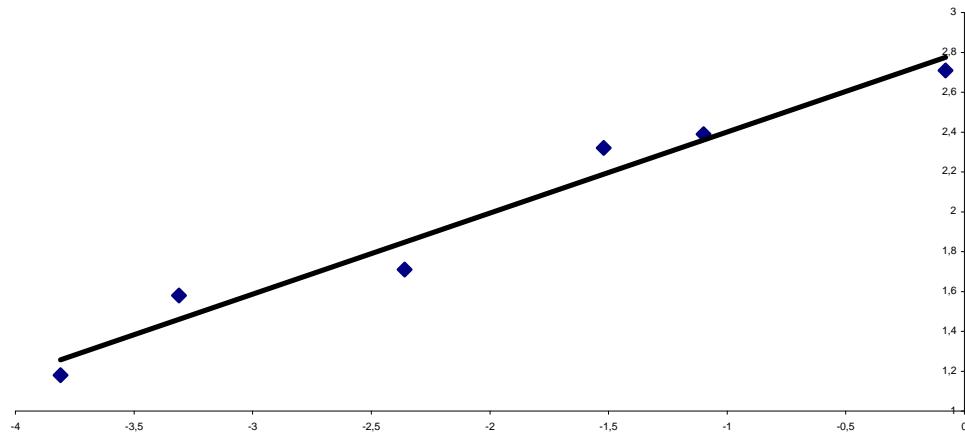
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The influence of substituent on electrophilic aromatic substitution for polychlorinated benzenes, biphenyls, diphenyl ethers and naphthalenes was calculated using Hammett equation $\log k_{\text{rel}} = \rho \sigma_s$. Values of $\log k$ in the table below correspond to the sum of partial rates in all positions except *ortho*-positions in PCB and PCDE.

Polychlorobenzenes		Polychlorobiphenyls		Polychlorodiphenyl ethers	
Cl	$\log k_{\text{rel}}$	Cl	$\log k_{\text{rel}}$	Cl	$\log k_{\text{rel}}$
1,2,3,4,5,6	2,69	2,3,4,5,6, 2',3',4',5',6'	2,71	2,3,4,5,6,2',3',4',5',6'	2,71
1,2,3,4,5	2,24	2,3,4,5, 2',3',4',5'	2,39	2,3,4,5,6,2',3',4',5'	2,39
1,2,3,4	1,81	2,4,5,2',4',5'	1,61	2,3,4,5,6,2',4',5'	2,32
1,2,3,5	1,69	3,4,5,3',4',5'	1,89	2,3,4,6, 2',4',5'	1,71
1,2,4,5	1,67	3,4,5,3',4'	1,52	2,4,5,2',4',5'	1,58
1,2,3	1,35	3,4,3',4'	1,24	2,4,6,2',4'	1,18

Correlation of calculated values for PCDEs with experimental values [1] for corresponding PBDEs gave good correlation:



Acknowledgement. This work was supported via NorthPOP project (www.northpop.no).

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EU-wide river water monitoring of polar organic contaminants

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The Institute for Environment and Sustainability (IES) of the Joint Research Centre (JRC) in Ispra (Italy) has started an initiative on environmental European-(EU)-wide monitoring assessments. The first campaign focused on polar organic pollutants in surface river waters. The objective of this study was to produce an EU-wide data set of environmental concentration levels of polar contaminants in river waters to be used for continental scale risk assessments and environmental fate studies.

More than 100 river water samples from 27 European Countries were analysed for 35 selected polar organic contaminants. Around 40 laboratories across Europe participated in this sampling and monitoring exercise. Analyses were performed at the JRC in Ispra by solid-phase extraction (SPE) of 400 ml water followed by triple quadrupole LC-MS-MS analysis using labeled internal standards for quantification.

Target compounds comprised selected pharmaceuticals (e.g. carbamazepine, ibuprofen, diclofenac), the antibiotic sulfamethoxazole, pesticides and their degradation products (e.g. bentazone, triazines, 2,4-D), perfluorinated acids (PFOS and PFOA), benzotriazoles (corrosion inhibitors), hormones (estrone, estradiol), and endocrine disrupters such as bisphenol A and nonylphenol.

The most frequently and at the highest concentration levels detected compounds were benzotriazole, caffeine, carbamazepine, tolyltriazole, and nonylphenoxy acetic acid (NPE₁C). Caffeine, ibuprofen, and carbamazepine (the widely used antiepileptic drug) were among the compounds with the highest maximum concentrations: 40, 31, and 12 micrograms per liter, respectively.

The most pristine rivers in Europe flow in regions with low population density such as Estonia, Lithuania, Norway, and Sweden. Only 10 per cent (11 of the 122 samples) of the samples contained virtually no chemicals.

Rivers with the relatively highest amounts of perfluorinated acids (PFOS and PFOA), were identified. The study suggests that the Rivers Po in Italy, Danube, Scheldt in Belgium and the Netherlands, Rhone in France and the Wyre in the UK contained significant amounts of PFOA, although not all major European rivers were tested. PFOS was found in similar amounts, but its emissions were more widely distributed throughout Europe. PFOS and PFOA discharges along the whole European river network to coastal areas in Europe have been estimated for the year 2007 to be in the order of 20 and 30 tons per year, respectively.

An analytical method was developed for the analysis of sucralose, a persistent chlorinated calorie-free sugar substitute, in surface waters, based on the same SPE-LC-MS-MS protocol. The EU-wide screening showed that sucralose, which is in use in Europe since beginning 2005, can be found in the aquatic environment, at concentrations up to ~ 1 µg/L. Sucralose was predominately found in samples from the UK, Belgium, the Netherlands, France, Switzerland, Spain, Italy, Norway, and Sweden, suggesting an increased use of the substance in Western Europe.

Correlation between alga and blue mussel concentrations of OH- and MeO-PBDEs?

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Several hydroxylated polybrominated diphenyl ethers (OH-PBDEs) and methoxylated polybrominated diphenyl ethers (MeO-PBDEs) have been shown to be natural products¹⁻⁴. OH-PBDEs have also been reported as metabolites of polybrominated diphenyl ethers (PBDEs)⁵⁻⁶. Many marine species, e.g. alga contain haloperoxide enzymes that can catalyse bromination of a suitable precursor in presence of bromine and hydrogen peroxide⁷.

Blue mussels (*Mytilus edulis*) and alga from several locations in the Baltic Sea were analysed for OH- and MeO-PBDEs. The blue mussels and alga were paired, sampled from the same site. Extraction and cleaned-up was done according to Jensen *et al.* (2009)⁸ and analysis with gas chromatography-mass spectrometry (GC-MS).

The major part of the OH- and MeO-PBDEs found in biota from the Baltic Sea is most likely naturally produced by primary producers such as algae and cyanobacteria. Blue mussels accumulate the substances through filtering of particles or through direct absorption of exudates. The levels in biota may vary with the occurrence and seasonal variations of algae and/or cyanobacteria. The study compares congener pattern and concentrations of OH- and MeO-PBDEs in blue mussels and algae from different locations along the Swedish coast line. The aim was to elucidate differences in retention of these compounds as well as to assess whether the alga is the primary source of exposure for the blue mussels.

Acknowledgement

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Combined field studies and modeling to characterize sources and processes controlling concentrations of semivolatile organics in air

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Concentrations of persistent semi-volatile contaminants (SVOCs) such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in air are controlled by many competing influences. Several studies of variability in concentrations of PCBs in air over diel (24-hour) periods have been reported in the literature and interpreted in terms of different controlling processes. We have developed a dynamic (Level IV) regional-scale multimedia model that provides a general description of variability in SVOC concentrations over diel periods. The model can be parameterized with local data on temperature, wind speed, atmospheric mixing height and hydroxyl radical concentrations to provide a process-level interpretation of field data. We applied this model to data reported in the literature to demonstrate that under weather conditions dominated by a stable high pressure system, four factors are sufficient to account for the variability of PCB concentrations in air over a diel period. These are: temperature, local atmospheric stability, hydroxyl radical concentration and source characteristics (1). Based on these insights, we designed two targeted field campaigns to evaluate the model and our understanding of controlling processes. First, PBDEs in air at a rural site in northwestern England were measured during a stable high pressure system. We observed higher concentrations during the day, which is consistent with inflow of PBDEs with air during the day and night-time depletion by deposition to the surface under a stable nocturnal boundary layer (2). In our second study, we measured PCBs and PBDEs in air during a stable high pressure system at two nearby sites simultaneously; the first site near the center of the city of Zurich, Switzerland, and the second atop a nearby hill outside the urban area. At the hilltop site, concentrations were higher during the day than at night, consistent with inflow at background levels during the day and nighttime depletion in the forest canopy. In contrast, in the city, concentrations were higher at night than during the day, indicating that the city is a source of both PCBs and PBDEs to the atmosphere, and that newly emitted pollutants are trapped at night under the stable boundary layer (3). From our combined field measurements and modeling, we estimate that the urban area of the city of Zurich was a net source to the atmosphere during the sampling period of 1600 g/day of PCBs, and 30 g/day of PBDEs.

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Using a sediment water test system to determine degradation kinetics and transformation products of pharmaceuticals

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Although many reports are available on the occurrence of pharmaceutical residues in aquatic systems, knowledge on the environmental fate of these compounds in rivers and river sediments is still sparse. To determine the potential of river sediment to act as a sink for several pharmaceuticals, we carried out sediment water tests. Moreover, we screened these tests for transformation products of pharmaceuticals that could be promising indicators for the assessment of microbiological degradation on the river scale.

One batch of sediment sampled from the river “Roter Main” (Northern Bavaria, Germany; sieved <2 mm) was used for this study. To obtain reproducible and well defined boundary conditions in the test system, we used a nutrient solution with a composition similar to river water instead of real river water. Sediment and water were incubated in 1 L glass bottles at a water:sediment ratio of approx. 6:1. Incubations were carried out in darkness at 15° C. After an initial equilibration period of 5-7 days where no pharmaceuticals were present, the supernatant was replaced by fresh nutrient solution containing the compound of interest at a concentration of 200 µg L⁻¹. The aqueous phase was continuously aerated to maintain oxic conditions in the test system. At regular intervals, water samples were taken and analyzed for the parent compound and potential metabolites using liquid chromatography interfaced to quadrupole-time-of-flight mass spectrometry (UPLC-QTOF-MS).

The screening procedure for transformation products was initiated by an a priori assessment of transformation pathways. To this end, predictions using the UM-BDD database (Ellis et al. 2006) and expert knowledge as well as literature data were used to generate a list of likely candidates for each pharmaceutical. Based on this list, the analyses were scanned for the exact mass of the transformation products and their expected fragment ions. Mass spectra and retention times of proposed degradation products were also matched against the corresponding data recorded from human metabolites detected in urine samples.

The first results of this investigation are promising, but no final results can be presented by the time this abstract is written since the experiments are not finished yet. We will present dissipation times for several frequently used pharmaceuticals like ibuprofen, diclofenac, metoprolol, and propranolol, and details of the screening procedure and transformation products that were tentatively identified using this test system.

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OH-PBDEs and MeO-PBDEs in blood plasma from Baltic flounder

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Methoxylated polybrominated diphenyl ethers (MeO-PBDEs) were initially detected in seal and fish¹ and later in several other Baltic Sea species²⁻⁴. Hydroxylated polybrominated diphenyl ethers (OH-PBDEs) were first identified in blood plasma from Baltic salmon³ and later in blue mussels, red algae, cyanobacteria^{4, 5} and in blood plasma from herring⁶.

One of the OH-PBDEs, 6-OH-BDE47, was recently shown to act as a strong inhibitor of oxidative phosphorylation in zebrafish⁷.

OH-PBDEs are known to be both natural products from marine environments and metabolites of polybrominated diphenyl ethers (PBDEs), whereas MeO-PBDEs appear to be solely natural in origin. The main part of the OH-PBDEs found in Baltic biota are most likely naturally produced by e.g. red algae and cyanobacteria.

Flounder (*Platichthys flesus*) in the Baltic Sea feed on blue mussels (*Mytilus edulis*), which live in coastal habitats also occupied by macroalgae, and are thereby exposed to algae exudates containing OH-PBDEs and MeO-PBDEs.

In the present study, plasma from flounders, collected on the east coast of Öland, an island in the Baltic Sea, were analyzed for OH-PBDEs and MeO-PBDEs. The plasma samples (1 g – 3.6 g) were extracted according to Hovander et.al.⁸ and analyzed using GC-MS (ECNI).

Several MeO-PBDEs and OH-PBDEs were detected and 6-OH-BDE47, 2'-OH-BDE68, 6-MeO-BDE47 and 2'-MeO-BDE68 were quantified in the samples.

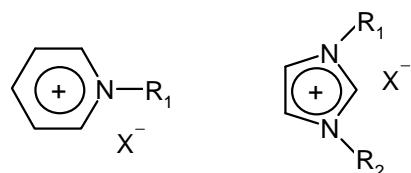
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Separation of selected ionic liquid cations by ion chromatography

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Ionic liquids (ILs) – salts having a melting point below 100°C – have recently attracted considerable attention as potential alternatives to conventional organic solvents in a variety of synthetic, catalytic and electrochemical applications. Ionic liquids are salts that typically consist of bulky organic cations such as alkylammonium, alkylimidazolium, alkylpyridinium, alkylpyrrolidinium, alkylphosphonium and inorganic anions, the most common are hexafluorophosphate or tetrafluorophosphate. These ionic solvents are composed entirely of ions, and strongly resemble ionic melts that may be produced by heating metallic salts, but are liquid at much lower temperatures. Their unique properties such as non-volatility, non-flammability, excellent chemical and thermal stability, negligible vapor pressure and selective dissolvability make them indispensable in several applications and allow the possibility for more efficient reactions and separations to occur. The uses of ILs in analytical chemistry include liquid phase and solid phase microextraction as well as liquid-liquid extraction, mobile phase additives for LC and CE as well as stationary phases for GC and LC. Most of the methods for separation and determination of ionic liquids reported so far involve high performance liquid performance with a variety of column packings and mobile phases^{1, 2, 3}. We focused our attention on separation of the most prominent pyridinium and imidazolium ionic liquid cations by ion chromatography with conductometric detection.



Cation exchange IonPac column with crown ether, carboxylic and phosphonic acids functional groups on the surface was employed. We investigated the mobile phase composition and pH effects on the retention and the separation of ionic liquid cations.

Acknowledgement

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Comparison of experimentally and theoretically determined oxidation and photochemical transformation rates of some organohalogens to promote prediction of persistence

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The diversity of choices we have to make everyday influence our environment and ourselves in more ways than most of us realise. Anthropogenic substances, such as flame retardants, date back as early as 450 BC when the Egyptians used alum to reduce flammability. The increasing demand for new articles has led to an increased production of chemical substances, for which many are commercially produced without complete knowledge on properties such as persistence, bioaccumulation and toxicology (PBT). Commercial compounds may be properly tested and denominated as “safe” regarding PBT properties, but their degradation products and/or metabolites may cause environmental impact.

The availability of uniform and accurate data for prediction of persistence is of key importance for the understanding of chemical fate. A method to determine the susceptibility of chemicals to undergo oxidation in water has been developed and applied on several organohalogens, including PBDEs and OH-PBDEs. The method was used to determine reaction rates and the group of OH-PBDEs were subsequently subjected to photolysis by use of UV-light. Hence, susceptibility to undergo both oxidation and photolysis for the OH-PBDEs were investigated and compared to previously reported degradation rates on PBDEs.

As a final step in promoting the prediction of persistence, quantitative structure-property relationship (QSPR) models were performed on a set of compounds which had undergone photolytic degradation under similar conditions. The QSPRs were used as a preliminary step in predicting photolysis half-lives for chemical substances and to determine which physicochemical descriptors are of greatest importance thereof.

This thesis presents the possibility of performing and assessing oxidation transformations on compounds of low and high water solubility, photolysis transformations in various media and using obtained data to predict behaviour via QSPR models, to promote predictions of persistence.

Cob(I)alamin reacts with sucralose to form an alkylcobalamin

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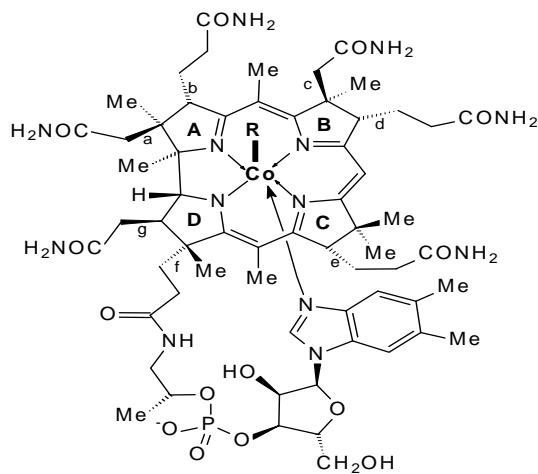
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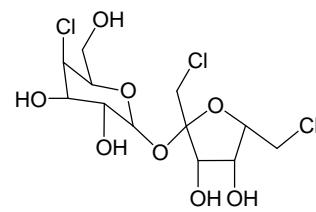
Sucralose (trichlorogalactosucrose) is a fairly new sweetener used in food and beverages. Because of three tightly bound chlorine atoms, sucralose has an exceptionally stable molecular structure. Due to its persistence in aquatic environment and lack of environmental data, it has been proposed that sucralose may be an environmental hazard.

Vitamin B₁₂ in its reduced form, cob(I)alamin (a supernucleophile), has earlier been used for dehalogenation and as a tool for analysis of electrophiles by formation of alkylcobalamins. The present study shows that cob(I)alamin reacts with sucralose and forms an alkylcobalamin (Suc-Cbl) with high yields. The Suc-Cbl was characterized by LC-UV and LC-ESI⁺-MS/MS. By mass spectrometry the alkylcobalamin was prominently observed as a doubly protonated molecule [M + 2H]²⁺, having *m/z* 846.5. Also seen were the doubly charged dechlorinated molecular ions corresponding to [M - Cl]²⁺ and [M - 2Cl]²⁺. The major fragment of the alkylcobalamin in product ion scan (PIS) was observed to be *m/z* 665.5, which is a doubly protonated fragment with loss of the alkyl (sucralose) moiety from the cobalt of the cobalamin. Other common cobalamin fragments *m/z* 359 and 972, were also seen in the PIS.

In this study we also present a new solvent system for extraction of alkylcobalamins, replacing phenol from the standard method. This system was applied for extraction of the Suc-Cbl. Further, we also investigate acid-induced decomposition of the Suc-Cbl that generates a sugar alkene, which was characterized by LC- ESI⁺-MS.



Vitamin B₁₂ (R = CN)



Sucralose

Organic pollutants in food and environmental samples of Bangladesh

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Organochlorine pesticides such as DDT, HCH and many others were commonly used by farmers in Bangladesh until 1980. Among them only DDT was produced in the country. After signing Stockholm Convention in the year 2001 use of all persistent organochlorine compounds were banned in the country. Nearly 500 metric ton unusable imported DDT is still stored at 4 stores of Directorate of Health Services. Similar amount of DDT was also found in Bangladesh Forest Research Institute (BFRI) which has been used earlier for preservation of wood. Most of transformers and capacitors in power generator sector contain PCB treated oils. A total of 140 samples which include fish, dry fish, soil, water & sediments from a closed DDT factory area and transformer & capacitor oils were collected and analyzed by gas chromatography (GC) coupled with an electron captured detector (ECD). The limit of detection of DDT and its metabolites, DDE & DDD were 0.05, 0.0025 and 0.005 ng/g, respectively. The amounts of DDTs were found to be 34-669 ng/g in the fresh fish samples. Most of the dried fish samples were found to contain DDTs in varying amounts (88-28,060 ng/g), some of which were above the maximum residual limit (MRL) value in food (5000 ng/g). These results indicated that extra DDT was used during fish drying processes and preservation in some localities. DDTs were found to be 10-51,000, 3-9,000 and 0.007-0.169 ppm in soil, sediments and water samples, respectively which were collected from different distances of the DDT store of the factory. The results indicated that DDT has been dumped into factory area from the store after closing the factory and thus is being spreading in the whole area during rainy season. The ranges of PCBs in transformer and capacitor oils were 0.55 to 9,076 µg/g. During change of oil of the transformer and disposal of the used oil there is a great chance to release of PCBs in the environment.

Bioremoval of 2-chlorophenol and lead from aqueous solutions by marine seaweed

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The use of marine seaweeds from Peruvian beaches *Lessonia nigrescens* Bory (A1) and *Macrocystis integrifolia* Bory (A2) as adsorbents for the removal of 2-chlorophenol (2-CP) and lead (II) ions from aqueous solutions was investigated. The experiments were carried out at room temperature in batch systems. Prior to the experiments, the seaweeds were characterized and adequately prepared for the adsorption. Equilibrium parameters such as pH, adsorbent dose and adsorbate concentration were evaluated. In order to avoid the partial dilution of the seaweed in the solution in presence of 2-CP, the seaweeds were cross-linked with calcium chloride to maximize their mechanical and chemical resistance.

The optimum pH values for both seaweeds A1 and A2 were 4 and 5 for Pb(II) and 3 and 2 for 2-CP, respectively. These results completely agree with the acid-base properties of the adsorbents that report an apparent ionization constant of 3.0. The effect of the adsorbent dose on the adsorption at two different concentrations showed a progressive saturation of the surface of the seaweeds. The use of 0.38 g of adsorbent was enough for both concentrations of 2-CP, whereas 0.06 g of both seaweeds was needed for the complete adsorption of Pb (II). From the results, it is concluded that the existence of more active sites does not affect the equilibrium nor improve the process. Conversely, at high adsorbent dose, partial aggregation of the adsorbent would reduce the number of available adsorption sites.

The effect of the presence of lead (II) on the adsorption of 2-CP was also evaluated. The results show that divalent cations do not compete for the adsorptive sites with 2-CP. According to the “egg-box” model, Pb(II) ions are exchanged by calcium ions that are present in the seaweed structure. On the other hand, the adsorption of 2-CP is mainly occurring on the external surface of the adsorbent, attracted by different intermolecular interactions.

Finally, the mathematical theories of Langmuir and Freundlich modelled the process. Langmuir isotherms showed a better description of the mechanism of adsorption of 2-CP and Pb (II) by both seaweeds. The maximum adsorption capacities for 2-CP were 61.3 and 34.6 mg/g and for Pb (II) were 893.0 and 730.0 mg/g with A1 and A2, respectively. The calculated parameters, mainly from the isotherm analyses, demonstrate an interesting adsorbent/adsorbate attraction and a maximum adsorption capacity value greater than the values reported in the literature. These results elucidate the potential use of both seaweeds in the elimination of 2-CP and/or Pb (II) from aqueous solutions.

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Comparative study of the removal of phenol by biological and non-biological adsorbents

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Exchanged clays and cross-linked algae were compared based on their properties for the removal of phenol from aqueous solutions at room temperature in batch experiments. Algae *Lessonia nigrescens Bory* (A1) and *Macrocystis integrifolia Bory* (A2) were cross-linked with calcium chloride to enhance their physical and mechanical properties. The natural clays were characterized by methylene blue (MB), XDR and BET analyses and chemically-exchanged with salts of tetramethyl ammonium (B1), hexadecyltrimethyl ammonium (B2) and bencyltriethyl ammonium (B3) ions to increase their affinity towards organic substrates.

The effects of the initial solution pH and adsorbent dose were evaluated. pH exhibited a strong effect mainly on the phenol aqueous chemistry. Moreover, pH showed a strong effect on the adsorption by algae, whereas, exchanged clays were almost unaffected by the initial solution pH. Adsorbent dose effect was also evaluated and revealed a lower mass required to reach saturation compared with reports in the literature with the same and other adsorbents.

Sorption isotherms were also carried out and fitted to Langmuir and Freundlich models, exhibiting a mixed adsorption mechanism. Langmuir and Freundlich constants indicate a better affinity between phenol and exchanged bentonites compared to marine algae. Equilibrium results and EDX analysis elucidate a surface adsorption of phenol on algal biomass and polar adsorption mechanism thus proposing the formation of hydrogen bonds. The same results also suggest that the organic phase derived from the exchanged quaternary ammonium ions was the primary adsorptive phase of phenol. The nonlinear sorption isotherms of phenol occur via a dual mode mechanism, in which partitioning of phenol into organoclays and surface adsorption onto marine seaweed takes place. These results provide further insight into the adsorption mechanism of phenol and analogues and their use as powerful and cost-effective adsorbents for the treatment of phenol-containing wastewater. Finally, a comparison between biological and non-biological adsorbent shows that for certain phenolic compounds, modified clays are more efficient than marine algae.

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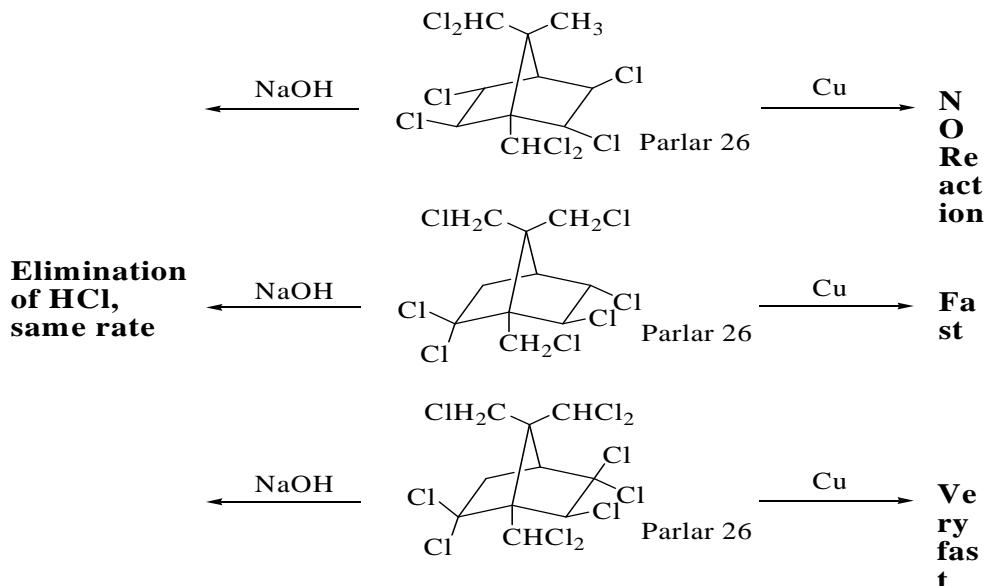
Selectivity of Toxaphene congeners and Polychloronaphthalenes in reactions with hard nucleophyles and Cu

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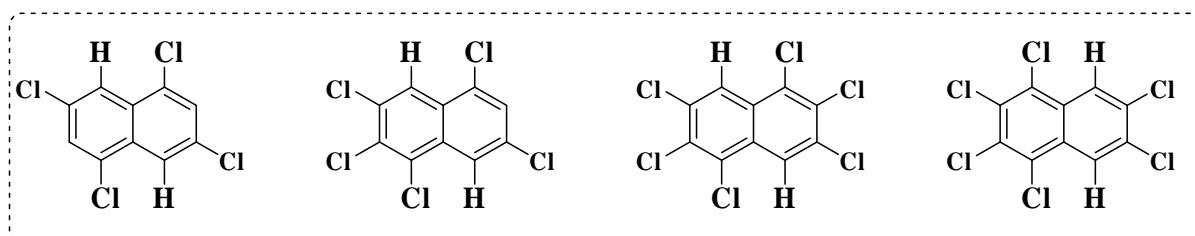
Selectivity of ecomodel reaction within a congener group may serve as a valuable criterion for its selection for reactivity-persistence correlations.

For example, reaction with hard nucleophyles like MeONa or NaOH is hardly a relevant model for Toxaphene congeners, as the most persistent, intermediate and least persistent congeners react with similar rates. In several cases persistent congeners were found even more reactive, than environmentally degradable ones:



On the other hand, dechlorination of the same set of congeners with Cu in acetic acid shows excellent correlation of reactivity and observed persistence. Persistent Parlar no. 26 is inert towards Cu, environmentally degradable Parlar no. 32 reacts fast and the least stable decachlorobornane Parlar no. 69 reacts extremely fast.

Moreover, selectivity of Cu correlates with environmental persistence also for Polychloronaphthalenes (PCNs). Most stable PCN congeners always have one Chlorine and one Hydrogen in *peri*-position:



All PCN congeners with 2 Cl atoms in *peri*-position easily react with Cu with substitution of one of the Cl atoms to H.

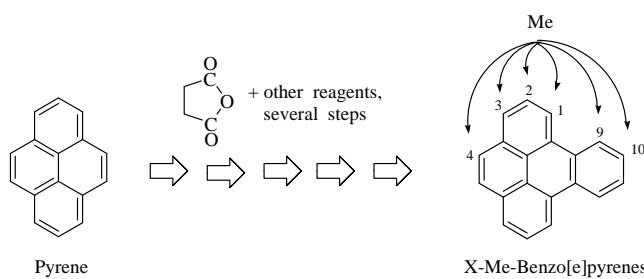
Synthesis of six methylbenzo[e]pyrene isomers from pyrene and succinic anhydride

Vladimir Nikiforov

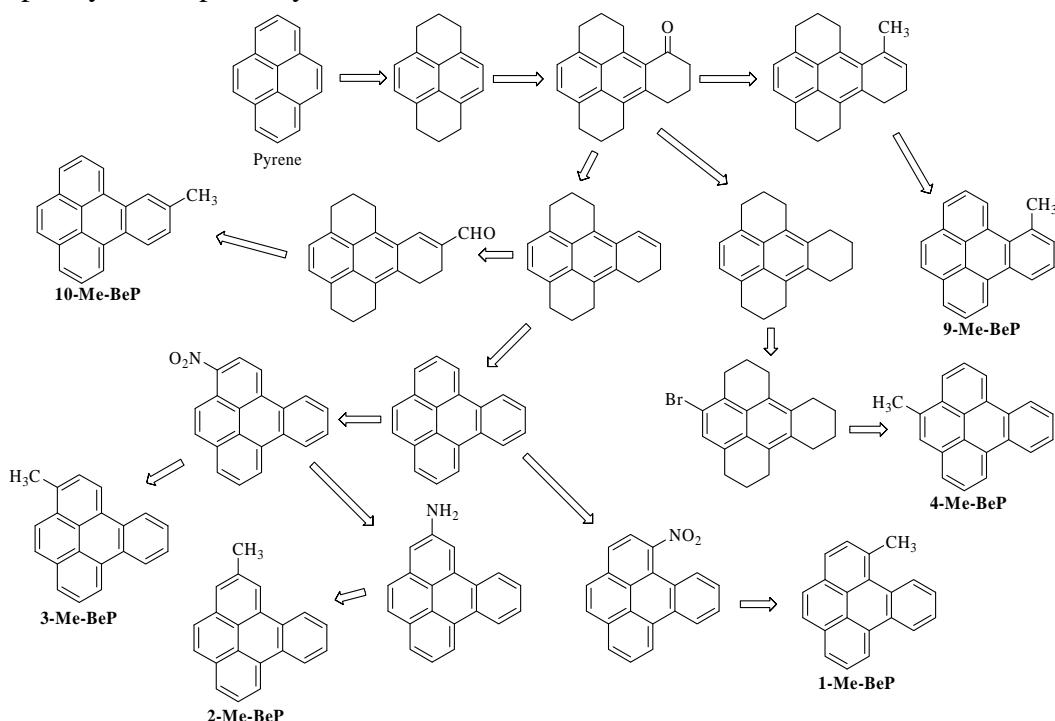
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Polycyclic aromatic compounds (PACs) are believed to be key toxicants for toxic, mutagenic and carcinogenic risks of contaminated sediments. Methylated benzo[e]pyrene isomers are a group of less studied compounds of this class.

Present report describes a general scheme for the synthesis of all 6 isomers of methylbenzo[e]pyrenes from single precursor, potentially applicable for the synthesis of $^{13}\text{C}_4$ -labeled reference material.



Developed synthetic pathways are summarized on the scheme below:



Yields are rather moderate with exception of 9-Methylbenzo[e]pyrene which was obtained in 56% yield calculated from hexahydropyrene.

Acknowledgement: This work was done as part of EC FP6 integrated project MODELKEY (contract no. 511237 GOCE)

Carbamazepine removal in microcosm constructed wetlands

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Recent studies have shown that pharmaceutical compounds (PCs) entering sewage treatment plants (STPs) are not fully removed and are discharged to the aquatic environment [1-2]. The release of these compounds in the environment has raised concerns over their effects as studies have shown their potential influence on wildlife and possible changes upon biological systems. Several published studies reported significant concentrations of PCs such as carbamazepine, clofibric acid, ibuprofen or diclofenac in tap water in several European countries [1-3]. Ubiquitous occurrences of these compounds have also been reported for surface and groundwaters worldwide [1-3].

Optimization of STP processes to decrease PCs incidence in treated wastewaters has been tried by increasing sludge residence times, use of membrane bioreactors, granular activated carbon filters, among others [1-2]. Many of these treatment options tend to reduce PCs load in effluents but they are not widely used for reasons of cost-effectiveness.

Subsurface flow constructed wetland systems (SSFCWs) are low cost wastewater treatment systems that have been recently used with success to remove some PCs from wastewaters [3-4].

In the present work SSFCW microcosm systems, established with an expanded clay matrix and planted with *Typha* spp. or *Phragmites australis*, were used to evaluate their ability to remove carbamazepine from contaminated wastewaters. Combined with an efficient SPE concentration step, the use of HPLC-DAD yielded an analytical method for carbamazepine quantification with very low LOQ and high reproducibility.

Overall removal efficiencies about 80% were achieved after a retention time of only 4 days in the control system (an unplanted expanded clay bed was used as control), due to sorption to the expanded clay matrix. However, no significant differences were observed in the microcosm systems planted with *Phragmites australis* or *Typha* spp. These experiments were carried out in winter greenhouse conditions, after the annual harvesting, which justify a minimal contribution by the plants. The removal kinetics was characterised by an initial fast step (removal of about 60% after just 24h) which is mainly attributable to adsorption on the matrix materials. In fact, under the winter conditions used in the experiments, the contribution of plants and of microbial populations are very low, although carbamazepine was already expected to show a limited removal by the microbial populations as it usually displays a recalcitrant behaviour.

Despite the fact that further tests using larger-scale systems are required to fully evaluate the carbamazepine behaviour in a constructed wetland system, this study points out to the possible application of these low-cost wastewater systems to treat carbamazepine contaminated wastewater.

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Degradation of ibuprofen in aqueous medium by heterogeneous catalytic oxidation

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Recent studies have shown pharmaceutical compounds (PCs) entering sewage treatment plants (STPs) are not fully removed and are discharged to the aquatic environment [1-2]. Residues of PCs and their metabolites have been detected in wastewaters, streams, groundwaters and even drinking waters worldwide [1-3]. Ibuprofen (2-[4-(2-methylpropyl)phenyl]propanoic acid) (IB), a non-prescription drug that is among the most consumed pharmaceuticals all over the world, is a well known non-steroidal anti-inflammatory drug. IB environmental contamination is a result of the very high amounts of this drug entering the STPs which, despite the high removal rates (up to 90%), still result in the discharge of contaminated effluent [4].

Advanced oxidation processes (AOP) have been used for the degradation of different organic pollutant (e.g. pharmaceuticals compounds). These processes are characterized by the formation of OH radicals, which ensure high reactivity and low selectivity [5]. Recently, it has been demonstrated that diclofenac present in aqueous solution can be efficiently degraded over a metal oxide catalyst, using H₂O₂ as oxidant agent [6].

In this work, we report the heterogeneous catalytic oxidation of ibuprofen with H₂O₂, over transition metal complexes (Ni(acac)₂) dispersed in polydimethylsiloxane.

Catalytic degradation of IB has been carried out through a series of laboratory batch experiments with the objective to evaluate the effects on catalytic activity of the following parameters: i) catalyst loading; ii) oxidant agent concentration (e.g. H₂O₂); iii) temperature effect and iv) catalytic stability. Degradation rates near 100% were obtained for IB in the presence of Ni(acac)₂ dispersed in polydimethylsiloxane, with H₂O₂ as oxidant agent.

These technologies are an emergent issue and can be useful in special cases such as drug manufacture and hospital effluents or treatment of drinking waters.

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Effect of sulfonamide antibiotics on soil microbial parameters

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Sulfonamide antibiotics are widely used in veterinary medicine, both for disease treatment and – especially outside of Europe – to promote growth or improve productivity. A major part of these compounds is excreted as unmodified compound or as metabolites. In concentrated animal feeding operations (CAFO), collected manure is typically applied as fertilizer to fields, and thus antibiotics can potentially enter the environment. In this context, aim of this study was to determine the effect of sulfonamide antibiotics on the soil microbial community, both from a structural and a functional point of view. To this end, incubation experiments using soil and manure from a dairy farm were carried out. Soil (*Oakdale sandy loam*) and manure were sampled at a CAFO located in the Northern San Joaquin Valley, California, USA. A mixture of three sulfonamide antibiotics was added to the soil at concentrations between 0.9 and 900 µg g⁻¹ dm. The soil water content was adjusted to 50 % of the water holding capacity with water, manure, or a glucose solution. At regular intervals, the activity of the enzymes urease and dehydrogenase was measured; at two time steps, we analyzed the phospholipid acid (PLFA) composition in soil to assess changes of community structure.

When sulfonamides were added in combination with pure water, no effect on the activity of both enzymes was determined. With the addition of glucose, all sulfonamide concentrations applied had an inhibiting effect on both urease and dehydrogenase compared to the control. This is due to the mode of action of sulfonamides which inhibit microbial growth rather than having a bacteriocidic effect. For urease, during the first 163 hours of the test the inhibition increased with increasing sulfonamide concentration; after 380 hours, the inhibition was independent from sulfonamide concentration. In contrast, the inhibition of dehydrogenase activity was highest at the lowest sulfonamide level and decreased with increasing sulfonamide concentration. The results for the manure treatments revealed an impact of “pure” manure which caused already an inhibition of urease activity; during the course of the experiment, urease activity was recovering from this initial inhibition. Only at 900 µg g⁻¹ dm, an effect of the sulfonamides on urease activity was observed in the manure treatments.

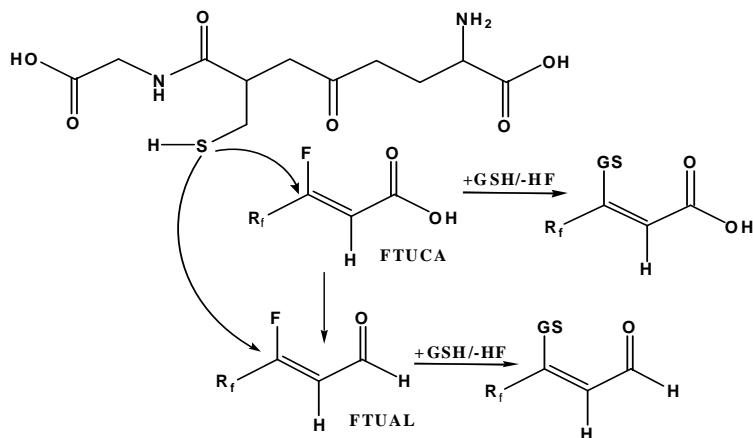
The PLFA analyses revealed a lower bacterial biomass in the glucose treatments that contained sulfonamides compared to the control experiment after 168 hours. Moreover, gram-positive bacteria were much more affected by the presence of the antibiotics than gram-negative ones, so the community structure shifted towards gram-negative bacteria. Since fungal biomass was not affected by sulfonamides, fungi gained relative importance in the soil microbial community compared to bacteria.

The result of this study demonstrate that sulfonamide antibiotics can potentially affect both activity and structure of soil microbial communities. The combined analysis of parameters that allow for the characterization of both functional and structural soil microbial parameters proved to be a promising approach to determine the effects of antibiotics on the microbial community level.

The reactivity of unsaturated fluorotelomer acids and aldehydes with Glutathione: Toxicological implications

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Fluorotelomer alcohols (FTOHs) are residual compounds created in the process of manufacturing higher weight fluoropolymers and surfactants used for commercial products. FTOHs are released to the environment and have been shown to degrade via abiotic and biotic mechanisms to perfluorinated acids (PFCAs), which are environmentally persistent and bioaccumulate in humans. The biodegradation of FTOHs forms intermediate saturated fluorotelomer acids (FTCAs), which are more toxic than PFCAs [1]. Unsaturated fluorotelomer aldehydes and acids (FTUALs and FTUCAs) are other intermediate species that form from the degradation of FTOHs and their toxicity may also be more significant than PFCAs. FTUALs and FTUCAs are strong electrophiles, likely to react with biological nucleophiles. Past studies have shown that these intermediate compounds form conjugates with a biological nucleophile, glutathione (GSH), the depletion of which may eventually lead to protein oxidation. The purpose of this study was to assess the reactivity of these intermediate compounds and to determine whether reactivity correlates to the fluorinated chain length. In vitro experiments were carried out in an aqueous buffer system (pH 7.4), where FTUCAs and FTUALs of varying chain lengths were synthesized and reacted with GSH. To quantify the reactivity of FTUCAs and FTUALs, the unreacted GSH was derivatized with 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB), its absorbance was measured at 412 nm, and the percentage of unconjugated GSH was calculated and plotted over time. The results of this study will be discussed, imparting a thorough understanding of the intrinsic reactivity and toxicity of these intermediate compounds in the presence of GSH.

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Contaminant uptake into plants: consideration of dynamic processes

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Models for the prediction of chemical uptake into plants are essential tools for human exposure assessment in chemical risk assessment, pesticide design, impact assessment of soil and air pollution and for environmental biotechnology such as phytoremediation. Steady-state considerations are often applied, because they simple and have a small data need. However, often the emission pattern is non-steady. Examples are pesticide spraying, or the application of manure and sewage sludge on agricultural fields. In these scenarios, steady-state solutions are not valid, and dynamic simulation is required.

We compared different approach for dynamic modelling of plant uptake in order to identify relevant processes and time-scales of processes in the soil-plant-air system. Based on the outcome, a new model concept for plant uptake models was developed. The approach combines a steady-state solution for concentrations in soil, roots, leaves and fruits with a matrix solution for non-steady and pulse input. This combination allows to mimick most input functions that are relevant in practice. This cascade model can be applied to the problems of pulse input (e.g. application of manure to soil), constant input over defined periods (e.g. application of pesticides) and background concentrations (Figure 1). The principles are explained and the model is applied to illustrative examples.

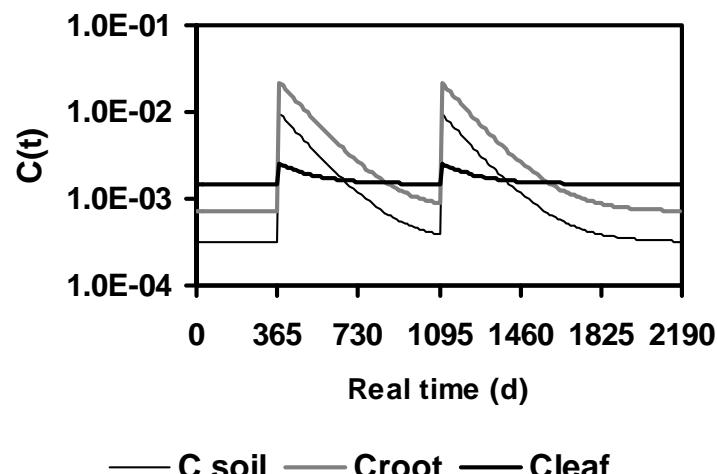


Figure 1. Simulation of concentrations in soil, roots and leaves with initial concentrations at background (steady-state) and pulse input at year 1 and 3.

Assessment of the safety and performance of a low-cost filter material for treatment of landfill leachate and industrial wastewater using an integrated approach based on ecotoxicological testing and chemical analysis

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¹ Mälardalen University, ² Örebro University

Ecotoxicological tests are frequently used as a complement to chemical analysis in hazard assessment of contaminated water, as they can detect toxic effects resulting from interactions of contaminants. They are, however, less commonly used in water treatment method development, where they can provide a rapid and low-cost means of evaluating the efficiency and safety of a new treatment method. This is particularly valuable when treating waters with a complex contaminant matrix, such as landfill leachates and industrial wastewaters.

Pine bark, which is an industrial by-product from the forestry industry, has been extensively investigated as a low-cost filter material and it has been shown to efficiently remove metals from solution, storm water run-off and landfill leachate. Additionally, it has also been demonstrated to retain phosphorous, uranium and organic compounds, such as lindane and pentachlorophenol, from water. Pine bark is therefore an interesting alternative to more expensive methods for treating waters contaminated with a mixture of organic and inorganic pollutants, e.g. activated carbon.

Although a promising low-cost sorbent, concerns have been raised about using pine bark for water treatment due to the leaching of organic acids and phenols from the unused filter material, particularly during the initial filtration phase. To ensure the environmental benefits and safety of using the filter material it is important to determine the extent and composition of the leaching of organic material from the unused material.

This study shows how an ecotoxicological test battery in combination with chemical analyses was used to evaluate the safety of using pine bark for water treatment. Leachates from the ISO standardized leaching test 12457-2 was analysed for metals, dissolved organic carbon (DOC) and phenols. The toxicity of leachates with and without pH adjustment was assessed using the freshwater crustacean *Daphnia magna*. The performance of the filter material when treating low-strength landfill leachate and industrial wastewater was assessed in batch tests followed by chemical analysis and a bioassay test battery consisting of bacteria, aquatic plants and invertebrates.

Levels of BDE-209 and other polybrominated diphenyl ethers (PBDEs) in wild Swedish mink (*Mustela vison*)

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Polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants incorporated, for example, into textiles and polymers. Since PBDEs were first analyzed in 1981, levels of PBDEs have been reported for various matrices world wide such as air, sediment and biota (De Wit 2002). PBDEs have shown to cause adverse effects in experimental in vivo models and due to their relatively high production volume and structural resemblance to other environmental organic contaminants, such as polychlorinated biphenyls (PCBs), PBDEs are a subject for environmental concern (Darnerud 2003).

In this study, wild mink (*Mustela vison*) from different regions in Sweden were autopsied at the Faculty of veterinary medicine and animal science in Uppsala and the PBDE analysis was performed at the MTM-Research centre in Örebro. Samples of 1-5 g of subcutaneous fat of 39 minks were homogenized with sodium sulphate and extraction and clean-up were performed with open column chromatography. PBDEs were analyzed by GC-MS system using a HP 6890 gas chromatograph coupled to a HP 5973 low-resolution mass spectrometer operating in the NCI mode. Quantification was carried out using the internal standard method using ¹³C labeled internal standards. A large number of BDE-congeners were found in the samples including BDE-209, which was found in 50 % of the minks (Fig 1). In general, BDE-209 is not commonly found in mammals and is analytically quite difficult to measure. However BDE-209 has been measured in for example grizzly bears and in adipose tissue of belgian red foxes, for which levels as high as 200 ng/g has been reported (Christensen et al. 2005, Voorspoels et al. 2006). In this study the range of BDE-209 was 0.1-7 ng/g fat. Finally, an evaluation of these results with regard to, for example, congener patterns will increase the knowledge of bioaccumulation of BDE-209 and other PBDEs in top-predators.

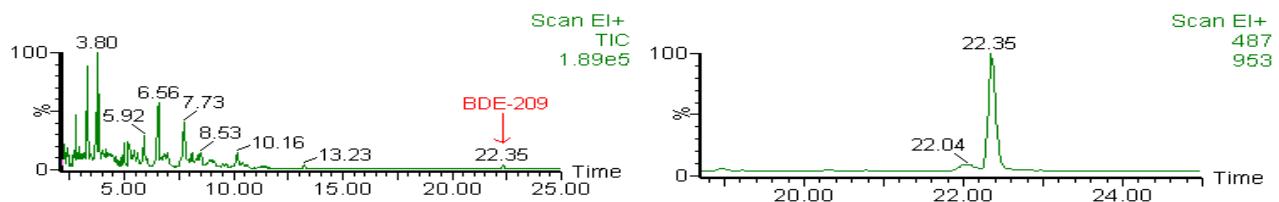


Fig 1. Chromatograms from a low-resolution GC/MS run (NCI) of a mink sample showing total ion current (TIC) and m/z 487, indicating the presence of BDE-209.

References

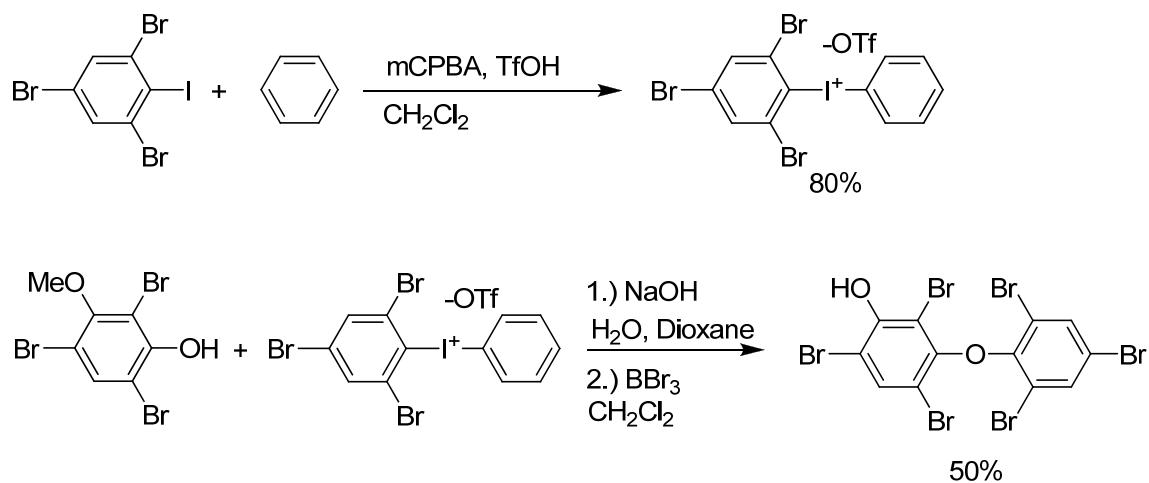
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Synthesis of hydroxylated polybrominated diphenyl ethers via symmetrical and unsymmetrical diaryliodonium salts

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Hydroxylated polybrominated diphenyl ethers (OH-PBDEs) are found as natural products, but can also be formed as metabolites from polybrominated diphenyl ethers (PBDEs), which have been widely used as flame retardants in e.g. furniture, textiles and computers. OH-PBDEs have been detected in mammals and humans.¹ Even though some of the congeners have been identified, some penta, hexa and hepta brominated OH-PBDEs are yet to be investigated.¹ The need for pure authentic reference compounds in order to identify these unknown OH-PBDEs calls for a synthetic approach. Previously, symmetrical diaryliodonium salts have been employed in O-arylation coupling of various phenols to obtain OH-PBDEs.² In this study we synthesized the novel unsymmetrical salt (2,4,6-tribromophenyl)(phenyl)iodonium triflate using previously reported methods.³ Coupling with 2,4,6-tribromo-3-methoxyphenol followed by demethylation gave 3-hydroxy-2,2',4,4',6,6'-hexabromodiphenyl ether (3-OH-BDE-155) in 50% yield (Scheme 1). The advantage of employing unsymmetrical salt in this synthesis compared to using the symmetrical 2,2',4,4',6,6'-hexabromodiphenyliodonium chloride, includes easier purification, better atom economy and higher yields. Other OH-PBDE congeners will be synthesised with similar methodology and these will be valuable in research concerning toxicity and the environmental occurrence of OH-PBDEs.



Scheme 1. Synthesis of 3-OH-BDE-155 via unsymmetrical diaryliodonium salt

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Precipitation scavenging of particle bound contaminants – a case study on PCDD/Fs

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The atmospheric wet deposition of PCDD/Fs to the Baltic Sea was estimated by collecting atmospheric bulk deposition samples and analyzing them for PCDD/Fs. Sampling was performed at a background location during the colder period of the year as previous studies have shown a clear seasonality in ambient air levels of PCDD/Fs. Bulk deposition samplers collect the PCDD/Fs associated with wet deposition (dominating process) and dry particle sedimentation¹. Dry particle impaction/interception and diffusion of gases and particles make a negligible contribution to the measured particle flux of PCDD/Fs².

The precipitation scavenging efficiency for particle associated PCDD/Fs originating from the same sources should be about equal for all congeners. However, scavenging ratios (S_R), calculated as the ratio between the PCDD/F congener concentration in rain (C_w) and the concentration on air particles (C_p), were systematically higher for the tetra- and pentachlorinated congeners, indicating that the concentrations of these congeners on air particles had been underestimated.

The PCDD/F concentrations on the atmospheric particles were estimated using a correlation between measurements of these concentrations at ground level and soot concentrations (also measured at ground level) derived in³. However, scavenging of atmospheric particles within clouds, where temperatures are often lower than at ground level, is a more important process than below cloud scavenging. At these lower temperatures, a larger fraction of the PCDD/Fs will be associated with particles than at ground level.

Replacing C_p with total air concentration (C_T) resulted in less variation in the scavenging ratio between congeners. However, the S_R values for the tetra- and pentachlorinated congeners were then systematically lower, which suggested that this approach overcompensated. A more refined analysis was conducted in which the C_p measured at ground level was corrected to the C_p at lower temperatures using a model of particle-gas partitioning of the PCDD/Fs. This gave very similar scavenging ratios for all of the PCDD/F congeners.

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Occurrence of antimicrobials in the Sava River

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A comprehensive study on the occurrence of antimicrobials in the Sava River was performed. Three different groups of antimicrobials, including sulfonamides, fluoroquinolones and macrolides, as well as trimethoprim, were monitored in our survey, which lasted from February 2007 till May 2008. In that period, water samples were regularly collected with a monthly frequency at 11 locations along the Sava River. Samples were enriched using solid phase extraction on Oasis HLB cartridges and analyzed by liquid chromatography – tandem mass spectrometry (LC-MS/MS) [1]. The most prominent analytes were human-use antimicrobials, especially those with extensive use in Croatia, while veterinary antimicrobials were rarely detected. Concentration of individual antimicrobials in the river was typically below 100 ng/L, which is comparable to the concentrations, reported for some other European rivers [2-5] and can be associated with the consumption of antimicrobials in human medicine. However, in some sampling periods, large increase in concentration was noticed for several antimicrobials. It was especially pronounced for sulfamethoxazole, azithromycin and the main metabolite of erythromycin - dehydroerythromycin. Their concentrations during spring 2008 were almost an order of magnitude higher than in most common situations. Our study indicated that this observation cannot be explained only by the variable hydrological conditions and seasonal consumption patterns. We hypothesized that these antimicrobials had an additional source of input into the Sava River, most probably the pharmaceutical industry. Indeed, facilities of the local pharmaceutical industry, including a significant production of macrolide antibiotic azithromycin, are located only few kilometers upstream of the city of Zagreb. Elevated concentrations of macrolide antimicrobials were determined at all stations, except for the location at Jesenice, situated upstream from the discharge point of wastewaters from pharmaceutical facilities. The hypothesis was additionally supported by the detection of azahomoerythromycin, an intermediate from azithromycin synthesis, which does not have any therapeutic application, in highly contaminated samples. Our results indicated wastewaters from the pharmaceutical industry as an important input of antimicrobials into the natural waters.

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Simultaneous determination of sulfacetamide and prednisolone by H-point standard addition method with simultaneous addition of both analytes in some biological fluids and pharmaceutical compounds

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Sulfonamides are bacteriostatic agents and the spectrum of activity is similar for all [1]. Sulfonamides inhibit bacterial synthesis of dihydrofolic acid by preventing the condensation of the pteridine with aminobenzoic acid through competitive inhibition of the enzyme dihydropteroate synthetase. Topically applied sulfonamides are considered active against susceptible strains of bacterial eye pathogens. Prednisolone is in a class of drugs called steroids.

Prednisolone prevents the release of substances in the body that cause inflammation. The combination of sulfacetamide and prednisolone is used to prevent or treat eye infections and treat swelling in the eye [2].

The absorption spectra of sulfacetamide and prednisolone under certain experimental conditions show that the maximum wavelengths of two compounds are very close to each other and their spectra are highly overlapped. Therefore, determination of sulfacetamide and prednisolone in the presence of each other is impossible by classical spectrophotometry.

In this work, the applicability of H-point standard addition method (HPSAM) with simultaneous additions of both analytes [3] is verified to the resolving of overlapping spectra. The results show that HPSAM is suitable for the simultaneous determination of two species in aqueous media. The limit of detection was 0.1 and 0.8 $\mu\text{mol L}^{-1}$ for sulfacetamide and prednisolone respectively. The proposed method has been successfully applied to the simultaneous determination of two compounds in some synthetic samples, plasma, urine and pharmaceutical compounds with satisfactory results.

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Investigation of nitrofuran antibiotics and organochlorine pesticides in shrimp cultivation in Bangladesh

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Shrimp industry is one of the foreign exchange earning sources in Bangladesh. Shrimp is being exported to EU, US, Canada, Japan and Middle East. Bangladesh fetched US\$ 459 million foreign exchange in 2005-2006 through frozen shrimp, along with fish, exports. However, in recent years several shrimp consignments from Bangladesh have been rejected by EU as they were found to contain traces of banned chemicals. Different types of chemicals such as nitrofurans, chloramphenicol, malachite green and organochlorine pesticides are widely used in fish and shrimp cultivation. They are used for protection against bacterial attack, as growth promoters or preservative of feed. The EU has forbidden the use of hazardous chemicals especially nitrofuran drugs in food producing animals. The four drugs i.e. furazolidone, furaltadone, nitrofurazone and nitrofurantoin belong to the group of nitrofuran antibiotics. In order to investigate the presence of nitrofuran antibiotics and organohalogen pesticides at any stage of shrimp cultivation, fifteen poultry feed, fifteen fish feed, six poultry feed ingredient, six fish feed ingredients, fifteen hatchery and twenty five Gher (shrimp growing out field) water samples were collected from different shrimp cultivation areas of Bangladesh. Nitrofurans and organochlorine pesticides were analyzed by HPLC with UV detection and GC-ECD & GCMS respectively. Out of fifteen poultry feed and fifteen fish feed samples, nine and eight samples were found to contain residual nitrofurazone in the range of 0.141-1.483 and 0.134-0.558 ppm, respectively. Residual nitrofurazone were found in the range of 0.294-0.516 ppm in feed ingredients. Although only one fish feed sample was found to contain furazolidone, nitrofurantion and furaltadone were not detected in any of the analyzed feed or ingredient samples. Nine hatchery water samples out of fifteen were found to contain residual nitrofurazone in the range of 3.261–411.072 ppm while twenty Gher water samples out of twenty five were found to contain residual nitrofurazone in the range of 3.806-9.806 ppm. Hatchery and Gher water samples were not found to contain any organohalogen pesticides. However, residual DDTs in poultry feed, fish feed, feed ingredient samples were in the range of 0.010-0.048, 0.008–0.432 and 0.007-0.087 ppm, respectively.

Relative contribution of volatile precursor substances and oceanic currents to long-range transport of PFOA

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Perfluorooctanoic acid (PFOA) is chemically inert, very persistent in the environment, and classified as toxic. Traces of PFOA have been found globally in different environmental media, fauna and humans. PFOA is dissociating in water and in this form has a low vapour pressure and high solubility, and is not volatile. Two different pathways are thought to be of importance for long-range transport of PFOA: transport with oceanic currents, and atmospheric transport of volatile precursor substances, which degrade into PFOA.

The environmental distribution of PFOA is studied using the global multicompartment chemistry-transport model MPI-MCTM. The model is based on a three-dimensional Earth system model, consisting of the atmospheric circulation model ECHAM-HAM with two-dimensional compartments (top soil and vegetation surfaces) embedded, and the oceanic circulation model MPIOM/HAMOCC. Sources of PFOA in the model include primary emissions for 1950-2004 and formation in air from oxidation of 8:2 fluorotelomer alcohol (FTOH). Primary emissions of PFOA consider emissions from fluoropolymer manufacturing facilities and APFO manufacturing facilities only [1-2]. Degradation of PFOA from 8:2 FTOH is based on a simplified oxidation mechanism as suggested by Wallington, 2006 [3]. The relative contribution of oceanic currents and atmospheric transport of 8:2 FTOH and subsequent deposition of PFOA for the transport into the Arctic is examined.

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Concentrations of chlorinated paraffins and brominated flame retardants in Greenland shark from the North-East Atlantic

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The Greenland shark (*Somniosus microcephalus*) is a long lived (possibly over 100 years) top predator in the Arctic marine food web and is therefore an excellent monitoring species of persistent organic pollutants and their metabolites in remote ocean waters. Previous work on this species has revealed concentrations of contaminants like polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) in the same range as in other high trophic Arctic species. Here we extend the knowledge about the contaminant burden in this living archive of human emissions with concentrations of chlorinated paraffins (CPs), complex technical mixtures used for example as flame retardants, as additives in metal-working fluids and as plasticizers. Furthermore we also present concentrations of pentabromoethylbenzene (PBEB), 2,3,5,6-tetrabromo-*p*-xylene (*p*TBX) and 1,2-bis(2,4,6-tribromophenoxy ethane (BTBPE), all used as brominated flame retardants (BFRs).

Short chain CPs (C₁₀-C₁₃, SCCPs) and medium chain CPs (C₁₄-C₁₇, MCCPs) were analysed with GC/HRMS (ECNI) in fifteen female Greenland sharks (liver samples) collected from the waters around Iceland between 2001 and 2003. Five of the individuals (liver samples) were also analysed for a set of flame retardants (FRs) (brominated and chlorinated) with GC/MS (ECNI). SCCPs were present above the method detection limit (MDL) in all but one sample with a median concentration of 380 ng/g fat (range: <92-870 ng/g fat). MCCPs were detected but not above the MDL in any of the samples analysed. Concentrations of SCCPs are lower compared to total concentrations of PCBs and DDTs measured in the same individuals. But compared to concentrations of PBDEs, the SCCP burden in these sharks is higher and the concentrations are also comparable to individual concentrations of for instance some PCB congeners and hexachlorobenzene (HCB). The profile of SCCPs was also examined and C₁₁ congeners with fairly low chlorine content were the most abundant, in agreement with other studies from the Arctic.

Among the FRs investigated the compounds identified so far other than PBDEs are PBEB, *p*TBX and BTBPE with mean concentrations of 7.5, 2.1 and 4.2 ng/g fat, respectively.

Environmental level distribution in river water in Japan and its implication to the environmental exposure assessment

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Environmental levels in river water and in other media apparently are not homogeneous over geographical scale. As the level distribution in the environment is significant, i.e., ranging over 4-6 orders of magnitude in Japan, exposure assessment based on the distribution information is the essential direction of assessment methodology. In this abstract, relation between environmental level distribution in river water in Japan estimated by geo-referenced model and monitoring data are discussed.

For the model estimation in this study G-CIEMS geo-referenced multimedia fate model is used for the simulation¹⁾. Segmented river water concentration of 38,000 river segments are simulated based on the model. Emission data is taken from PRTR program in Japan. Monitoring data is taken from several national monitoring programs in Japan.

Figure 1 shows the plots of environmental level information by model and monitoring data compilation for bisphenol-A. Level distribution from modelling approach shown in Figure 1 consists of three box-whisker summaries. First box-whisker shows the level distribution of whole simulation output of 38,000 river segment data. Second and third box-whiskers show the extracted data for residential area and for highly-populated area from whole outputs, respectively. It is clear that when data are extracted by population density the simulated range of level distribution approaches to the range of monitoring data. This could indicate the importance of geographical representativity to estimate the reference level and distribution for exposure assessment, especially when going to use highly-resolved model outputs.

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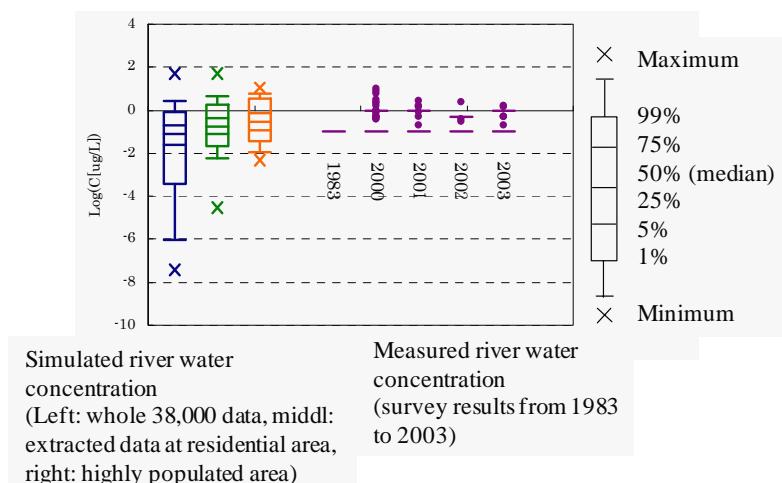


Figure 1 Simulated and measured river water concentration distribution of bisphenol-A in Japanese river system

Synthetic photoproducts of Diclofenac—Standards for environmental fate studies

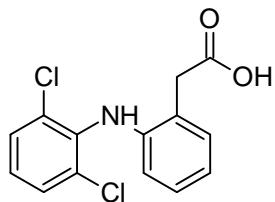
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Organic compounds containing electron-donor and electron-acceptor groups linked through a conjugated system may absorb energy from ultraviolet radiation, resulting in excited states with very high dipole moments. Such structural elements are frequently found in high production volume chemicals (HPVC), including pharmaceutical substances. Upon exposure to UV-radiation these compounds may undergo photochemical transformation reactions, forming products with decreased internal energies, i.e. compounds of enhanced stability. It is known that even relatively low-energy UV-light may initiate transformation reactions of pharmaceuticals.

A vast number of pharmaceutical compounds has been found downstream of waste water treatment plants (WWTPs). The structural complexity of individual compounds along with their susceptibility to undergo transformation reactions implies a challenging work for environmental chemists. The research concerned with the environmental fate of these emerging contaminants is consequently receiving more attention. It should also be emphasized that the application of UV-radiation in water treatment may provide a direct source for the introduction of phototransformation products to the aquatic environment.

The aim of this work was to synthesize the proposed transformation products of the non-steroidal anti-inflammatory drug diclofenac, in order to gain deeper insight into the mechanistic, kinetic and ecotoxicological aspects associated with the photochemical transformations.



Diclofenac

Exploring promiscuous activities in a lipase

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Nature has created living systems with diverse biochemical reactions mediated and regulated by enzymes. Enzymes are known to be specific for their substrates and reactions. However, some enzymes have wider substrate and reaction recognition. Today, this enzyme quality is well-known as enzyme promiscuity.^[1-5] The enzyme *Pseudozyma antarctica* lipase B, formerly known as *Candida antarctica* lipase B, has been well-explored for both its native and promiscuous activities and it is used in numerous applications within the field of Biocatalysis. We have explored two promiscuous activities of *Pseudozyma antarctica* lipase B, conjugate additions^[6-8] and direct epoxidations^[9], in detail by laboratory experiments and molecular modeling to demonstrate how these reactions occur inside *Pseudozyma antarctica* lipase B.

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Non-BDE flame retardants in Lake Winnipeg (Canada) biota

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With the voluntary phase out of penta- and octa-BDE formulations by industry in 2004 and with tighter regulations being placed on the use of decaBDE in North America it is likely that other non-BDEs type flame retardants will emerge as replacement chemicals. Evidence for this has already emerged: 1,2-bis(2,4,6-tribromophenoxy)ethane, for example, is thought to be the replacement chemical for applications in which the octaBDEs formulation were used. In this study, archived extracts of biota which were analyzed previously for BDEs and which represent components of a Lake Winnipeg food web were analyzed for a suite of emerging bromine-based chemicals. Of particular note is the detection of octabromotrimethyl-phenylindane, bis(2-ethyl-1-hexyl)tetrabromophthalate and 2-ethylhexyl-2,3,4,5-tetrabromo-benzoate at small ng/g (lipid weight). Other mono-cyclic BFRs, notably hexabromobenzene, pentabromotoluene and 2,3,5,6-tetrabromoxylene, were also detected. Overall, ΣBDEs still account for the majority of BFRs detected.

Debromination products of decabromodiphenyl ether detected in sediments and periphyton of DecaBDE-ammended mesocosms

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Decabromodiphenyl ether (DecaBDE) is a brominated flame retardant found in a variety of consumer products. Although recently banned in the European Union, DecaBDE continues to be used in other countries. A legacy of DecaBDE remains in lake sediments worldwide. The use of DecaBDE is controversial because of its potential to break down into lower-brominated diphenyl ethers, which are generally more readily absorbed and more toxic. Laboratory studies have shown that DecaBDE can be degraded by light, by anaerobic microbes, and in fish. Whereas debromination has been clearly demonstrated under laboratory conditions, the extent to which this process occurs in the natural environment is largely unknown. We are examining the fate of DecaBDE in a boreal lake at the Experimental Lakes Area in Ontario, Canada, to determine: i) the extent to which DecaBDE is debrominated in the littoral zone of a boreal lake; and ii) the bioavailability of DecaBDE and its potential breakdown products to aquatic biota. In 2007 and 2008, we installed 10-m diameter mesocosms in the littoral zone of a remote, oligotrophic, temperate lake. The mesocosms are open to the atmosphere and sediments and contain a natural littoral food web. We added a single dose of DecaBDE (BDE-209) to three mesocosms, and a fourth mesocosm served as a control. We are collecting environmental and biotic samples over a 2-year period. Our study will be the first to determine, under realistic field conditions, if DecaBDE is debrominated in the aquatic environment and whether these more toxic breakdown products are subsequently bioaccumulated by aquatic biota. In this poster, we will present results from sediment and periphyton samples which show that DecaBDE was debrominated to lower-brominated congeners (nona- through to hexa-BDEs) within weeks to months.

Dioxins and PCB in fermented Baltic herring and pickled herring

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Pickled herring is usually made of Atlantic herring and is served at for example Midsummer celebrations, Smorgasbord and at Christmas buffets in Sweden. The fish used for *fermented Baltic herring* is usually caught in the Bothnian Sea in early summer and then treated in brine for around three to four weeks at controlled conditions. In the beginning of August it is an old Swedish tradition to eat the fermented Baltic herring, usually outdoors.

Within the official control program of food in 2008, the National Food Administration has tested a few samples of fermented Baltic herring and pickled herring for the dioxin and PCB concentrations. The levels of these organic pollutants are usually elevated in fish with a high fat content from the Baltic Sea. The results are presented in the table below.

	Σ total TEQ*	Σ PCDD/F TEQ*	Σ Indicator PCB*	Σ PCB TEQ*	Σ mono ortho PCB TEQ*	Σ non ortho PCB TEQ*
Pickled herring (N=5)						
Mean	0.62	0.32	4080	0.30	0.10	0.20
Median	0.74	0.36	4300	0.33	0.11	0.21
Min	0.26	0.12	2600	0.14	0.06	0.08
Max	0.80	0.48	5100	0.39	0.13	0.27
Fermented Baltic Herring (N=4)						
Mean	12.2	8.93	47250	3.23	1.43	1.77
Median	12.1	8.95	47500	3.25	1.45	1.80
Min	8.60	6.80	40000	1.80	1.10	0.68
Max	16.0	11.0	54000	4.60	1.70	2.80

*) Concentrations in ng/kg fresh weight. TEF factors from 1998¹ are used for the calculations. Concentrations below LOQ have been set to LOQ. \sum Indicator PCB is the sum of PCB 28, 52, 101, 118, 138, 153 och 180.

As can be seen, elevated concentrations of dioxins and PCB were found in the samples of fermented Baltic herring whereas the levels found in the selected samples of pickled herring were relatively low. The levels found in the fermented herring reach or exceed the maximum limits set by EU (1881/2006/EC). However, the levels found are comparable to concentrations analyzed in fresh herring from the Baltic Sea and since Sweden has derogation from the maximum limits in fish the fish may still be sold at the national market.

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Identification of an abundant substituted brominated diphenyl ether isolated from whale blubber

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A previously unidentified organobromine compound was isolated from whale blubber and analysed with nuclear magnetic resonance spectroscopy (NMR). The compound was identified as 6'-Methyl-2'-methoxy-2,3',4,5'-tetrabromodiphenyl ether.

Result and discussion

After extraction and purification of 16 kg whale blubber the unidentified compound was isolated with preparative capillary gas chromatography (PCGC). This method enables isolation of large amounts of single compounds in high purity by collection of fractions during repeated GC runs (Fig 1).

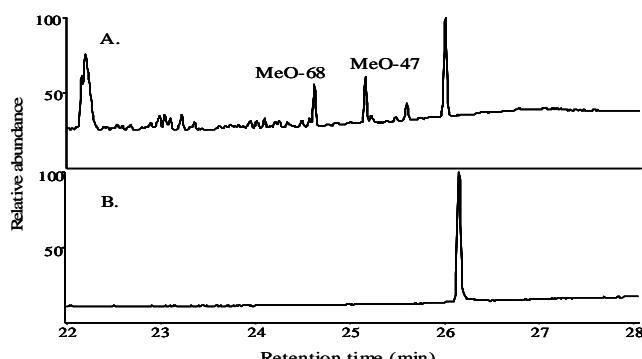


Fig 1: Fullscan GC-MS chromatogram a) before and b) after PCGC. MeO-68 and MeO-47 are abbreviations for 2'-methoxy-BDE-68 and 6-methoxy-BDE-47 respectively.

Fullscan GC-MS showed a single compound with four bromines and a mass-to-charge ratio of 526. ¹H-NMR data proved the isolated compound to be a brominated diphenyl ether with one methyl and one methoxyl group. ¹³C shifts were obtained for protonated carbons through heteronuclear single quantum coherence (hsqc) and supported the suggested structure (Fig 2).

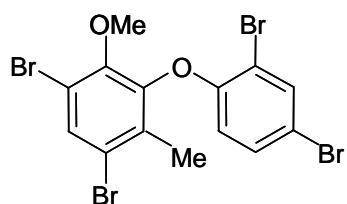


Fig 2: Structure of 6'-Methyl-2'-methoxy-2,3',4,5'-tetrabromodiphenyl ether isolated from whale blubber.

**Partitioning of tetra- and pentabromo diphenyl ether and
benzo(a)pyrene among water,
dissolved and particulate organic carbon along a salinity gradient
in coastal waters**

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This study assessed the partitioning of 2,2',4,4'-tetrabromo diphenyl ether (BDE-47), 2,2',4,4',5-pentabromo diphenyl ether (BDE-99) and benzo(a)pyrene (BaP) among water, dissolved organic carbon (DOC: 4.93 to 8.72 mg L⁻¹) and particulate organic carbon (POC: 191 to 462 µg L⁻¹) along the salinity gradient (0 ‰ to 5.5 ‰) of the Baltic Sea. Equilibrium dialyses and two solid phase extraction techniques using polyoxymethylene polymer (POM) were used to determine partitioning coefficients (*K*). Experiments using artificial coastal water (ACW) with Nordic fulvic (NoFA) and Nordic humic acids (NoHA) were used to assess effect of salinity (0 and 5.5 ‰) to the DOC–water partitioning of the model compounds. All three compounds bound more (2.2 to 3.8 fold) to the HA than to the FA. Increasing salinity from 0 to 5.5 ‰ decreased sorption to dissolved humic substances in the ACW and Baltic Sea water samples. Along the salinity gradient the sorption of compounds to organic material decreased when the salinity increased. Particulate organic matter sorbed model compounds per unit of carbon more than dissolved organic matter. Along the studied salinity gradient freely dissolved portion increased from 10-29 % to 52-80 % in the coastal water samples mainly due to the increasing salinity and changes in the DOC and quality of POC.

Isopropyl alcohol: An effective, powerful, 'green', solvent for the preparation of ketoconazole and thiazole derivatives as antifungal agents

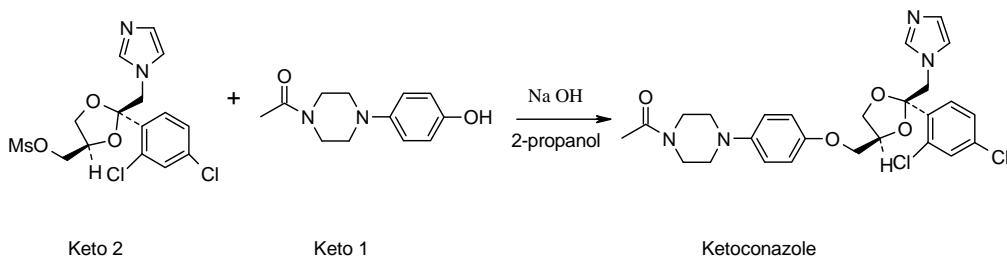
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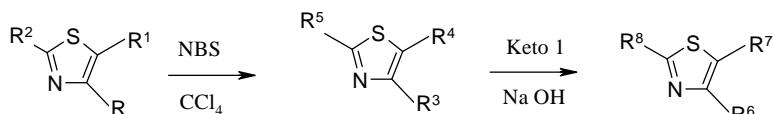
³Department of Chemical Engineering, Islamic Azad University, Ayatollah Amoli branch, Amol, Iran

Azole antifungals represent one of the largest classes of antifungal agents today acting as sterol biosynthesis inhibitors in fungi [1]. Despite intensive research efforts over the years, azole antifungals still remain a viable lead structure in the pursuit of a more efficacious, broad spectrum, systemic fungicidal drugs [2-3]. In this work we prepared ketoconazole from commercial available materials 1-Acetyl-4-(4-hydroxyphenyl)piperazine (keto 1) and cis-2-(2,4-dichlorophenyl)-2-(1H-imidazole-1-ylmethyl)-1,3-dioxalon-4 ylmethylmethanesulfonate (keto 2) in presence of sodium or potassium hydroxide in 2-propanol (Scheme 1).



Scheme 1 Preparation of ketoconazole

Also, we prepared some thiazole derivatives of ketoconazole by reaction of bromomethylthiazoles with Keto 1 in presence of NaOH in 2-propanol. The bromomethylthiazoles were synthesis from selective bromination of thiazoles with NBS (Scheme 2). The new materials have low biological activities in compare to ketoconazole.



Scheme 2 Preparation of thiazole derivatives

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Determination of poly- and perfluorinated compounds (PFC) in the marine atmosphere of the Baltic Sea

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Volatile and semivolatile perfluorinated compounds (PFC) such as fluorotelomer alcohols (FTOH) and perfluorosulfonamides have been identified as precursors of the persistent perfluorooctanoate and perfluorooctanoate sulfonate. Here, we present the distribution of polyfluorinated compounds in ambient air in the Baltic Sea region. Neutral and ionic PFC were determined in 27 air samples collected onboard the German research vessel Maria S. Merian during a cruise in the Baltic Sea in June and July 2008. Fluorotelomer alcohols, fluorotelomer acrylates, perfluoroalkyl sulfonamides, and perfluoroalkyl sulfonamido ethanols in the gaseous and particulate phase were enriched onto PUF/XAD-2/PUF cartridges and glass fiber filters. Perfluorinated carboxylates and sulfonates were only determined in the particulate phase. Total gas phase concentrations Σ PFC ranged from 20 pg m^{-3} to 164 pg m^{-3} . FTOH are the most frequently observed class of PFC. 8:2 FTOH was the predominant substance in all samples. Trajectory analyses revealed the importance of air mass origin. They indicated increased PFC contamination in air masses which arrived from potential source regions in Western Europe as well as the Gulf of Finland.

Studying sarin, soman and sulfur mustard stability in drinking water

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At the present time possible chemical terrorist acts (or “chemical terrorism”) are considered to be a serious threat to the national security.

Among the large number of potential terrorist chemical agents, of special importance are chemical warfare agents: sarin, soman and sulfur mustard, particularly in the case of releasing these agents in water supply system.

The research carried out previously shows the regularities of the sarin, soman and sulfur mustard behaviour in deionized water.¹ In particular, it was determined that the pH has a considerable influence on the hydrolysis rate.

In this connection it was rather useful to collect data about the stability of the agents in actual drinking water, which has certain buffer properties compared to deionized water.

The report covers the results of studying sarin, soman and sulfur mustard in actual drinking water.

The kinetic research was carried out for completely dissolved sarin, soman and sulfur mustard at 10°C, 20°C for sulfur mustard, and 20°C, 30°C for sarin and soman. The concentrations of the researched substances in water ranged between 230 – 260 mg/dm³.

The hydrolysis of sarin, soman and sulfur mustard was controlled by the gas chromatography with flame photometric detection.

The final detectable concentrations made $2.5 \times 10^{-2} - 5.0 \times 10^{-2}$ mg/dm³ for sulfur mustard (0.01 – 0.02% of the initial concentration) and 2×10^{-5} mg/dm³ for sarin and soman.

Based on the obtained kinetic data hydrolysis parameters (rate constants, a half reaction time (τ_{50}), and a 99% hydrolysis time (τ_{99})) were calculated.

The results have shown that the sarin and soman stability in drinking water is higher than in deionized water. Stability of sulfur mustard in drinking and deionized water does not differ significantly.

The obtained results allow making scientific decisions on the ways of treating water and on the opportunity of its use after sarin, soman or sulfur mustard contamination.

The present research work was financially supported by ISTC and was carried out within the framework of the Project # 3642p (in the partnership with USEPA).

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Determination of pharmaceuticals in water samples of the Belgian coastal zone and the Scheldt estuary using LC-MS

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Pharmaceuticals are the active substances of medicinal products used in human and veterinary medicine. They are excreted either in their native form or as a metabolite and are discharged to the sewer system [1]. Via the sewage water pharmaceuticals reach the waste water treatment plant where they are not completely degraded, resulting in a continuous release of pharmaceuticals in the aquatic environment [2]. In recent years, numerous monitoring studies have demonstrated the occurrence of pharmaceuticals in the aquatic system at concentration levels from the low ng.l⁻¹ up to µg.l⁻¹ concentration level [3,4]. Based on current evidence, little is known about the occurrence and the persistence of pharmaceuticals in the marine ecosystem [5]. The objectives of this study were at first to develop and validate an analytical approach for the determination of 15 pharmaceuticals in surface water, including sea- and freshwater. Secondly, the method was applied to samples of the North Sea and the Scheldt estuary in order to know more about the presence of pharmaceuticals in marine environment and their transfer to estuarine and marine ecosystems. This study, which is part of the INRAM project (www.vliz.be/projects/inram), is the first to report the detection of concentrations of pharmaceuticals up to 0.855 µg.l⁻¹ in the marine environment.

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Genotoxicity/antimutagenicity of humic acids extracted from regenerated and modified lignite

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Humic acids produced for this study were extracted from regenerated and modified lignite using the standard alkaline method with 0.5 NaOH and 0.1 Na₄P₂O₇. For chemical oxidation nitric acid (5%, 10% and 20%) and hydrogen peroxide (2% and 5%) were used. For physical modification acetic acid (20%) and citric acid (20%) were used. The attempted goal of such lignite pre-treatment is the production of humic acids with a certain standard of desirable and well defined properties. Humic acid from original lignite was extracted too.

Antimutagenicity tests were performed with the yeast *Saccharomyces cerevisiae* using the method first described in Zimmermann, 1984. 4-nitroquinoline-N-oxide was used as mutagen to achieve tryptophane conversions and isoleucine reverse mutations on their selective media. Numbers of grown yeast colonies were used to calculate percentage of inhibition of mutagen in the presence of humic sample according to the equation %_{inh} = 100 - [(X₁/X₂) * 100], where X₁ is the number of the yeast colonies in the presence of mutagen and humic sample and X₂ is the number of the yeast colonies in the presence of mutagen without humic sample. Four different concentrations of humic solution (0.03%, 0.06%, 0.125% and 1%) were tested. This assay was performed on all samples in form of potassium and ammonium humates with the aim to evaluate and compare the suitability of individual regeneration/modification as well as the influence of counterion from point of view of genotoxicity/antimutagenicity.

As for the influence of counterion, our results show that potassium humates are more suitable for this study as they show better solubility and stable pH values. Yet, we were able to compare both lines with an interesting outcome that the effect of pre-treatment was exactly the opposite in potassium humates than in ammonium humates. Specifically, in potassium humates the original sample demonstrates high antimutagenicity but with increasing strength of HNO₃ this positive effect declines. Thus, although the whole HNO₃ line is harmless only 5% HNO₃ regeneration is profitable in terms of antimutagenicity. In ammonium humates, all samples in HNO₃ line including the original one supported mutagen activity, the worst case being 5% HNO₃ regeneration. Regeneration with H₂O₂ bolstered positive effect in ammonium humates, especially in 5% H₂O₂ regenerated sample. On the contrary, H₂O₂ line of potassium humates supported mutagen activity with the only exception of high sample dilution (0.03%). Regeneration with organic acids produced mostly harmless humates, with positively outstanding results for highly diluted samples (0.03%). An important conclusion is that according to lethal controls no humate was genotoxic itself. When preparing a material with certain properties it is necessary to contemplate the availability of toxic groups and take into account anomalies occurring at specific concentrations in combination with particular counterion.

Acknowledgement:

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Assessing PBT properties of PFOA – Overview and outlook

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Substances of very high concern (SVHC) will be listed in Annex XV of REACH. Decision on inclusion is made on the basis of properties of the substance in question. A substance is of very high concern if it is either classified as CMR (carcinogenic, mutagenic or toxic to reproduction), shows PBT properties (persistent, bioaccumulating, toxic) or there is an equivalent concern (provisions cf. Article 57 of REACH; process cf. TGD chapter R.11).

Although some substances may not clearly meet CMR- or PBT-criteria they may nevertheless be of very high concern, as it is in the case of Perfluorooctanoic Acid (PFOA).

For several years some producers of polyfluorinated polymers generated PFOA data to train for REACH and to improve data situation. German agencies commented the whole process, advised and assessed the data.

This poster shows the assessor's view: why we think PFOA meets the criterion of equivalent concern based on the available information and how we intend to proceed.

In-silico tools in risk assessment

Poster abstracts

Sil P1-P16

SP-LFERs are obsolete

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Initially, environmental chemists were uncertain how to best approach the partitioning behaviour of organic compounds into important environmental media, such as soils and sediments. The biggest difficulty was accounting for the chemical activity in these diverse environmental phases. Thus, to deal with this, simplifying assumptions were made, such as the environmental sorbing phase being an ideal solvent (Raoult's Law) or proportional to the chemical activity in octanol. A classic example is $\log K_{oc} = a \log K_{ow} + b$, where K_{oc} is the partitioning constant in natural organic carbon, K_{ow} is the octanol-water partition coefficient, and a and b are constants fitted by linear regression. These simplified approaches came to be known as single-parameter linear-free energy relationships (SP-LFERs).

As environmental chemistry as a discipline developed, the shortcomings of SP-LFERs become increasingly evident. Amongst the biggest concerns are that they have to be recalibrated for various compound classes (especially polar compound classes), and they do not account for the diversity of complex environmental media. In response, more explicit alternatives to SP-LFERs have been developed.

One such alternative is poly-parameter linear free energy relationships (PP-LFERs), which separate the contributions of specific sorbent-sorbate interactions. Even when using a diverse set of polar and apolar compounds, PP-LFERs boast a much higher degree of accuracy than SP-LFERs, and can often be calibrated to predict partition coefficients within a root mean square error of 0.3 to 0.4 log units for complex environmental phases. PP-LFERs, unfortunately, suffer the disadvantage of requiring molecular descriptors that are not as commonly available as K_{ow} values. Thus, there are many cases in which PP-LFERs cannot be utilized though SP-LFERs still can (though the number of such cases is decreasing).

Another alternative to SP-LFERs are molecular structure based approaches, which are based solely on the molecular structure of the sorbent and sorbate. These include quantum chemical approaches (e.g. COSMOtherm) and the SPARC online calculator. To validate such models, only measured environmental partition coefficients are needed, and no other experimental data. Thus, they are inherently more chemically robust than SP-LFERs and require less experimental data as input. Further, based on work done so far, validated molecular based approaches can predict environmental K values for a wide set of compounds usually with an rmse of 0.6 to 0.8 log units, and are thus more accurate than SP-LFERs.

In this presentation, an overview of PP-LFERs and molecular-structure based approaches will be presented, as developed for terrestrial aerosols, humic acids, contaminated sediments and other phases. These modelling techniques show a far greater potential than that conceivable with SP-LFERs, in terms of accuracy, practicality and chemical robustness. Thus, we argue that environmental chemists should abandon the early, simplifying assumptions regarding chemical activity behind SP-LFERs, as there are continuously less reasons to keep assuming them, especially for emerging contaminants.

QSAR studies on mouse inhalation LC₅₀ data of perfluoro-compounds

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Perfluoro compounds have been very useful for chemical and mechanical industries mainly due to the stability of C-F bond, hydrophobic effect and thermal resistivity, but the fluorinated residues released in the environment are not quite degradable and are leading to environmental bioaccumulation, bio-persistence and health problems [1]. The mammalian toxicity of some of Perfluoroalkylated (PFA) compounds are studied in laboratory [2] but there are very few data available for developing Quantitative Structure-Activity Relationship (QSAR). Analysis of the structure of these compounds indicates that many congeneric fluorinated analogs are available and can be present in the environment. There is a general agreement that similarity in structure and properties indicates similar environmental fates and human health concerns. Thus, a dataset was prepared to study several perfluoro- and multi-fluorinated compounds with different functional groups as alcohols, acids and esters (**Fig.1**).

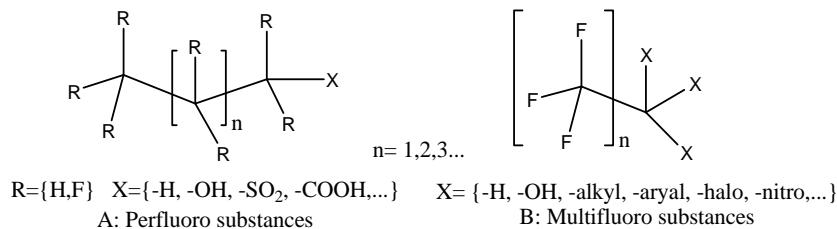


Fig.1: Depiction of Perfluoro- and Multifluoro- compounds included in the dataset.

QSAR modelling by Multiple Linear Regression (MLR) is used as an *in silico* screening tool to predict the Mouse Inhalation (LC₅₀) toxicity data of 56 perfluoro-compounds including other congeneric multifluoro-compounds which has not been yet tested for toxicity. The models are developed according to the OECD principles [3]. The data set was split in two different ways: a) based on response value, and b) based on structural similarity verified by Self Organizing Map (SOM), in order to propose reliable predictive models, developed on the training set and externally verified on the prediction set. 1D- and 2D- physico-chemical descriptors were calculated using DRAGON [4a] and MOPAC [4b]; Genetic Algorithm-Variable Subset Selection (GA-VSS) method was used to find the best combination of descriptors for modelling. The performance of the QSAR models was assessed by both internal and external validation, Y-scrambling, and bootstrap method. The robustness of the models and their applicability domain will be discussed. The predicted (Mouse Inhalation LC₅₀) response value of other congeneric PFAs based on the best selected models and on a consensus model will be presented. (*Financial support by European Union through the project CADASTER FP7-ENV-2007-1-212668*)

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CoZMoMAN: A dynamic mechanistic model of the link between environmental emissions of POPs and human body burdens

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Different factors affect how Persistent Organic Pollutants (POPs) released into the environment over time distribute and accumulate, enter various food-chains, and potentially cause toxic effects in wildlife and humans. A sound risk assessment for POPs thus requires the determination of the quantitative relationship between emissions and human exposure. For this purpose an integrated, mechanistic, non-steady state environmental fate and human food chain bioaccumulation model (CoZMoMAN) has been developed. Building upon earlier evaluations of the sub-models upon which CoZMoMAN is based, an overall model evaluation for selected polychlorinated biphenyls (PCBs) in the western part of the Baltic Sea drainage aims to establish further confidence in the integrated model. CoZMoMAN-predicted PCB concentrations in 11 key model compartments are typically within a factor of 2 to 4 of measured values. CoZMoMAN was further used to explore the validity and implications of the steady-state assumption frequently made in risk assessment models. A steady-state approach may fail to properly describe the long-term behaviour of more persistent POPs in environmental media that respond slowly to emission changes (e.g. soil, humans). The results also illustrate the potential difficulties in defining a steady-state emission inventory for substances for which the rate of release may have fluctuated over several orders of magnitude during the time-scales relevant for exposure assessment. Possible implications with respect to a sound understanding and management of chemicals with similar use and fate properties are discussed.

Screening chemicals for the potential to be POPs

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Based on a quantitative understanding of the relationship between chemical properties and environmental behavior, it is becoming possible to identify the properties of substances that qualify as contaminants of concern. For example, we now can determine what chemical characteristics make an organic substance susceptible to accumulation in the Arctic physical environment¹. Similar approaches seek to constrain the properties of substances bioaccumulating in human food chains². It should thus be possible to screen the multitude of chemicals of commerce for those that do possess such properties, and which therefore are most likely to be found in environmental and human tissue samples.

A chemical must traverse a complex pathway to become a contaminant in the Arctic food chain; emission, long range transport, deposition, exposure, bioconcentration and biomagnification all play a role. A mechanistically based screening method relying on the modelling study by Czub et al.³ screens the partitioning properties of chemicals for the potential to be environmentally transported to the Arctic and bioaccumulated in the Arctic food chain. To filter out chemicals which are quickly degraded in the atmosphere and therefore have low long range transport potential, an atmospheric OH oxidation half-life cut-off is used.

Chemicals which have already been identified as contaminants in the higher trophic levels of the Arctic food chain must have the correct combination of chemical properties to traverse the entire pathway from emission to human. These properties are themselves governed by chemical structure, implying that there may be a limited number of possible combinations of structural features that give rise to the properties of an Arctic contaminant. Indeed many known Arctic contaminants share a number of structural characteristics and these are used to screen chemicals for structural similarity to known contaminants.

Within a dataset of more than 100,000 chemicals the Arctic contaminant screening methodology identifies 913 chemicals which are known Arctic contaminants or are structurally similar to known contaminants. An additional 1250 chemicals fulfil the criteria of partitioning properties and atmospheric persistence, yet are dissimilar to known Arctic contaminants⁴.

Several aspects of the mechanistic screening method warrant further investigation. Long range transport is typically associated with atmospheric transport, but ocean currents can also act as a transport mechanism. Another issue is the effect of intermittent rain; model calculations of physical transport to the Arctic assume constant rainfall, and this may cause the long range transport potential of some chemicals to be underestimated.

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Controlled indoor experiments on the wind speed dependence of contaminant uptake in XAD-based passive air samplers

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Passive air samplers (PAS) intend to measure the time-averaged concentrations of semi-volatile organic contaminants in the atmosphere. To obtain quantitative data from a PAS the sampling rate should be constant and measurable. There are several criteria that need to be met for this to be true. The sorption medium must have a large enough capacity for the contaminant that the uptake over the entire sampling period is within the linear range where equilibrium has not yet been reached. In order to compare the results from PAS deployed at different sites, it is further imperative to understand the influence of environmental factors such as temperature and wind speed on the uptake and retention of chemicals. An ideal PAS will thus have a sampling rate that is independent of environmental conditions such as temperature and wind speed. Alternatively, it is necessary to understand the influence of environmental factors quantitatively so as to account for them in the data interpretation.

Whereas early wind tunnel experiments and fluid mechanics simulations for the XAD-based PAS by Wania et al.¹ seemed to indicate that the sampler housing largely eliminates the influence of variable wind speed on the uptake rate, subsequent studies have called this into question². For example, compounds known to have relatively uniform atmospheric concentrations, such as hexachlorobenzene, regularly display higher sequestered amounts in PAS deployed at windy locations, suggestive of a higher sampling rate. Also, the uptake in other PAS with different housing design has been shown to depend on wind speed³. The goal of the current study was to resolve the issue of variable sampling rates by performing experiments under tightly controlled wind conditions indoors.

Three sets of twelve XAD-based PAS were exposed to different wind conditions indoors. The different sets of samplers were exposed to (i) wind still conditions, (ii) constant wind blowing perpendicular to the sampler housing, and (iii) constant wind blowing at a fixed angle. To assure comparable wind fields for each sampler, wind was generated by individual electric blowers directly aimed at each sampler housing. Duplicates from each set were retrieved after time periods ranging from 1 to 5 month, and analyzed for PCBs and PAHs typically present in indoor air. Active samples taken in the same room as the PAS allows for an independent determination of the air concentrations during the deployment period. Plotting the amount of SOCs sequestered versus time of deployment, sampling rates can be determined from the slope of the resulting uptake curves and the average air concentration.

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School students working as environmental scientists – “Global POP”

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The world of today is facing large environmental threats such as climate changes and spread of contaminants. Environmental awareness has become a part of our daily lives. In order to engage youth in environmental issues and ignite their interest for natural sciences, we are running a scientifically based project where students participate with environmental research on dioxins in fish. In the International Polar Year project "Global POP", school students follow a scientific protocol for fish sampling; they record and publish to web important field- and fish-data, and label, pack and ship the samples to NILU (Norwegian Institute for Air Research) for BDS CALUX dioxin analysis. The project has demonstrated that pupils are very conscientious and follow scientific instructions meticulously.

At present the results from the first sampling are finished, and field- and fish data from some of the participating schools are already published on the web page (sustain.no/projects/globalpop). We have made an effort to engage more schools in the project and expanded the fish sampling period to the spring 2009. From a scientific research point of view we are very happy for being able to serve this large and important dataset to the scientific community and authorities. At present 50 school classes have sent fish samples for analysis and 37 schools have uploaded their data into the database on the web page. We have received and delivered results on approximately 160 samples of 22 different fish species of which some species have not previous been analysed for their dioxin level. The majority of the samples had TEQ concentrations well below maximum limits set by WHO and the EU commission. We conclude that collaboration between schools and research institutions are beneficial for both partners. This dataset, which would be difficult to obtain without the effort of the involved schools, is providing novel results on dioxins in fish.

Atom-Centred Fragments in QSAR Modelling

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Atom-centred fragments (ACF) models work by decomposing molecules into individual atoms, and characterizing the atoms by selected atomic properties, bonds to other atoms, next neighbour atoms, and optionally more than next neighbours. They can be used as a new tool to improve model predictions, to select appropriate models from a set of models, to apply read-across approaches, and to determine the chemical domain of models. This talk focuses on ACFs for read-across models and chemical domain analyses.

In read-across approaches, ACFs can be used to run k next neighbour models. ACFs are employed to select the most similar compounds. Working examples are shown for the consistent prediction of the acute aquatic toxicity for both baseline and excess toxic compounds.

In the chemical domain analyses, ACFs are employed to examine whether a test compound is covered in the training set of a model with respect to its chemical composition. A study is presented to optimize the use of ACF for the model domain characterization of quantitative and classification models for physical-chemical properties and ecotoxicological endpoints.

This study has been financially supported by the EU projects OSIRIS (IP, contract no. 037017), CAESAR (contract no. 022674), and 2-FUN (contract no. 036976).

Effect of Different Tautomers on QSAR Models: Comparison between Several Levels of Tautomer Recognition

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The application of quantitative structure-activity relationships (QSAR) requires the input of the proper chemical structures of the respective compounds. However, in case of tautomers chemical structures are ambiguous. The positions of the mobile hydrogen atoms in the actual structures may affect the results.

To figure out the differences between tautomers we developed a new tautomer enumeration algorithm based on InChI (The IUPAC International Chemical Identifier). This algorithm generates tautomers for heteroatoms, marked in the InChI mobile layer. Applying the generated structures in QSAR models, significant differences in the results for tautomers of the same compound have been detected.

However, is it sufficient to focus on heteroatoms, or are there significant effects regarding carbon acceptors and triple bond connections too? Moreover, numerically heteroatom tautomerism covers only a small part in the entire field of tautomerism.

This study examines the differences between several levels of tautomer recognition with regard to atom and bond types and properties for ca. 1,000 input structures. Calculation methods for some compound descriptors as well as estimation models for several properties were applied to the generated tautomer sets, and the ranges of the results have been compared.

This study has been financially supported by the EU projects OSIRIS (IP, contract no. 037017) and 2-FUN (contract no. 036976).

Decision Tree for Toxicity Estimation in the *Tetrahymena pyriformis* Assay

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The ciliates *Tetrahymena pyriformis* are used as alternative bioassay in both human and environmental toxicology.

For the 48h growth inhibition as toxicity endpoint, we have collected approx. 1350 experimental data from literature. Employing our in-house software system ChemProp, we derived a decision tree for toxicity estimation based on mechanistic considerations and different structural alert models. The models employs different major structural alerts representing substructural features, some of which contain various related subgroups.

Regarding possible risks for human health and environment, the focus in model development was to correctly classify compounds to be at narcosis level. The presented model correctly classifies more than 99% of the narcosis-level compounds, and more than 90% correct predictions for excess-toxic compounds are achieved. The application domain for correct excess toxicity prediction is limited by the chemical domain of available data. Therefore, compound classes with rare data are classified separately as compounds with a potential environmental risk.

The study was supported by the EU Integrated projects NoMiracle (contract No. 003956) and OSIRIS (contract No. 037017).

Prediction of the partition coefficient between air and body compartments from the chemical structure

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For PBPK modelling, partition coefficients between tissues and environmental compartments are required. A simple approach starts with the system blood/air, fat/air, and fat/blood. Employing thermodynamic relationships, one of the three coefficients can be calculated from the other two values. With respect to available human and mammal data, modelling efforts focus on the blood/air and fat/air partition coefficient.

Respective data sets from literature have been collected and evaluated. The chemical domain of the sets is presented in terms of chemical structure, complexity, and polarity. Data gaps have been identified.

The blood/air partition coefficient data set has been applied to a validation of literature models, with particular remark on the performance for specific compound classes. A preliminary new model is presented.

The study was supported by the EU projects 2FUN (contract No. 036976) and OSIRIS (IP, contract No. 037017).

Prediction models for the acid-base dissociation constant

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Acid-base dissociation constant, pK_a , which defines the ionization degree of organic compounds, is an important parameter for their toxicity and environmental behavior and fate. At present there are numerous studies on theoretical prediction of pK_a values.

In order to compare the performance of different methods in pK_a prediction referring to special dissociation groups, we selected three typical methods, which are quantum chemical method (QC), sophisticated increment method SPARC including MO theory and fragment-based ACD, and carried out calculation on ca. 1200 organic acids and bases.

For the whole dataset, there isn't clear superiority for any method. Then subsets (6 acid and 9 base subsets) according to dissociation function groups were studied and different substitution position on aromatic ring were taken into consideration. During this process the discrepancy of three methods emerged. But it is really interesting that no obvious improvement get when dividing chemicals subsets by the position of substituent on aromatic ring and maybe because of diverse variability of molecular structure in complete chemical subsets.

The results of three methods on monoprotic molecules were also emphasized and compared with original results in order to exhibit the effect of existed multi-dissociation function groups on pK_a calculation.

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Air-water partition of organic chemicals in a wide range of environmental conditions

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Thermodynamic description of aqueous organic solutes is needed for modeling and/or process design in a variety of applications such as partitioning of chemicals into environmental compartments, cleanup of aqueous effluents by air stripping or by using high-temperature water as a medium for decomposition of hazardous organic waste, in petroleum exploration in sedimentary basins, for chemical speciation and phase equilibrium calculations in power cycle chemistry and in natural or technological hydrothermal solutions. This array of applications is traditionally covered by several disciplines – environmental chemistry, chemical engineering, geochemistry, power cycle chemistry – which have developed their own data bases and modeling concepts, often without a reference to the achievements reached in the other fields. Major interest for environmental chemists is directed towards the various partition coefficients (Henry's law constant, air-water partition coefficient, relative volatility, etc.), usually ignoring its variation with temperature and pressure¹ or describing it by the simplest thermodynamic integration². In chemical engineering the property of interest is either the limiting activity coefficient or the Henry's law constant, full equations-of-state for standard thermodynamic properties are needed in hydrothermal and geochemical applications³.

The thermodynamic properties of hydration that provide a theoretical basis for development of high-temperature models include the Gibbs energy of hydration, resulting from the air-water partition coefficients or from limiting activity coefficient, and their derivatives such as the enthalpy and heat capacity of hydration/solution and partial molar volume at infinite dilution (accessible from calorimetric and volumetric experiments). In many cases these derivative properties provide an essential source of information, because experimental results on the Gibbs energy level are for many solutes scarce or missing at all.

The purpose of this presentation is twofold. First, to assess in quantitative terms the errors associated with application of various modeling approaches to the prediction of air-water partitioning at higher-than-ambient conditions. Second, to report on the project under the auspices of IUPAC and IAPWS whose objective is to establish a reference database of thermodynamic properties of hydration for selected organic solutes that can be used as a standard for testing and establishment of new prediction schemes of interest for chemical engineering, environmental chemistry and geochemistry.

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Modelling human bioaccumulation using poly-parameter linear free energy relationships (ppLFERs)

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Mechanistically based bioaccumulation models are used for exposure assessment and for understanding organic chemical behaviour in food chains. Chemical partition coefficients between environmental media and biological tissues are a key component of such models. Currently, this partitioning behaviour is described using partition coefficients amongst the three reference phases octanol, air and water. The partitioning into defined organic phases in biota (such as lipids, proteins, carbohydrates and lignin) is correlated to the partitioning into octanol. The underlying assumption on which such single-parameter linear free energy relationships (spLFER) are based is that the same type of intermolecular interactions rule the energy cost/gain associated with the partitioning between water-octanol and water-organic phase. The correlations are thus specific for sets of chemicals exhibiting the same functional groups and variations in their apolar moieties.

The spLFERs commonly applied in bioaccumulation models are usually derived using apolar or weakly polar chemicals. The partitioning of neutral polar chemicals (i.e. chemicals that undergo hydrogen bonding) into organic phases is thus not well described by the spLFERs used today. Poly-parameter LFERs (ppLFERs) for partitioning between various matrices include chemical specific descriptors for H-bond accepting/donating properties and van der Waals interactions and are derived by multiple linear regression. These ppLFERs are thus valid for chemicals participating in both nonspecific interactions and hydrogen bonding. To date, ppLFERs for biotic matrices have been deduced mainly for human organs and tissues (e.g. fat, muscle, blood, skin, brain, liver) and a few non-human matrices (algae, tomato cuticle).

In this study, a ppLFER based model for organic chemical bioaccumulation in humans is presented. Chemical partitioning into the human body is described by a body-water partition coefficient estimated as a volume weighted average of the ppLFER derived partition coefficients for the major organs and tissues constituting the human body. This model is compared to a corresponding spLFER model where the human body is treated as a mixture of lipid (\approx octanol) and water. A large dataset of organic chemicals is used to illustrate the differences between the two modelling approaches. The underlying mechanistic explanations for the deviations are explored.

Influence of the choice of partitioning property estimation method on the results of the screening for new persistent organic pollutants

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In the past decade, various approaches have been developed and applied in which large numbers of organic chemicals are screened for their potential to cause environmental harm (1, 2). Most of the screening methods rely to some extent on numerical values of the chemical's equilibrium partition coefficients between air, water and octanol (i.e. K_{OA} , K_{AW} and K_{OW}). In particular, the potential for bioaccumulation and long range transport is often assessed based on a comparison of a chemical's partitioning properties with threshold values (1, 2). Since measured partition properties are available for only a few of the large number of organic chemicals being screened, the partition coefficients typically need to be predicted from molecular structure using Quantitative Structure Property Relationships (QSPRs). QSPRs differ widely in terms of their underlying approach, their applicability domains, and their suitability for predicting the properties of large numbers of chemicals. The predictions of these models presumably could deviate considerably as well, which may cause false positive or false negative chemical screening results. Here we explore the extent to which the outcome of screening efforts depends on the choice of a partitioning property estimation method.

We used three QSPRs, namely the fragment-based EPISuite (3), the molecular level descriptor based SPARC (4, 5), and the quantum chemistry based CosmoFrag (6) to estimate K_{OW} , K_{AW} , and K_{OA} for a set of 232 organic High Production Volume (HPV) chemicals, which had been highlighted in an earlier screening effort (1). EPISuite and SPARC only require the input of the organic chemical's SMILES string, whereas CosmoFrag needs to be supplied with a pre-optimised three-dimensional molecular structure. Preliminary result shows that EPISuite and SPARC can calculate partitioning properties for 220 of the 232 chemicals. Partition properties calculated by the two methods can vary widely, in the case of K_{OA} by as much as eight orders of magnitude. When the two different sets of partition properties are used as input in a chemical screening for persistent organic pollutants based on the Arctic Contamination and Bioaccumulation Potential (AC-BAP), 43 of the 220 chemicals are classified differently. In the presentation, we will identify the chemicals and functional groups that lead to discrepancies between the prediction methods and explore whether it is possible to judge one set of predictions superior to others. We will also look at the impact of QSPR selection on the outcome of other screening methods using K_{OW} and K_{AW} .

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Combining exposure- and pharmacokinetic modelling tools for elucidating the sources of human exposure to PFOA

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Biomonitoring studies of human serum show that the general population in a majority of the sampled countries has a mean concentration of approximately 5 ng/ml of perfluorooctanoate (PFOA), whereas blood serum levels for human populations near to areas of contaminated drinking water or occupation exposed individuals are significantly higher. Despite extensive efforts in analysis of a wide range of exposure media the sources of human exposure to PFOA are still poorly understood. In this study, a probabilistic approach for back-calculated internal exposures using a one-compartment pharmacokinetic model was evaluated by comparing model predictions with forward-calculated exposure estimates for two distinct human populations; i) those exposed to high concentrations of PFOA in their drinking water (Emmett et al., 2006; Hölzer et al., 2008) and ii) those with low level “background” exposure. A preliminary exposure analysis showed that drinking water intake is the dominating source of exposure (>75% of total daily intake of PFOA) when water concentrations of PFOA exceed 500 ng ml⁻¹. Thus, data from populations with measured serum concentrations in response to chronic intake of PFOA from areas with high drinking water concentrations provides an evaluation of the one-compartment pharmacokinetic model. A reasonable agreement of a factor 1.5–5.5 was found between back-calculated internal exposures from serum levels and estimated daily intakes derived from drinking water concentrations in the drinking water districts of Arnsberg, Germany and Little Hocking, US. A re-analysis of serum concentrations from a background exposed population in Bavaria, Germany in 2005 (Fromme et al., 2008) showed that the measured median intake from food is a factor of 2.6 lower than back-calculated intake from matched serum measurements. This study indicates that serum concentrations of PFOA in a background exposed population are close to reflecting contemporary exposure intakes dominated by food. Given the model uncertainty and slight overestimation of intake from back-calculated serum concentrations this study further indicates that the findings of food being the most important contemporary exposure source are consistent with a higher historical exposure (Olsen et al., 2008).

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Mobilisation of prioritised contaminants in soil and at the soil/water interface - Results from the PERSPEC project

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The aim of the PERSPEC project was to investigate and predict the impact of hydrological and atmospheric processes on the mobilisation of contaminants to, within, and from soils at a remote catchment where the major input of substances is related to diffuse pollution. The project included priority substances according to the European water framework directive (WFD), such as metals (e.g. mercury, lead and aluminium), and persistent organic pollutants (POPs; e.g. PAHs, HCB, PCBs and dioxins). Metals and organic contaminants have, in the past, often been studied separately, mainly due to their different chemical properties. However, in the environment they coexist and are subjected to the same environmental processes.

The results showed increased soil and soil pore water concentrations with increased amount of organic matter (OM) in soil profiles for both metals and POPs, with maximum values in the top layers of the riparian soil. This indicates that spring flood and other hydrological events heavily affect the stream water levels and loads of contaminants. It is also clear that wet and dry atmospheric deposition pollution fluxes in the Krycklan area show seasonality, which may be extrapolated to assess the impact of future climate change scenarios. Levels of POPs in surface water along the water path from Krycklan to the Gulf of Bothnia were measured and results show that atmospherically derived diffuse pollution has impact in addition to downstream point sources. In parallel to the field measurements, stream water pollutant mass balance models were developed and these were validated vs. the field data for the studied catchment and the following water path.

In conclusion, it is evident that a full understanding of the baseline contribution and the soil-to-water processes controlling the transport of priority substances at catchment scale is a prerequisite for assessing the variation of priority substances in water streams and river basins on a seasonal and regional scale. Such basic knowledge is also needed for estimations of the impact of diffuse sources in relation to point sources, and as research support to decision makers in risk assessment work towards well-founded regional and national threshold values. It is also clear that headwater atmospherically derived diffuse pollution may have an impact in addition to downstream point sources. Furthermore, the study clearly indicates that climate change scenarios including changes in temperature and precipitation, will affect both the accumulation and mobility patterns of contaminants in northern latitude boreal regions. The findings within the PERSPEC project are applicable to a wide variety of north European catchments systems and provide an integrated, process-based, understanding of base-line contamination of major catchments.

The execution of PERSPEC was possible under the umbrella of the European Commission's 6th Framework Programme project SNOWMAN (contract no ERAC-CT-2003-003219).

Sustainable Chemistry

Poster abstracts

Sus P1-P16

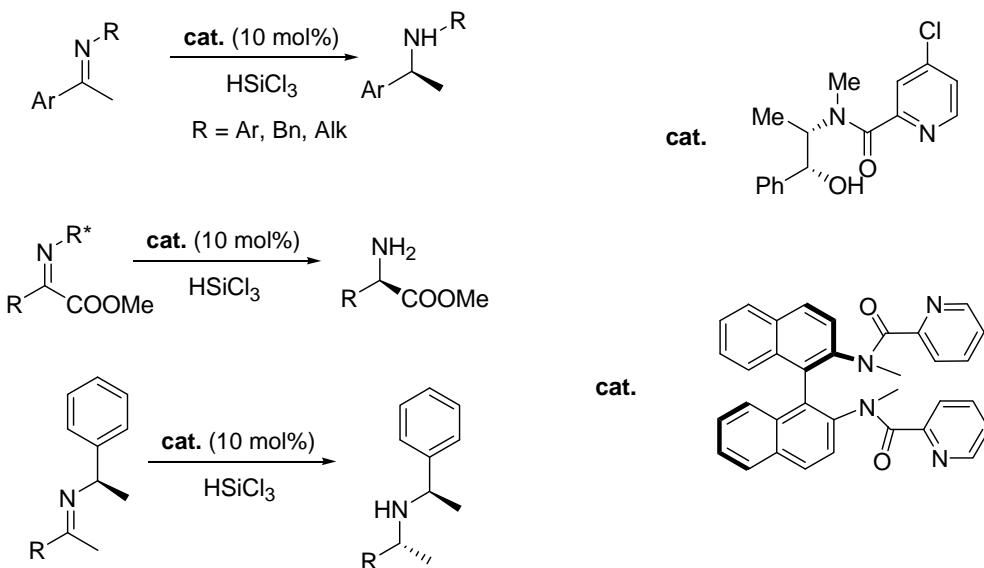
Metal-free catalytic enantioselective reduction of imines

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The synthesis of enantiomerically pure amines is a topic of paramount importance due to the centrality of these compounds in different classes of relevant chemicals such as pharmaceuticals, fragrances and agrochemicals. Despite several reported methodologies, the development of a new simple, low cost, efficient, and sustainable route to enantiomerically pure amines would be of extraordinary interest, also because it would offer the possibility to bypass existing patented strategies. In this context we wish to present an extremely efficient chemical and stereochemical synthesis of chiral amines in high ee through the Lewis-bases activated trichlorosilane reduction of ketoimines.

The very cheap, metal-free catalysts were easily prepared in one step from commercially available products, namely a chiral aminoalcohol and picolinic acid derivatives; after performing the imines reduction a simple aqueous work up allowed to obtain chiral amines often in very high chemical yields and high enantioselectivity. The extremely simple experimental procedure, the mild reaction conditions, the low cost and the easy preparation of the catalyst, the wide applicability to a large variety of structures, the high chemical and stereochemical efficiency and the possibility of recovering the catalyst are all positive features which make the present system possibly suitable also for large scale applications.



The combination of a low cost metal-free catalyst easily prepared in one step only from cheap commercially available substrates and an inexpensive chiral auxiliary such as α -methyl benzyl amine allowed to reduce ketimines with different structural features often with total control of the stereoselectivity. The method has been also successfully applied to the preparation of natural and unnatural α -amino ester.

Role of salt marsh plants on TBT biological remediation in sediments

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Butyltin compounds (BTs) introduced into marine and estuarine sediments, despite strict regulations, pose a long-term risk to aquatic life due to their toxicity and persistence in sediments. It is necessary not only to control the release of tributyltin (TBT) and its degradation products from polluted sediments but also to develop remediation forms. When pollutants are in low concentration, rhizoremediation alone can be an economical and effective remediation strategy.

Studies using coastal vascular plants for TBT rhizoremediation are still scarce. TBT degradation on natural environments, as salt marshes, still pose an open field of research. The aim of this work is to report results on TBT biological remediation produced by the salt marsh plants *Spartina maritime*, *Sarcocornia fruticosa* and *Halimione portulacoides* in estuarine and lagoon sediments of Portugal.

Three sets of experiments were carried out: (1) a nine month *ex-situ* study at *Sado* River estuary; (2) a twelve month laboratorial scale study in sediments collected at *Cávado* River estuary; and (3) an *in-situ* study in salt marshes of *Marim* channel, in *Ria Formosa* lagoon. In studies (1) and (2) the plant *Halimione portulacoides* was used. In study (3) the roles of both *Sarcocornia fruticosa* and *Spartina maritime* were investigated. Determination of BTs were carried out using the method described in Carvalho *et al.* (2007).

Study (1), which was carried out with transplanted plants and very polluted sediment revealed that the presence of *H. portulacoides* caused 30% of TBT remediation, whereas a TBT natural degradation was not statistically significant. In study (2), which was carried out in sediment relatively clean but initially doped with TBT, DBT and MBT standards, the presence of plants caused a TBT remediation of about 75%. In study (3) TBT residues could only be detected and quantified in non-vegetated sediments, suggesting that the presence of plants enhanced TBT rate of degradation.

In terms of microorganisms abundance (determined by *total cell count*), higher abundances were found in the rhizosediment than in the non-vegetated sediments, showing a positive influence of the plants in the community of microorganisms of the rhizosphere. However, rhizosediment (2) displayed higher microorganisms abundance than rhizosediment (1), which is compatible with the higher percentages of remediation obtained in study (2). This may be a result of the sediment used in the study (1) that is highly polluted with different substances including trace metals, which can be toxic for microorganisms.

This study demonstrated the potential of the salt marsh plants for biological remediation of TBT in salt marsh sediments, either *in-situ* or *ex-situ*.

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Simultaneous reduction of CO₂ and NO₂⁻ using modified electrodes with new poly-tetraruthenated porphyrins

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The catalytic conversion of carbon dioxide to fuel products is a critical goal that would positively impact the global carbon balance by recycling CO₂ into usable fuels [1]. CO₂ is an extremely stable molecule generally produced by fossil fuel combustion and respiration [1]. Another product generated by burn fossil fuels are nitrogen oxides, which causes serious problems for the global environment (acid rain) and the human body (metahemoglobin generation) [1]. Many efforts have been focused to find electroic surfaces that present the possibility of recycling CO₂ in fuels or starting materials for organic products [2]. The electroreduction of nitrogen oxides also has been studied [3, 4]. It is interesting that CO₂ and nitrogen oxides can be simultaneously removed [3, 4]. The electrochemical conversion of CO₂ with nitrite ions into a useful material consisting of C-N bond has attracted much attention [3, 4].

In this work, we propose an electrochemical method of CO₂ and NO₂⁻ simultaneous conversion, using glassy carbon-modified electrodes with new tetraruthenated porphyrins. These sort of tetraruthenated porphyrins consists in tetrapyridyl porphyrins units (metal-free porphyrin and metal (II) porphyrin) with four groups of [Ru(5-NO₂-phen)₂Cl]⁺ coordinated to the pyridyl moieties. These supramolecules promote the effective formation of conductive polymers onto electroic surfaces because the nitro substituents are able to generate radicals species that initiate the process of electropolymerization. On the other hand, tetraruthenated porphyrins can operate as a source of electrons generating multielectronic transfers achieving the efficiency to the electroreduction reactions. The experiments by cyclic voltammetry showed that these modified electrodes present electrocatalytic activity in CO₂ reduction, NO₂⁻ reduction and both simultaneously, in comparison with the bare electrodes, this behavior was demonstrated by the increment in the cathodic currents and the low overpotential required in the reduction process. The determination of reaction products was developed using spectrophotometric methods. The products obtained were urea, ammonium, hidrazine, formic acid and formaldehyde.

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Antifungal Activities, Compositions and the Main Fungitoxic Components of the Brazilian *Ocimum basilicum* L.

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Antifungal activities of the essential oil (EO) and the hexane extract (HE) of the Brazilian *Ocimum basilicum* L. were evaluated by the food poisoning assay using eight post-harvest deteriorating fungi (*Aspergillus flavus*, *A. glaucus*, *A. niger*, *A. ochraceous*, *Colletotrichum gloesporioides*, *C. musae*, *Fusarium oxysporum* and *F. semitectum*). Good antifungal activities (51 to 92% inhibition at a concentration of 0.075%) were obtained with both extracts against the eight fungi. The components of the EO and the HE were identified by Kováts retention indexes using gas chromatography (GC) and gas chromatography-mass spectrometry. The compounds were quantified (area %) by GC. Thirty-two components were identified in the EO and twenty in the HE. Bioautography-TLC was used to identify the fungitoxic fraction on both the EO and HE. Our data suggest that the major fungitoxic component of *O. basilicum* was eugenol. Nevertheless, a synergistic effect involving other components of the EO, probably linalool, α -terpineol and methyl chavicol, is conceivable since the HE had slighter fungotoxicity, though it containing larger relative percentage of eugenol, compared to the EO.

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Influence of ozonation on the removing of fulvic acids by biologically active carbon

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Fulvic acids (FA) is the main type of natural organic matters (NOM) present in the water of the Dnepr River. Their content is 80-90% of the concentration of total organic carbon (TOC). These matters are difficult to remove with traditional technologies, which are typical for the most of the Ukrainian water treatment plant (coagulation – sedimentation – filtration – post-chlorination). Therefore it is important to investigate the removal of FA by such methods, which provide the most complete their removing.

The purpose of this work was to study the impact of the previous ozonation and aeration on the performance of biofiltration of FA solutions. It is known that the effectiveness of the water purification from NOM by biofiltration depends on the fate of biodegradable organic carbon (BDOC) in the total organic carbon content. It was studied how to improve performance of biofiltration by modifying the content of BDOC. BDOC was decreased by aeration and increased by ozonation.

Effectiveness of biofiltration of NOM through the biologically active carbon (BAC) should be assessed by comparing the value of equilibrium and dynamic adsorption capacity of AC. The dynamic adsorption capacity of AC is usually lower than the equilibrium value unless there is accompanying biodegradation processes. Comparison of dynamic and equilibrium adsorption capacity is made to evaluate the contribution of biodegradation component in cumulative effect. Excess dynamic adsorption capacity of the equilibrium is due to bioregeneration of AC.

We filtered aerated, ozonated and aerated - ozonated solutions of FA through AC filter. In all cases, dynamic capacity exceed the equilibrium one. It was shown, that the process of bioregeneration of AC starts at the concentration, which lies within the <50% breakthrough. Even in case of aerated solution of FA with very low concentration of BDOC, dynamic capacity exceeded equilibrium. It show higher biodegradation potential of microorganisms on AC. Further ozonation of aerated solutions of FA at low TOC increases content BDOC and efficiency of biofiltration. It should be noted that the comparison of TOC in treated water after filtration of identical volumes of FA solutions that in the case of consecutive aeration and ozonation solution the advanced extraction of TOC is observed. In this case, it is provided obtaining biologically stable water (i.e. containing 0.3 mg BDOC/dm³).

Uranium removal by *Bacillus polymyxa* IMV 8910 from aqueous solution

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Uranium is a long-lived radionuclide that is an ecological and human health hazard. The mining and processing of uranium for nuclear power plants and nuclear weapons production have resulted in the generation of significant amounts of radioactive wastes. The treatment of low charge effluents, conciliating economic and technical constraints is impossible with traditional physical-chemical processes. It has been suggested that biomass could be used to decontaminate these wastes and to concentrate metals [1]. Biological methods are the most ecologically appropriate techniques. The major advantages of microbial treatment are self-reproducibility, adaptability, recyclisation of bioproducts, specificity, and good cost/benefit ratio.

This study focuses on uranium sorption mechanism by exopolysaccharide producing bacterium, *Bacillus polymyxa* IMV 8910. The main characteristics of this process were determined. The rate and extent of U (VI) uptake were subject to such parameters, as biosorbent properties, pH, concentration of radionuclides, interference by certain anions and cations [2]. The pH plays an important role in biosorption phenomena, mainly by its influence on metal or cell wall chemistry. It is shown, an optimal range of pH for uranium sorption is 4.0-6.0. The experimental data showed that process of uranium sorption by *B. polymyxa* IMV 8910 can be described well by the Langmuir isotherm with $q_{\max} = 1000 \mu\text{mol/g}$, $k = 11.11$, $R = 0.9921$.

Uranium (VI) removal by *B. polymyxa* IMV 8910 cells occurs on the biosorption mechanism whereas metal uptake does not require the metabolic activity and does not dependent of temperature. Therefore, based on the results of IR-spectral analysis it is may assumed that active groups on the cell wall and the mucilage of *B. polymyxa* IMV 8910, which may take part in U (VI) binding, are carboxylic, hydroxylic, phosphate, amine and amide groups. The important role of carboxylic groups in the adsorption process has been clearly demonstrated while measuring of sorption capacity microbial biomass after blocking of COO^- groups: U (VI) uptake reduced on about 27 %.

A number of desorption agents have been tested for their ability to release bound UO_2^{2+} ions from cells of *B. polymyxa* IMV 8910. The highest levels of bound uranium removing by extraction of microbial cells with Na_2CO_3 and NaHCO_3 (85.5 and 75.2% respectively) are caused by forming stable soluble anion complexes with U (V) - $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ [3].

So, the use of microbial cells of *B. polymyxa* IMV 8910 as biosorbent for uranium (VI) offers a potential alternative to existing methods for decontamination or recovery or both of radionuclides from low charge waste streams.

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Synthesis of TiO₂ and TiO₂/SiO₂ coupled nanoparticles from inorganic precursor and evaluation of their photocatalytic activities in degradation of a model organic pollutant

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Among the transition metal oxide semiconductors, TiO₂ is widely used in photocatalysis due to its high photocatalytic efficiency, chemical and physical stability under the reaction conditions, safety and non-toxic properties and also its economic feasibility [1,2]. In this work, TiO₂ and TiO₂/SiO₂ nanoparticles were prepared by sol-gel method and photocatalytic activities evaluated at photocatalytic degradation of C.I. Acid Red 27 (AR27) as a model contaminant from textile industry.

TiCl₄ was used as a main starting material. Appropriate amount of TiCl₄ was added to bi-distilled water and HNO₃ added to suspension as a catalyst, then at 70 °C and vigorous stirring was digested for 24 h, to prepare TiO₂/SiO₂, appropriate amount of Tetraethyl Orthosilicate (TEOS) was added to suspension and stirred for 1 h, then oven dried and finally calcinated at different temperatures. Catalysts were characterized with XRD, FTIR, SEM-EDS, UV-Vis spectrophotometer.

TiO₂ and TiO₂/SiO₂ nanoparticles can be obtained by sol-gel method from inorganic TiCl₄ precursor. XRD analysis results for TiO₂ and TiO₂/SiO₂ with molar ratio 70/30 particles calcinated at 400 °C indicates TiO₂/SiO₂ particles have broader peaks than TiO₂ particles at $2\theta=25.2^\circ$ which means that the TiO₂/SiO₂ particles are smaller than TiO₂ particles also TiO₂ crystals are in both anatase and rutile phases but TiO₂/SiO₂ has pure anatase phase which means that SiO₂ acts as a phase stablizing agent to keeps crystals in anatase phase. Crystal's size are determinated 5 nm and 13 nm using Scherrer's equation for TiO₂/SiO₂ in molar ratio of 70/30 and TiO₂ crystals, respectively. The modification of Titania sol with silica can enhance chemical, physical and photo stability of particles, also it can reduce particle's size from 13 nm to 5 nm in Si coupled particles [2,3].

According to the FT-IR results, the spectra reveal three major absorption bands at about 1090, 960 and 460 cm⁻¹, which represent the characteristic bonds of Si—O—Si asymmetric stretching (near 1090 cm⁻¹), Ti—O—Si asymmetric stretching (near 960 cm⁻¹) and stretching vibration of Ti—O bonds in Ti—O—Ti (near 460 cm⁻¹) [3].

AR27 was used as a model pollutant to investigate the photodegradation with illuminations of UV light. Results indicate both of TiO₂ and TiO₂/SiO₂ photocatalysts have proper photocatalytic activity in presence of UV light. In TiO₂/SiO₂ photocatalyst, molar ratio 70/30 of Ti to Si respectively, has an optimum photocatalytic activity in comparison with other molar ratios.

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Synthesis of pure TiO_2 and $\text{TiO}_2/\text{SnO}_2$ coupled nanoparticles by citric acid complexing method under ultrasonic irradiation and study of their photocatalytic activity

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In the past decade, metal oxide semiconductors such as TiO_2 , SnO_2 and WO_3 have attracted a great deal of attention in the areas of water, air and wastewater treatment since they can catalytically decompose organic compounds under the illumination of UV light. Coupled semiconductor photocatalysts may increase the photocatalytic efficiency by increasing the charge separation and extending the photo-responding range [1]. The aim of the present study is preparation of pure TiO_2 and $\text{TiO}_2/\text{SnO}_2$ nanoparticles with different ratios of these particles at different conditions and evaluation of their photocatalytic activities at photocatalytic degradation of C.I. Acid Red 27 (AR27) as a model organic contaminant from textile industry.

Nanosized TiO_2 and $\text{TiO}_2/\text{SnO}_2$ photocatalysts were prepared using the citric acid complexing method in the presence and also absence of citric acid. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and TiCl_4 were used as the starting materials, and citric acid was used as the complexing agent. Photocatalytic degradation was performed in batch photochemical tubular reactor with UV-C light and HALOGEN visible light lamps. Catalysts characterized with XRD, FT-IR, SEM-EDS techniques.

The XRD spectra has confirmed that the crystal forms in the pure TiO_2 , also composite $\text{TiO}_2/\text{SnO}_2$ are in anatase and rutile phases. Diffraction signals assigned to the anatase structure at $2\theta=25.2$ and rutile structure at $2\theta=27.5$, were clearly observed in both TiO_2 and $\text{TiO}_2/\text{SnO}_2$ nanoparticles. Beside the anatase TiO_2 , there exist the rutile SnO_2 diffraction peaks ($2\theta= 26.60, 33.92, 37.94, 51.82$ and etc.) [2]. The diffraction patterns also show that the diffraction peak width of the composite $\text{TiO}_2/\text{SnO}_2$ is broader than pure TiO_2 , indicating the average diameter of the composite $\text{TiO}_2/\text{SnO}_2$ particles are smaller than pure TiO_2 particles. This can be attributed to the existence of SnO_2 that reduce the growth rate of particles. Citric acid has a great effect on stabilizing the precursor solution, and slows down the hydrolysis and condensation processes. In the absence of citric acid, the precursor hydrolysis and condenses are in an uncontrollable manner and the obtained nanoparticles are comparatively larger in size [3]. EDS analysis shows that both titanium and tin are present in the particles. The SEM images demonstrate uniform morphologies. The FT-IR spectra has confirmed the peak at $1740\text{-}1880\text{ cm}^{-1}$ probably corresponded to the COOR groups. The vibration at 560 cm^{-1} is related to the terminal oxygen vibration of Sn-OH and the peak at $600\text{-}660\text{ cm}^{-1}$ is attributed to the OXO bridge functional groups (OSnO). The photocatalytic activity of coupled nanoparticles reached their maximum when loading of SnO_2 on TiO_2 was 1 % Wt.

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LCA as decision tool for ASR management

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ELV (End-of-Life Vehicles) produces from 9 to 10 million tonnes of wastes per year in Europe. According to Directive 2000/53/EC and ISO 22628, the actual ELV treatment chain consists of pre-treatment, dismantling, shredding metal separation and post-shredder ASR (automobile shredder residue) recycling technologies.

In order to optimize ELV plants ecological and economical impacts, in this specific study LCA is used as a tool to monitor all the different improving steps and to highlight the consequent environmental impact saving. Starting from an existing plant the authors intend to exploit the LCA potential for assessment not only as a simple “snapshot” of the shredding plant’s mass balance but as a “film” of the output evolution due to the installation of new parts of the plant. Actually the core of the plant is a 4000HP hammer mill followed by the aeraulic separation system, that generates the light ASR fraction during a first cleaning of the shredded metals . Then, a magnetic separation system removes ferrous metals from the remaining output flow, consisting of heavy ASR and non-ferrous metals that are removed later by an Induction Sorting System. The resulting materials, light and heavy ASR are landfilled today.

This paper describes the first step of a PhD thesis that aims at using LCA as a tool for decision making on further technological evolutions of the plant like a flotation plant, a copper wire separation and recycling machinery as well as an evaluation of innovative processes designed for material and energy recovery from ASR. Concerning the latter aim, studies have already been performed in that plant in order to characterize ASR in terms of material composition and chemical-physical properties.

Synthesis of acrylic acid from renewable materials – economical prospects and limitations of technology

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oral presentation

A dynamic growth has been observed recently in the demand for acrylic acid and its derivates (acrylic monomers) in the Polish market. Propylene, derived from crude oil processing, is the main raw material in the industrial production of acrylic acid. The process is based on a two-stage oxidation of propylene. The local demand for propylene is supplimented by import due to low propylene production. This reason , as well as the schrinking reserves and high price of crude oil has prompted research into the use of biocomponents as raw material base for the production of acrylic acid.

The limitations and prospects of development of this technology as well as the economic implications are the bases of research.

The minimum percentage of biocomponents in fuels is expected to be reach 5,75% by 1st January 2010. (EU directive). The biocomponents mainly consist of methyl esters of Fatty Acids FAME whose production has recently caused the occurence of large amounts of glycerol in the market. The large-scale production of the glycerol by-product has resulted in a decline in its price therefore making it an attractive raw material for organic synthesis. Glycerol as raw material for acrylic acid production can be considered a cheap and environmentally friendly alternative to propylene.

The production of acrylic acid from glycerol is a two – stage process. In the first stage glycerol is dehydrated to acrolein which is there after oxidized to acrylic acid in the second stage. This work covers the first stage in which glycerol is dehydrated to acrolein at the 290-400°C temperature range under atmosheric pressure. The liquid feed containing 40-90wt% of glycerol in water was evaporated and the vapors passed through an industrial catalyst based on alumina-silicas. The liquid product was collected in a cold trap and analized by GCMC to calculate the over all glycerol conversion and acrolein yield.

The results have been presented in a Polish patent application P-379283 as well as in European applications 07 104654.4 and EP 1860090. This work is the first part of the project "Operational Programme Innovative Economy 2007" – National Cohesion Strategy in Poland. The project has been accepted for further adaptation with partial financial support from the European Regional Development Fund – ERDF.

Development of biodegradable chitosan hydrogel materials to encapsulate nitrification inhibitors

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The objective of the project is to develop a simple, environmentally friendly, inexpensive release technology for the sustained delivery of nitrification inhibitors (Fig. 1). Nitrification inhibitors are chemicals used on farms to slow the process by which microorganisms convert ammonium into nitrate in soil and slurry and thus reduce nitrogen losses to ground water. In Ireland there is an increased interest in using such inhibitors due to the implementation of the Nitrates Directive (91/676/EEC). The development of a slow sustained release delivery system would aid the farmer as it would reduce the number of applications of the inhibitor required. The material used to develop a delivery system for the nitrification inhibitors was chitosan (Fig. 2).

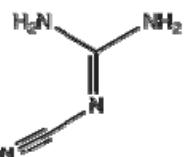


Figure 1 Nitrification inhibitor dicyandiamide (DCD)

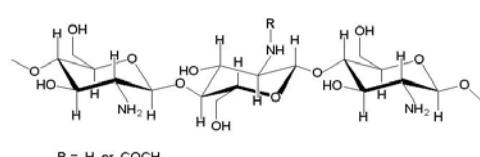


Figure 2 Chemical structure of chitosan

Chitosan polymers can be cross-linked to form hydrogel materials in which the inhibitor can be encapsulated. The chitosan hydrogel was formed as spherical beads with diameters in the range of 1.18 – 1.40 mm as measured by a Gilson Autosiever. When placed in contact with water the hydrogel swells and the encapsulated inhibitor diffuses out. Our results show that it is possible to manipulate the release rate of the nitrification by altering the conditions used to form the beads such as molecular weight of chitosan, percentage of cross-linker used and curing time. The release rate is also altered by the properties of the release solution such as pH. The release of DCD is monitored using Uv-vis spectroscopy. A typical release profile for DCD from the beads is shown in Fig. 3.

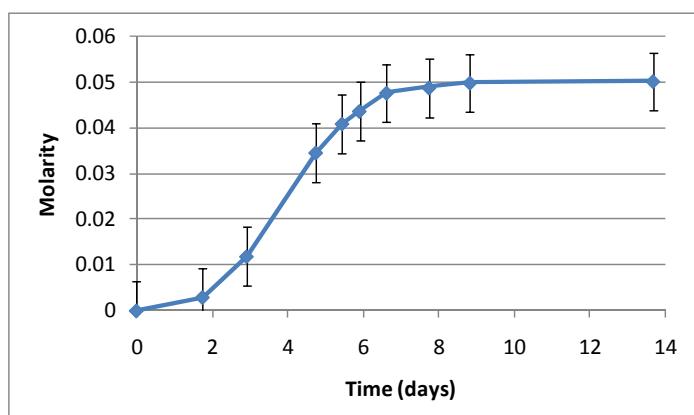


Fig. 3 20 chitosan beads are placed in 400 cm³ of Millipore water and the DCD is released into solution is monitored as a function of time

Catalysts of Na₂S oxidation on the base of non-aggregated immobilized metal phthalocyanines

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Substituted metals phthalocyanines (PcM) have been successfully investigated in our laboratory for a long time [1]. These complexes as catalysts were used in different processes, for instance, in oxidation of leucobases to triarylmethane dyes [2], N,N'-bis(dimethylamino)diphenylmethane to Michler's Hydrol [1], aromatic amines oxidative dimerization to benzidine derivatives [3], 1,5-dihydroxynaphthalene catalytic and photooxidation to 5-hydroxy-1,4-naphtoquinone (juglone) [1,4], aromatic hydrocarbons oxidative chlorination to chloroderivatives [5] and others. Besides ascorbic acid oxidation as the base of catalytic therapy of cancer has been studied [1].

Application of phthalocyanine complexes in catalysis is considerably retarded by the lack of sufficiently developed methods for their heterogenization. There are two available methods of forming surface layers where the interaction of PcM molecules is weak or totally absent, namely equilibrium adsorption and chemical attachment to carrier [6-8].

This report is devoted to investigation of catalytic activity of some substituted PcCo immobilized on different carriers by equilibrium adsorption and covalent bonding in Na₂S oxidation.

The catalytic Na₂S oxidation by air oxygen in aqueous solution has depended on the nature of substituents (PhS- *t*-Bu, PhSO₂, PhSO₂-*t*-Bu, (Et₂NCH₂)₄, (ClSO₂)₃₋₄) in PcCo molecule. Na₂S conversion has reached in the best cases more than 90% in 60 min of the reaction in the presence of (3-PhSO₂)₄PcCo, (ClSO₂)₃₋₄PcCo and (Et₂NCH₂)₄PcCo, immobilized on 3-aminopropyl-functionalized SiO₂. Catalyst activity does not change during at least seven cycles and depends on amounts of PcCo on carrier. The data obtained are better than published ones [9, 10].

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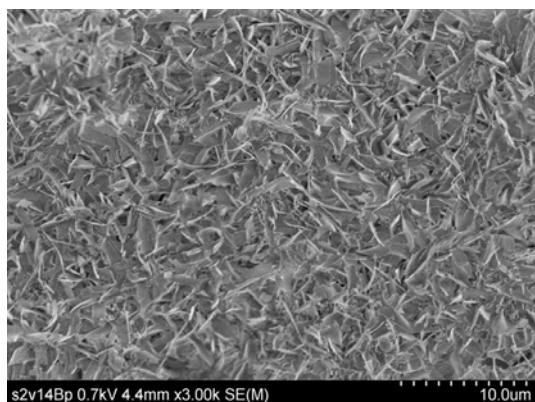
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Preparation of superhydrophobic coatings using supercritical CO₂ as a solvent

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A novel process has been developed for preparing superhydrophobic[1] surfaces without the use of organic solvents or fluorinated compounds by spraying Alkylketenedimer (AKD) dissolved in supercritical CO₂ through a nozzle, into ambient conditions, onto the substrate to be coated. The particles produced by using Rapid Expansion of Supercritical Solvents (RESS) [2] to form a coating of merged flake shaped particles [3,4]. This surface shows two favourable properties for a superhydrophobic surface, namely, a relatively high hydrophobicity of the used material combined with a rough surface geometry with steep features (see figure). Initial tests show that a wide variety of surfaces could be coated with this method and that other waxy substances such as stearic acid could also be used to produce a superhydrophobic coating. In the case of AKD the production parameters such as pressure and temperature of the CO₂, and the distance to the surface from the nozzle has been varied and the results were validated with SEM and contact angle measurement to water giving values between 160°-170°. Results showed that the distance to the surface to be coated to be of critical importance.



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Artificial soils – design of a long term field experiment

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Artificial soil production, incineration, landfilling, ground storage and land application are the most commonly implemented alternatives for the management of sewage sludge in Slovenia. Being rich in high amounts of organic and inorganic plant nutrients, the introduction of sludges can also result in water and soil pollution and can pose a serious threat to humans, when sludge introduced to the environment contains high (extractable) concentrations of metals, organic pollutants and pathogenic organisms.

In October 2009 we designed a field experiment; eight fields were set up with different artificial soil mixtures and one field with control soil. Lysimeters were constructed and integrated under the research field for the study of leaching with precipitation (rain water, snow). With the design setup of a field experiment, we are aiming to study the environmental impacts and the processes, that could influence the behaviour of metals in artificial soil mixtures (metal speciation, monitoring of metal mobility, plant accessibility and human oral availability). Metals, observed in our study, are: copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), nickel (Ni), chromium (Cr), mercury (Hg) and arsenic (As).

The first sampling of artificial soil mixtures was performed in November 2009. A set of methods was used to assess the potential hazard of metals, determining the "ground-zero" state. Metal concentrations were determined by *aqua regia* digestion, water extraction and by a modified Tessier's six-step sequential extraction procedure; potential for phyto-availability was assessed with diethylenetriamine pentaacetic acid (DTPA) and mobility and leachability the Toxicity Characteristic Leaching Procedure (TCLP). Growth experiments will also be performed, in spring time, followed by metal plant uptake assessment.

The first results showed different metal mobility and extractability among mixtures; the phytoavailable fraction was observed to be higher than the mobile (leachable) fraction, determined by TCLP test. Water extraction test showed very low extractability of metals. According to the sequential extraction test, metals were observed to be bound mostly to soil organic matter and to the residual fraction. Oral bioavailability of metals, assessed by PBET test, showed differences among different mixtures.

Chemicals in statistics – a source for information on environmentally relevant compounds?

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Detailed information on the use of chemicals, like the Swedish Products Registry, is not available in most countries. Commercial confidentiality also severely limits the use of such information. Yet another source of information is the official trade and manufacture statistics based on the Combined Nomenclature eight digit codes (CN) of the European Union. The CN consists of the Harmonized Commodity Description and Coding System (HS) nomenclature with further subdivisions. Each CN code for chemicals is linked to one or several Chemical Abstract (CAS) registry numbers, which provide unique identifiers for the specific compound in question.

Here we have screened the trade statistics for compounds with PBT-properties by applying two QSARs for baseline toxicity and atmospheric persistence, respectively [1-3]. 10 578 compounds matching the applicability domain for both QSARs were ranked, and the 100 compounds with highest ranking were selected for further study. Many of these environmentally relevant compounds belong to the same groups of chemicals, where halogenated derivatives of aromatic hydrocarbons was the largest with 25 members, followed by halogenated derivatives of methane, ethane or propane (halogenated only with fluorine and chlorine, i.e. HCFCs) with 20 members.

The net use of chemicals (import and manufacture minus export) in each group of chemicals was followed in the trade statistics (1998-2005). Additional data was also requested from the Products Register of the Swedish Chemicals Agency (2000-2005). The results were ambiguous and thus difficult to interpret. One data source indicated a declining import of compounds classified as halogenated aromatics while the other indicates an increase. Similar problems with the data evaluation also occur with the statistics for HCFCs.

A preliminary conclusion from this study is that the statistics may need further validation. Some possible measures to improve its usability — for evaluating the accomplishment of the environmental objectives at a more detailed level — are discussed. For compounds and compound groups of particular environmental relevance it also seems necessary to trace the statistics back to the primary source to further examine the accuracy of the data.

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Evaluation of Nutrient Supply from Indian Fly ash and Human Urine

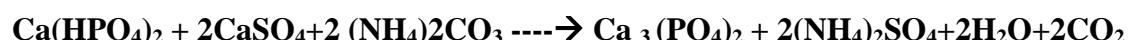
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In India installed capacity of electric power generation was 140,000 Mw as on 31 st march 2008,.Currently ,120 million metric tones of fly ash is being generated annually in India with 65,000 acres of India being occupied by ash ponds (Kumar 1996).Fly ash contains high content of elements which are very essential to plants(chatterjee et al 1988) .There is need for full exploitation and utilization of all locally available organic and inorganic sources of nutrients like fly ash, urine etc.it is being reported that soil enzyme activities strongly influenced by the presence of oxides of iron ,manganese and zinc in fly ash (yeledhalli et al 2005).The present research is focused to asses different forms of metal fractions by single extraction techniques,i.e. total and potentially bioavailability fractions from fly ash and extraction of nutrient from human urine of an Indian .The research finding will be helpful to find the simple ways to handle urine to prevent nitrogen loss and its utility along with fly ash with respect to its fertilizer value.Indian fly ash are mostly bituminous and sub bituminous in nature which can supply essential elements which can improve the fertility of soil, but fly ash generally devoid or low amount of major nutrients like nitrogen , phosphorus and potassium , on the other hand human urine can supply major nutrients like nitrogen ,phosphorus and potassium. An attempt has been made to study fly ash from different thermal power plants mixed with human Urine for its total metal content, exchangeable forms of metals are analysed by using Diethyl triamine pentaacetic acid -Calcium chloride solution. Nitrogen is mostly in ammonium form in human urine which are fixed by neutralizing with 2.5 gm of single super phosphate to pH-6.8-7.2.and converted into tricalcium phosphate and ammonium sulphate which prevent the loss of ammonia .this can be explained with the help of following equation.



Potassium and remaining phosphate are adsorbed on this salt or in liquid fraction , this product is then soaked on fly ash at the rate 3.57gm of ash per ml of urine ,with this amendment the total N content increases from 0.002 to 0.39%, available P from 0.003% to 0.045%,available K from 0.052 % to 0.195%,available DTPA-Fe 3.5-6.8 ppm,DTPA- Mn 2.1-3.98ppm,DTPA-Cu 2.4-3.0 ppm, DTPA-Zn 1.10-1.32 ppm.As the ash under study are found to be alkaline pH is found to be 7.5-7.8 and Electrical conductivity is found to 0.68-0.78dS/m.where as pH of urine amended ash was found to be 6.7-6.9 and EC 16.5-17.5dS/m.

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Chemical Environmental Toxicology

Poster abstracts

Tox P1-P37

Branched PFOS isomers and shorter perfluorocarboxylates are more efficiently transmitted through the human placenta

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Perfluorochemicals (PFCs) have been manufactured on an industrial scale for decades and given their unique chemical and physical properties they have been extensively used in many consumer products. PFCs are detectable in the general population, some are known to cross the placenta, and there are concerns about their developmental toxicity. For example, studies done on rodents and data on multiple birth cohorts are suggestive of an inverse association between cord serum perfluorooctane sulfonate (PFOS, C₈F₁₇SO₃⁻) and low birth weights. The mechanism of toxicity to the fetus is unclear, and the extent to which perfluorinated chain-length and alkyl branching affects transplacental transfer has not been systematically examined. Serum samples collected from a cohort of 20 mother-baby pairs (15 week gestation/cord) were analyzed by a solid-phase-extraction isomer-specific tandem mass spectrometry method to investigate the structure activity of placental transfer.

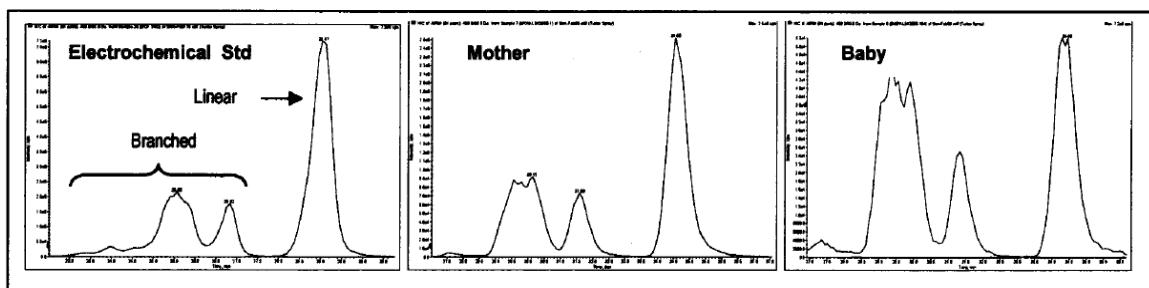


Fig 1: Chromatograms showing relative amounts of PFOS linear and branched isomers.

Our data indicate that linear PFOS isomers and longer-chained perfluorocarboxylates were more effectively blocked by the placenta. This is, for example, shown by the consistently higher ratio of total branched: linear isomers in babies compared to mothers (Fig 1). Matched house-dust samples were also examined for each mother-baby pair, and the isomer patterns were useful for source elucidation. Isomer specific transfer of PFOS to the fetus in humans may have implications for interpretation of toxicity studies in animals, exposure source elucidation, and could also affect the accurate quantification of “total PFOS”.

Tissue distribution of perfluorooctane sulfonic acid in mice after exposure to an environmentally relevant low dose

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Low levels of Perfluorooctane sulfonic acid (PFOS, $C_8F_{17}SO_3^-$) have been detected in both the serum and tissues of occupationally exposed, as well as general human populations, and in various aquatic mammals (e.g., seals, sea lions and dolphins), birds and fish, with highest levels in the blood and liver. The average serum level of PFOS in general human populations is 20 – 30 ng /ml (= 40-60 nM). The aim of this study was to determine the tissue distribution of PFOS in mice with similar serum concentrations.

Material and Methods

^{35}S -PFOS (90% chemical purity, and specific activity of 59 mCi/mmol) synthesized by Maria Sundström and Prof. Åke Bergman (Environmental Chemistry, Stockholm University) was mixed with standard laboratory chow to obtain a concentration of 0.0000156% (w/w) and 20-22-g male C57Bl/6 allowed free access to this diet for 1, 3 or 5 days. Following this period of exposure, the animals were sacrificed and blood and organs removed for determination of PFOS by scintillation counting. In addition, the hemoglobin content of the different organs was measured in order to correct for the radioactivity due to contaminating blood.

Results

Our results showed that the uptake of PFOS was 30% and 20% respectively to the time points, with the highest distribution in the liver (11%) and in the blood (6% after one day of dietary exposure and 2% after 5 days of dietary exposure). The apparent concentrations in the liver were 98 nM and 450 nM after 5 days of dietary exposure. The apparent concentrations in blood were 58 nM and 94 nM after 5 days of dietary exposure. Significant, although considerably lower concentrations of PFOS were also detected in all other organs examined, and in particular in the lungs, kidneys and pancreas. The contribution made by contaminating blood to organ levels of radioactivity was negligible in all cases.

Conclusion

At an environmentally relevant dose, PFOS distributes, as expected, primarily to the liver and blood, with the hepatic concentration being approximately up to 5-fold higher than that in the blood. Bioaccumulation was observed during the 5-day regimen of exposure employed here. Moreover, all of the tissues examined contained low, but significant levels of PFOS at all time-points evaluated.

Acknowledgement

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Perinatal tissue distribution of perfluorooctane sulphonate (PFOS) in mice

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Perfluorooctane sulfonate (PFOS) is an industrial chemical that has been used as a surfactant and surface protector for more than fifty years. It has during the last decade emerged as an environmental contaminant due to its widespread presence in humans and wildlife and its persistent, bioaccumulative and toxic properties. PFOS is developmentally toxic and late *in utero* exposure in rodents affects neonatal survival and growth. Observed symptoms suggest impaired pulmonary function, but the cause of the mortality has not been clarified. The purpose of this study was to determine the perinatal tissue distribution of S³⁵-labelled PFOS in mice using whole-body autoradiography (WBA) combined with liquid scintillation counting (LSC). Pregnant C57Bl/6 mice were dosed orally on gestation day (GD) 16 and sampled on GD18, GD20 and postnatal day (PND) 1 (dams + pups). The results from the WBA and the LSC were unequivocal. In dams, PFOS accumulated primarily in the liver, but also the lungs contained levels higher than the blood. PFOS was readily transferred to the fetus. At GD18 general PFOS levels were higher in the fetus than in the blood of the corresponding dam with accumulation in the liver. At GD20, general PFOS levels remained higher in the fetus than in the dam, with substantial accumulation also in the lung. The accumulation in the lung persisted at PND1. Our results show that the fetus is exposed to higher levels of PFOS than the dam and point towards the lung being the main perinatal target organ of PFOS.

Toxic effects of toluene and its metabolites in rats

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Predominant step of toluene phase I biotransformation is hydroxylation of toluene to form benzyl alcohol. This step is responsible for the formation of 95% of toluene metabolites. It was reported in *in vitro* studies that cytochrome P-450 2E1 (CYP2E1) is the most active cytochrome P-450 (CYP450) isozymes in forming benzyl alcohol, and cytochrome 2B6 (CYP2B6) in production of p-cresol. Glutathione-S-transferases (GST) catalyse conjugation of glutathione (GSH) to GSH-adducts in toluene phase II biotransformation.

This study was designed to investigate the effects of toluene treatment on total CYP450 content, CYP2E1, CYP2B6 contents and GST from rat liver microsomes as well as histopathological changes in the rat organs. Wistar rats were divided into four groups of 12 each: control (I group), the group treated i.p. with toluene in propylene glycol daily for 12 days, at doses of 0.38 mM/kg bw (II group), and daily for 6 days at doses of 5 mM/kg bw (III group female and IV group male). Rats were sacrificed killed by deep anaesthesia with ether 24 h after the last administration. Microsomes were isolated from the liver according to procedure described by Mayer. Total CYP content were estimated according to the method of Omura and Sato. CYP2E1 and CYP2B6 content immunoblot analysis was performed according to the method of Towbin. The membranes were then incubated with a primary CYP2E1 and CYP2B6 antibodies, detected with horseradish peroxidase-conjugated secondary antibodies. Glutathione-S-transferase (GST) activity was measured with CDNB and GSH according to the method described by Habig. Tissue preparation animals were fixed in 10% paraformaldehyde in phosphate buffer saline (pH 7.4) to prepare paraffin blocks.

Toluene exposure resulted in a significant increase in the total CYP450 content and the level of liver microsomal CYP2E1 and decreased the level of CYP2B6 in all exposed groups ($p<0.05$ or $p<0.001$). Microsomal GST activity was enhanced by toluene in all groups compared to the control group ($p<0.001$). These results suggest that toluene influence total CYP 450 content, levels of CYP2E1 and CYP2B6 isoforms. CYP2E1 enzymes can produce superoxide (O_2^-) anion and hydrogen peroxide (H_2O_2) through the breakdown of oxygenated intermediates of the enzyme. O_2^- and H_2O_2 , in the presence of transition metals, can produce the highly reactive hydroxyl radical which can cause extensive cell damage (1). Pathological study was demonstrated that exposed toluene relate to parenchyma degeneration, granular in hepatocyte cytoplasm and cardiomyocytes as well as vacuolated kidney tubules cells. These changes, dose and sex-dependent. Exposure to high concentration toluene results in permanent and fatal damage both in the liver and other organ systems and in increased risks of various cancers in humans and animals.

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Dynamics and risks of DDT applied indoors for malaria control

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The continued use of DDT for Indoor Residual Spraying (IRS) of dwellings to interrupt malaria transmission in many parts of Africa remains controversial due to the various toxic effects of DDT and its close proximity to inhabitants. Little is known about the dynamics of DDT in indoor air and other surfaces following application. A better understanding of the dynamics of the different isomers might enable the identification of uptake and risk reduction interventions.

Air and floor dust samples were collected from 30 dwellings during the IRS programme of 2007 and compared to levels from 12 dwellings outside the malaria control area. Air sampling was done using high volume sampling and high density polyurethane foam discs before and after DDT application at -1 hr, 0, 1, 2, 4, 8 and 24 hours, and at 84 days. Floor dust samples were collected using vacuum suction and trapped on glass micro-fibre filters at -1 and 1 h.

Major differences were seen in ΣDDT levels depending on the size of packaging used. On Monday, small product packages were used and ΣDDT levels at 0 h were 13 times higher than during the other days of the week when larger packs were used (mean 145 and 11 µg/m³, respectively). At 1 h, the mean ΣDDT in air was 9.6 and 5.6 µg/m³, and at 2 h 16.5 and 7.4 µg/m³, for Monday and weekday dwellings, respectively. The major isomer in air in the Monday-sprayed dwellings was p,p'-DDT, but o,p'-DDT was higher in the weekday-sprayed dwellings. After 84 days, the air concentrations were 3.4 and 3.7 µg/m³ for Monday- and weekday-sprayed dwellings, respectively. p,p'-DDT was the major isomer in floor dust, and the mean floor dust concentration in Monday-sprayed dwellings ranged between 0.18 to 12 mg/m², and the week-day-sprayed dwellings from 0.67 to 31 mg/m². The packaging type, (small and large packages) influenced the mixing conditions (foaming, etc), and probably caused the differences between Monday- and weekday-sprayed dwellings.

Inhabitants spend 6-8 hours per day inside dwellings, every day. Especially babies with higher relative ventilation volumes, and babies, children and adults coming into contact with dust will experience almost continuous exposure. Risks assessments and guideline values in air for occupational exposure will therefore not be applicable, as otherwise more susceptible age and gender groups will be exposed almost every day of the year. In particular, the differential risks due to the estrogenic and anti-androgenic isomers need to be taken into account. We present further assessments of the data, and elaborate on possible risk reduction measures and intervention options, based on these findings.

6-2 Fluorotelomer alcohol hazard evaluation

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6-2 Fluorotelomer alcohol [6-2 FTOH, $\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OH}$] is a raw material used to manufacture polymers and surfactants. This paper will present the results of acute, genetic, sub-chronic, reproductive, developmental, and aquatic toxicity studies.

6-2 FTOH was slightly toxic by the acute oral and dermal routes with an oral LD₅₀ of 1750 mg/kg and a dermal LD₅₀ > 5000 mg/kg in rats. 6-2 FTOH did not produce a dermal sensitization response in mice. 6-2 FTOH was not mutagenic in the bacterial reverse mutation test or in the mouse lymphoma assay and was not clastogenic in a chromosome aberration assay in human lymphocytes. 6-2 FTOH is not genotoxic. 6-2 FTOH was moderately toxic to aquatic organisms. The 96-hour LC₅₀ in fathead minnows was 4.8 mg/L, 48-hour EC₅₀ in *Daphnia magna* was 7.8 mg/L, and 72-hr EC₅₀ in *Pseudokirchneriella subcapitata* was 4.5mg/L.

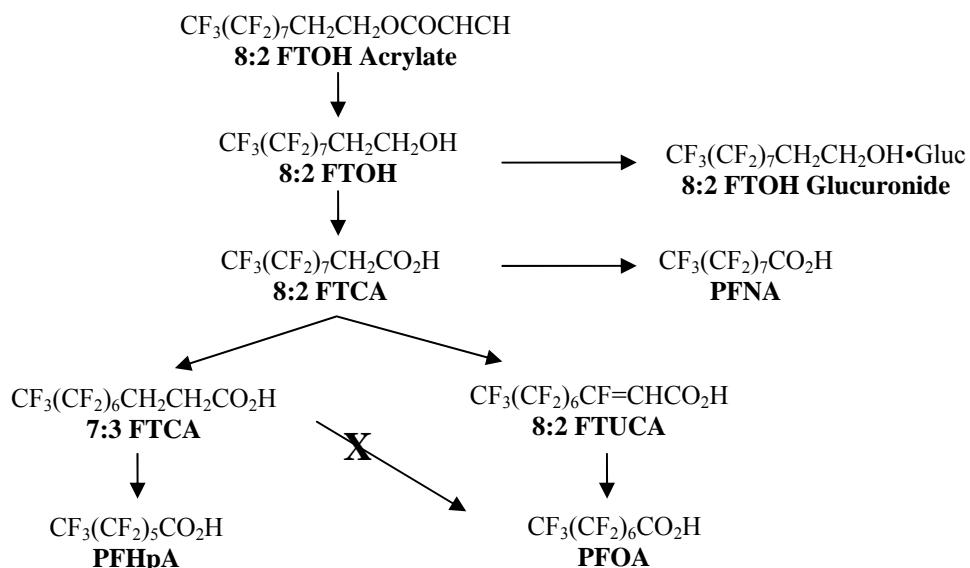
In repeated-dose sub-chronic, one-generation reproduction, and developmental toxicity studies, 6-2 FTOH was administered to rats by oral gavage. Mortality was observed in the sub-chronic study at 125 and 250 mg/kg/day; the deaths occurred after about three weeks of dosing and continued sporadically. Other effects observed at 125 and 250 mg/kg/day included decreased body weights, changes in organ weights, and pathological findings involving the liver and kidneys as well as effects on the teeth. Observations at 125 and 250 mg/kg/day in the reproductive study included reduced litter size, increased pup mortality during lactation, reduced uterine weights, and reduced offspring weights. Effects in the developmental study were limited to increased incidences of skeletal variations, lower maternal body weights and food consumption at 125 and 250 mg/kg/day. There was no maternal mortality nor were there any test substance-related gross observations in the developmental study. There were no effects on fetal body weight or litter sex ratio and there were no effects on the incidences of fetal resorptions or malformations at any dose level. Reproductive and developmental effects in pups were observed only when adverse effects were also observed in dams. These data indicate 25 mg/kg/day is the repeated-dose NOAEL for this test substance. The sub-chronic, one-generation reproduction and developmental effects observed in these studies are similar to those reported for a commercial FTOH mixture that included 6-2 FTOH as a major constituent.

Biotransformation studies of the 8:2 fluorotelomer acrylate and intermediate metabolites in rainbow trout

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In recent years, it has become evident that perfluorinated carboxylates (PFCAs) are detected in wildlife throughout the globe. Despite this apparently ubiquitous presence, the source of PFCAs in biota remains unclear. Recent studies have shown that precursor compounds can be metabolized by humans and animals to yield PFCAs. One potential precursor is the 8:2 fluorotelomer alcohol (8:2 FTOH) which has been shown to yield perfluorooctanoate (PFOA) and trace levels of perfluorononanoate (PFNA) in various biological systems. However, this metabolic pathway is not well understood. Our previous research has demonstrated that rainbow trout can rapidly biotransform another PFOA precursor, the 8:2 FTOH fluorotelomer acrylate (8:2 FTOH acrylate), to initially form the 8:2 FTOH followed by the 8:2 saturated and unsaturated fluorotelomer acids (8:2 FTCA & 8:2 FTUCA), 7:3 FTCA and PFOA. The 8:2 FTCA & 8:2 FTUCA were rapidly depurated. In contrast, the 7:3 FTCA and PFOA showed a delayed depuration, suggestive of formation from intermediate precursors. An additional study was performed to further elucidate this metabolic pathway. Juvenile rainbow trout were exposed via the diet to 8:2 FTCA, 8:2 FTUCA, 71 µg/g 7:3 FTCA, separately. Whole blood and liver were collected and analyzed for suspected metabolites by LC-MS/MS. Results indicated that exposure to the 7:3 FTCA yielded the 7:3 FTUCA and a novel metabolite, perfluoroheptanoate (PFHpA). PFOA was not detected during the 7:3 FTCA exposure. In contrast, PFOA was formed during 8:2 FTCA and 8:2 FTUCA exposure. In addition, delayed depuration of PFOA during 8:2 FTCA exposure was suggestive of PFOA formation from this intermediate metabolite. *In vitro* biotransformation rates and products were also investigated using the hepatic cytosol fraction (S9) isolated from rainbow trout.



Kinetic glutathione chemoassay – A non-animal component of integrated testing strategies to identify compounds with an electrophilic potential for reactive toxicity

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In aquatic toxicology, baseline narcosis forms a convenient frame of reference. For organic narcotics, acute aquatic toxicity can be predicted through hydrophobicity-based quantitative structure-activity relationships (QSARs), removing those compounds from the priority list of substances to be experimentally tested in detail. By contrast, correspondingly general models are not available for reactive or specifically acting toxicants. Accordingly, discrimination between narcotic-level and excess-toxic compounds would be a valuable tool to reduce animal testing at an early stage of chemical safety evaluation. A prominent route to excess toxicity proceeds through a primary electrophilic attack of the compound at endogenous targets. Here, the kinetic glutathione (GSH) chemoassay allows one to quantify chemical reactivity – in terms of reaction rate constants – towards the thiol group, the latter of which represents an abundant nucleophilic site in organisms. The kinetic GSH chemoassay thus provides an option as non-animal component of integrated testing strategies (ITS) for REACH, allowing one to identify compounds that have an electrophilic potential for exerting excess toxicity. In this communication, we demonstrate the use of this chemoassay to assess the electrophilic potential of α,β -unsaturated carbonyl and carboxyl compounds, epoxides, and sulphones. The discussion includes a comparison with literature data on toxicity, and an analysis in terms of structural alerts discriminating between narcosis-level and excess toxicity. This study was supported by the European Union through the projects CAESAR (Contract No.: SSPI – 022674 - CAESAR) and OSIRIS (contract No.: GOCE-CT-2007-037017).

Toxicokinetics of the adrenocortical toxicant 3-MeSO₂-DDE in mother and offspring following oral administration to lactating minipigs

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3-MeSO₂-DDE is a persistent and bioaccumulative metabolite of DDT, formed through biotransformation of DDE [1] and characterized by a high and tissue-specific toxicity in the adrenal cortex in mouse fetuses [2], suckling pups and adult mice [3]. 3-MeSO₂-DDE also targets the human adrenal cortex kept in tissue-culture *ex-vivo* and human adrenocortical H295R cells *in vitro* [4,5]. 3-MeSO₂-DDE is accumulated in human adipose tissue and is known to be excreted in human milk [6,7].

The present study was designed to examine the excretion of 3-MeSO₂-DDE in milk and the maternal and neonatal toxicokinetics following a single oral dose to lactating minipigs 2 days *post partum* (15 mg 3-MeSO₂-DDE/kg b.w.). Milk, maternal fat, and plasma were collected at regular intervals during four weeks and at autopsy adrenals, liver and body fat were sampled.

The levels of 3-MeSO₂-DDE in milk were about 30 times higher than in maternal plasma on fresh weight basis but on lipid weight basis the ratio plasma/milk was about 1. The 3-MeSO₂-DDE plasma levels in the piglets were about five times higher than in the mothers throughout the investigation. A strong accumulation of 3-MeSO₂-DDE was observed in fat tissue and a moderate accumulation in adrenals and liver of mothers and offspring. The retained tissue levels in the piglets were higher than in the mothers. It is concluded that suckling offspring were more exposed than their mothers despite the offspring's weight growth during the study. The results suggest that human risk assessment of the adrenocorticolytic environmental pollutant 3-MeSO₂-DDE should be focussed on breast-fed infants who are more vulnerable to exogenous compounds as their body is not fully developed. Also in highly DDE exposed marine mammals, the risks posed by 3-MeSO₂-DDE are likely most pronounced during the postnatal period.

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Pesticide residues in medicinal herbs of North Africa

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Even though the use of pesticides has been playing globally a very important role in the increase of agricultural productivity of a large number of crops however the irrational use of pesticides believed to have an adverse effects on the environment. Among those pesticides the organochlorines are thought to be indeed the most persistent organic pollutants in the environment. In fact the chlorinated pesticides are well known of their bioaccumulation in animals and in humans and of their toxicity. There for it becomes to be imperative that regular monitoring of even those occasionally consumed medicinal herbs by a wide spectrum of the general public particularly in developing countries. In fact monitoring both of pesticide and heavy metal contents in the environment is of immense importance.

Large number of samples of several claimed wild medicinal herbs know to grow in north Africa were collected from wilderness locations believed to be more prone to both of water and borne pollution. The planets identities were confirmed by the botany department of our university.

The dust and the attached soils were kept to dry away from the direct sunlight after which they were grounded into a homogenous powder.

The samples were then extracted with acetonitrile then treated with sodium chloride and homogenized for five minutes. The acetonitrile layer centrifuged at high speed then concentrated to a smaller volume under nitrogen. The samples were transferred to SPE tube and the pesticides were eluted with a mixture of acetonitrile: toluene (3:1) then concentrated to near dryness. Final volumes were made in n-hexane.

The method was subjected to a complete and careful validation procedure. The percent recoveries were in the range of 70 to 89%

The residues were analyzed using GC with capillary column 14% cyanopropyl phenyl 86% dimethylsiloxane, 30x0.25mm, ID 0, 15 micrometer film.

The concentration levels of the determined species were investigated in terms of location and the possible source of contamination.

Targeted analysis and screening of intracellular metabolites in zebra fish and surrounding water after exposure to cadmium

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Standard ecotoxicity tests focus on macroscopic endpoints such as death, reduced motility and/or inhibited reproduction. In this study we attempted to find more sensitive endpoints by focussing on the relative change in concentration of 90 nitrogen containing native metabolites, such as amino acids, peptides and (phosphorylated) DNA bases. These metabolites can serve as stress indicators and may have the potential to predict the type of stressor in case of an unknown toxic stress.

Zebra fish eggs (*Danio rerio*) were exposed to increasing concentrations of cadmium. At each exposure concentration 6 eggs were hatched. After 96 hours the experiment was stopped. The macroscopic effects ranged from undisturbed hatching at the three lowest exposure concentrations (and control group) to disturbed hatching in the two highest exposure concentrations. After the experiment the hatched embryos, unhatched eggs and exposure water were frozen until extraction.

Extraction was performed by 10 minutes of sonication in water followed by centrifugation of the extract. A subsample of the supernatant liquid was combined with acetonitrile and injected on the LC-LTQ-Orbitrap MS (Full scan range m/z 50 to 600 with a resolution of 30.000). The samples of the surrounding water were injected directly. For the targeted analysis the retention time and the exact mass of the 90 nitrogen containing metabolites was used to identify and quantify the peak areas of the compounds. The results were expressed as relative to the peak areas in the control experiment.

The first results show that 66 metabolites were detected in the extracts and 30 in the exposure water. The results show concentration changes (both increasing and decreasing) in target metabolites relative to the control even before macroscopic effects are detectable. With the mass resolving power of the Orbitrap and statistical software like Sieve, it is possible to find significant changes between the different levels of exposure.

The current set of metabolites will be expanded as more compounds are identified for the full scan data set. Current experiments involve *Daphnia magna* and may be expanded to other trophic levels, such as bacteria and algae, which are relevant species for water quality assessment.

Desorption kinetics of phenanthrene and lead from a contaminated soil

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Heavy metals and polycyclic aromatic hydrocarbons (PAHs) exist naturally in soils in acceptable concentrations. However, recent studies proved the simultaneous accumulation of PAHs and heavy metals in soils surrounding urban complexes, gas stations, metalliferous mines, coking plants and major roads [1]. Therefore, it is important to predict and prevent the transport of these contaminants through soils. Various studies have been made in order to describe the sorption kinetics and equilibrium of different contaminants [2], but little attention is paid to desorption processes and their enhancement. To our concern this is a very important issue, since the (bio) availability of these contaminants depends on desorption and consequently affects the efficiency of a (bio) remediation process.

The objective of this experiment is to evaluate the influence of simultaneous contamination in the desorption kinetics of heavy metals and PAHs. Phenanthrene and lead were chosen as representative contaminants of each class. A soil historically contaminated with 5000 mg/kg of Pb, spiked with phenanthrene, was used as soil specimen. Soil sample was allowed to contaminate for more than one week. Batch desorption tests were performed using different desorption solutions, in order to evaluate and compare their efficiency. Namely, deionised water, solutions of ethylenedinitrilo tetraacetic acid disodium salt (Na-EDTA), polyethylene glycol dodecyl ether (Brij® 35 P), polyethylene glycol sorbitan monooleate (Tween® 80), and composed solutions of Na-EDTA/ Brij® 35 P and NA-EDTA/ Tween® 80.

The experiments were carried out in flasks containing 2 g of soil and 10 mL of desorption solution, agitated in a shaker at room temperature for different contact times. This method allowed keeping the equilibrium undisturbed. The pH of the supernatant was measured after centrifugation of the samples. Proper duplicates were undertaken.

The experimental data from each desorption run were fitted by commonly used kinetic models like Elovich, Lagergren, Second Order Equation and an Empirical Power function. The tested solutions showed very high efficiency desorbing both contaminants, comparing to water. Hence, there are good perspectives in the application of these solutions as enhancers of remediation processes.

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Ergosterol and FAME biomarkers as indicators of changes in soil microbial communities in a uranium mine area

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It is well known that soil microorganisms are sensitive to environmental stresses and degradation and severe impacts on microbial community can occur following disturbance, both in terms of total biomass and species composition.

Thus, included in the tier 3 of a site specific risk assessment that is being carried out in an abandoned uranium mine (Cunha Baixa uranium mine, Centre of Portugal), fatty acid methyl esters (FAME) and sterols (ergosterol, cholesterol, cholestanol and coprostanol) were analysed to assess the impact of soil contamination with metals and radionuclides, in the structure of the microbial community, in seven sampling sites at different distances from the mine (A-D-E-F-G-H-I). Surface (0-20 cm) soil samples (10 replicas) were collected in those sampling sites in the different seasons of the year (November, February, May and August). After extraction and methylation, FAME's were quantified by gas-chromatography coupled to a mass spectrometry (GC-MS); sterols were also quantified by GC-MS after extraction and derivatization procedures. Two-way analysis of variance and principal component analysis (PCA) were performed on FAME's and sterols data. Statistical significant differences were obtained among sampling sites and seasons for all detected and quantified FAME's as well as for ergosterol, cholesterol, cholestanol; no coprostanol was detected in any analysed sample. Through PCA analysis two distinct groups were set apart along the first two components. One group included sites at a great distance from the mine (E, H and I) which where correlated with higher contents of *i*C15:0 and *i*C16:0, both indicators of gram-positive bacteria, as well with the three sterols. The second group in turn was composed by sampling sites (A, D, F and G) most impacted by ore exploration, *in situ* leaching of poor ore, and sludge from the effluent treatment pond. These sites where correlated with higher contents of *i*C16:0 (gram positive bacteria indicator), *cy*C17:0 (generally common in gram negative bacteria) and C18:0 and C17:0 (indicators of actinomycetes). The profile of FAME's obtained in the sampling sites revealed different predominance of groups of bacteria which are a clear indication of differences in the soil microbial communities that are directly related to the environmental conditions prevailed in the uranium mine area.

Plant litter decomposition in a uranium mine area: The effect of litter quality *versus* local contamination

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In the third tier of the ecological risk assessment of contaminated sites, structural and functional features of ecosystems are usually assessed under field conditions. Organic matter (OM) breakdown is a mandatory endpoint to be assessed, as it is a crucial function for the sustainability of terrestrial ecosystems. The effect of metal pollution in organic matter decomposition is well described and the subsequent accumulation of OM in mineral soil affect a wide spectrum of soil characteristics compromising possible reclamation processes. The main goal of this study was to analyse the impact of soil contamination with metals/radionuclides in the litter decomposition, within Cunha Baixa uranium mine area (Portugal). To attain this goal nylon litterbags (1 mm mesh size) were filled with dried material (70°C, for 48h) of the most representative tree species from the area (*Salix* sp., *Quercus robur* and *Pinus sylvestris*), individually or mixed in equal proportions, and buried in the upper 50cm of soil, in 5 different sites (A-B-D-F-I), at different distances from the mine pit. The litter bags with a mixture of the three species aimed to assess if the diversity of litter material enhances their degradation. Three replicated litterbags for each species and the mixture were withdrawn from the field after 3, 6, 9 and 12 months. Extracted litter bags were rinsed with tap water; litter was dried at 70°C for 48h and weighed to determine leaf biomass loss. Organic and inorganic matter, ash and ammonium-nitrogen content were evaluated in initial and decayed litter. Fourier Transformed Infra-red spectrometry (FTIR) was additionally performed to analyze if the profile of organic compounds of leaf litter changed throughout decomposition. Species, mine site and buried time revealed to have a statistical significant effect ($p<0.01$) on leaf biomass loss; higher percentages of loss (>40%) were obtained for oak leafs, especially after 9 months in local I (reference site) which was correlated with a high decrease in organic matter (15 to 20%). Pine leaf showed the lowest decrease in OM matter especially in sites A, B and D impacted by mining activities. Inorganic matter in decayed leafs increased throughout time and more significantly in sites B, D and I for willow and oak species, which also presented substantially higher content of ash. Higher content in ammonium-nitrogen was registered in oak leafs for all 5 mine soils, after 6 months of exposure of litterbags. Pine-tree litter presented the lowest values of ammonium-nitrogen content. According to FTIR spectrum, a different pattern of evolution of organic compounds, throughout time and for the different mine sites, was observed for the 3 leaf species. In general, the absorbance decreased over time, for oak leafs, with some variability between sites. The opposite was observed for pine and willow leafs since an increase of absorbance is generalized for all the sites. Oak litter was the species which in general suffered higher decomposition after 12 months especially in local I. No enhanced degradation was observed for litterbags with mixed litter. The study demonstrated that organic matter decomposition ability seemed to be disturbed in soils most impacted by mining activities; however, this observation is extremely species dependent.

Effect-directed analysis of contaminated sediment from highly industrialized area in Serbia

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Industrial area in the city of Pancevo in Serbia is represented by a big industrial complex consisting of a petrochemical factory, an oil refinery and a chemical fertilizer factory. All industrial effluents are released in the wastewater canal (WWC) whose main environmental receptor is the River Danube.

In the present study, effect-directed analysis (EDA) was applied to evaluate the contribution of the monitored target organic compounds in the WWC sediment to potential hazards of the complex contamination and to suggest additional potentially relevant compound groups as a basis for further toxicant identification and monitoring.

The present EDA study is based on two toxicological endpoints including EROD induction in H4IIE rat hepatoma cells as a biomarker for exposure to hazardous aromatic compounds with arylhydrocarbon receptor (AhR) – mediated activity, measured as 7-ethoxyresorufin-*o*-deethylase (EROD) activity and tetrazolium salt reduction cell cytotoxicity/proliferation assay (MTT) for examination of effect of selected fractions on cell growth. These bioanalytical tools were combined with an automated multistep normal phase fractionation of sediment extracts and chemical analysis based on gas chromatography with mass spectrometry (GC-MS).

Fractions characterized by different-sized polycyclic aromatic hydrocarbons (PAHs) exhibited high sample potencies relative to the 2,3,7,8-TCDD standard (TCDD-EQs) in EROD bioassay ($0.3\text{--}31 \times 10^3 \text{ pg g}^{-1}$ dry wt.). Chemical analysis of the most active fractions revealed great concentrations of PAHs (up to $290 \times 10^2 \text{ ng g}^{-1}$ SEQ), methylated PAHs (up to $900 \times 10^2 \text{ ng g}^{-1}$ SEQ), and other alkyl-substituted PAHs. Instrumentally derived toxic equivalents (TEQs) were calculated where it was possible, and compared to TCDD-EQs to see how much of the biological response can be explained by the analytical findings. Major parts of TCDD-EQs for fractions could not be attributed to analysed compounds indicating the presence of toxicologically important EROD-inducing unknowns in the WWC sediment. Results of the cell cytotoxicity/proliferation assay on H4IIE cell line suggest the presence of sediment pollutants with pronounced potency to disturb cell growth. Further investigations, concerning identification of suggested potentially relevant compound groups have been recommended.

Soviet polychloropinen - non-racemic source of Toxaphene congeners in the environment

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Polychloropinen was a major insecticide product in the USSR, produced by hydrochlorination and subsequent chlorination of natural pinene. It was shown that both addition of HCl and free-radical chlorination proceed with preservation of enantiomeric purity and this process was used for preparation of pure enantiomers of Toxaphene congeners[1].

A specimen of Polychloropinen was separated on SiO₂/Hexane column and fractions, containing two major persistent congeners, Parlar no. 26 and Parlar no. 50 were analyzed on GC-MS with a chiral stationary phase. Standard solutions of racemic Parlar no. 26 and Parlar no. 50 and these compounds, prepared from optically active (1S)-(-)- α -pinene were analysed under the same conditions. Satisfactory enantioseparation was achieved. Preliminary results suggest that:

- 1) The specimen of Polychloropinen contains non-racemic Parlar no. 26 (er = 1.5) and Parlar no. 50 (er = 1.5)
- 2) Parlar no. 26 and Parlar no. 50 obtained from the specimen of Polychloropinen and from (1S)-(-)- α -pinene are enriched in different enantiomers. Therefore major enantiomers in the specimen of Polychloropinen made in USSR are (1S)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane (Parlar no. 26) and (1S)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane Parlar no. 50

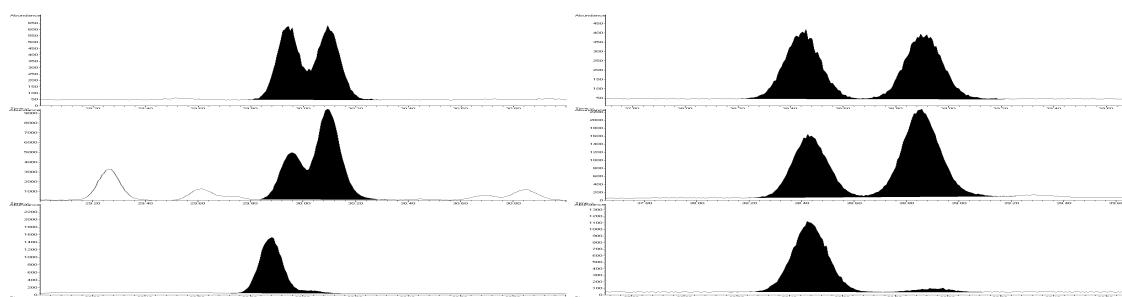


Fig. 1. Chiral separation of Parlar no. 26 (left) and Parlar no. 50 (right). Upper line – racemic standard, middle line – fraction of Polychloropinen, lower line – (1R)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane (Parlar no. 26) and (1R)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane Parlar no. 50

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Absolute configuration of Toxaphene congeners Parlar no. 26, 32 and 50

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Pure enantiomers of important Toxaphene congeners Parlar no. 26, 32 and 50 were obtained *via* hydrochlorination of optically active (1S)-(-)- α -pinene. Structure of isolated enantiomers were resolved by RCA and/or determined with VCD method. Now we report separation of racemic standards of these compounds on a chiral GC phase (BGB 172 (BGB analytics, Waedenswil, Switzerland) 30 m, 0.25 mm, 0.25 umchiral separator: 20% tert-butyldimethylsilyl-beta-cyclodextrin dissolved in BGB-15 (15% phenyl-, 85% methylpolysiloxane) and assignment of absolute configuration of first and second eluting enantiomers.

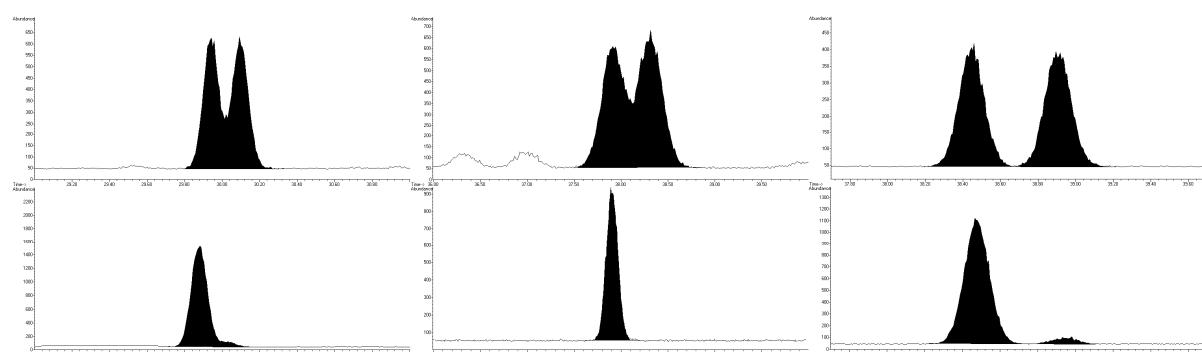


Fig. 1. Chiral separation of Parlar no. 26 (left), Parlar no. 32 (center) and Parlar no. 50 (right). Upper line – racemic standard, lower line – (1R)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane (Parlar no. 26) (1R)-2,2,5-*endo*,6-*exo*,8,9,10-Heptachlorobornane (Parlar no. 32) and (1R)-2- *endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane Parlar no. 50.

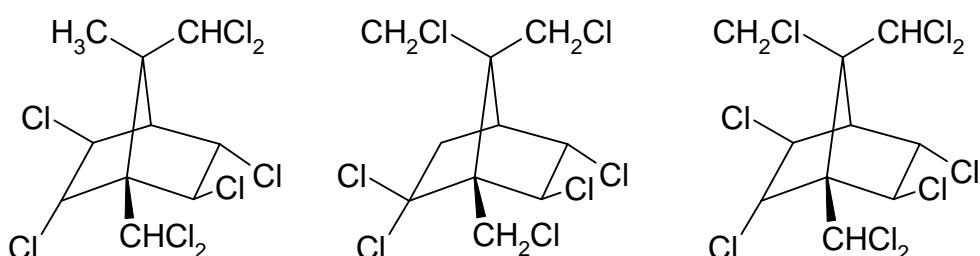


Fig. 2. Absolute configuration of first eluting enantiomers of Parlar no. 26, 32 and 50

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OH-PCB and OH-BDE in mother/offspring pairs of polar bears (*Ursus maritimus*) at Svalbard

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High levels of polychlorinated biphenyls (PCB) and hydroxylated metabolites of PCBs (OH-PCBs) have been reported in polar bears (*Ursus maritimus*) at Svalbard, Norway^{1,2}. In contrast, relatively low levels of polybrominated diphenyl ethers (PBDEs) and their hydroxylated metabolites (OH-BDEs) have been found in polar bears³. OH-PCBs play a major role in thyroid hormone disruption in heavily exposed animals^{4,5}. The aim of the present study was to investigate levels of OH-PCBs and OH-BDEs in mother-offspring (3-4 month old) pairs of polar bears at Svalbard. Plasma samples collected in March/April 1997/1998 were analysed at the Laboratory of Environmental Toxicology which is accredited according to the requirements of NS-EN ISO/IEC 17025 (TEST 137). The multicomponent analytical method used for determination of POPs and metabolites is based on a method modified by Løken⁶.

The results showed significant levels of OH-PCBs in the cubs as well as the mothers. Levels of OH-PCBs were generally higher in the mothers than in their cubs (Fig. 1). The most dominant metabolite was 4-OH-CB187 which constituted about 35% and 50% of ΣOH-PCBs in cubs and mothers respectively. Levels of 4'-OH-BDE49 and 4-OH-BDE42 were just above detection limits in some of the bears. The levels and pattern in the mothers are consistent with earlier reports of OH-PCBs and OH-BDEs in adult polar bears². High levels of OH-PCBs may indicate a high risk for toxic effects for both newborns and adult polar bears. Studies are in progress to investigate disposition and effects of PCBs and OH-PCBs in mothers and offspring. The project is part of the International Polar Year 2007-2009, and is funded by the Norwegian Research Council.

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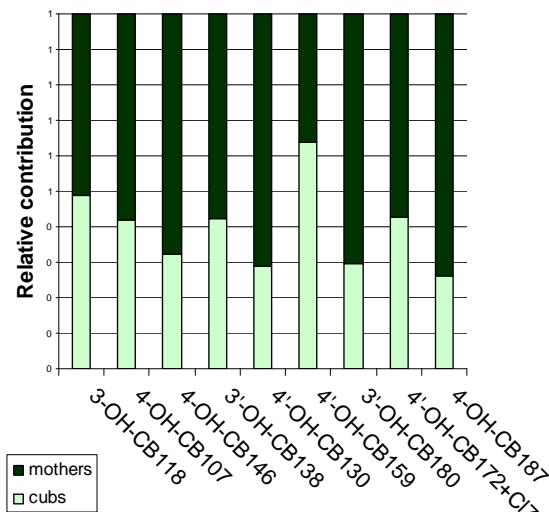


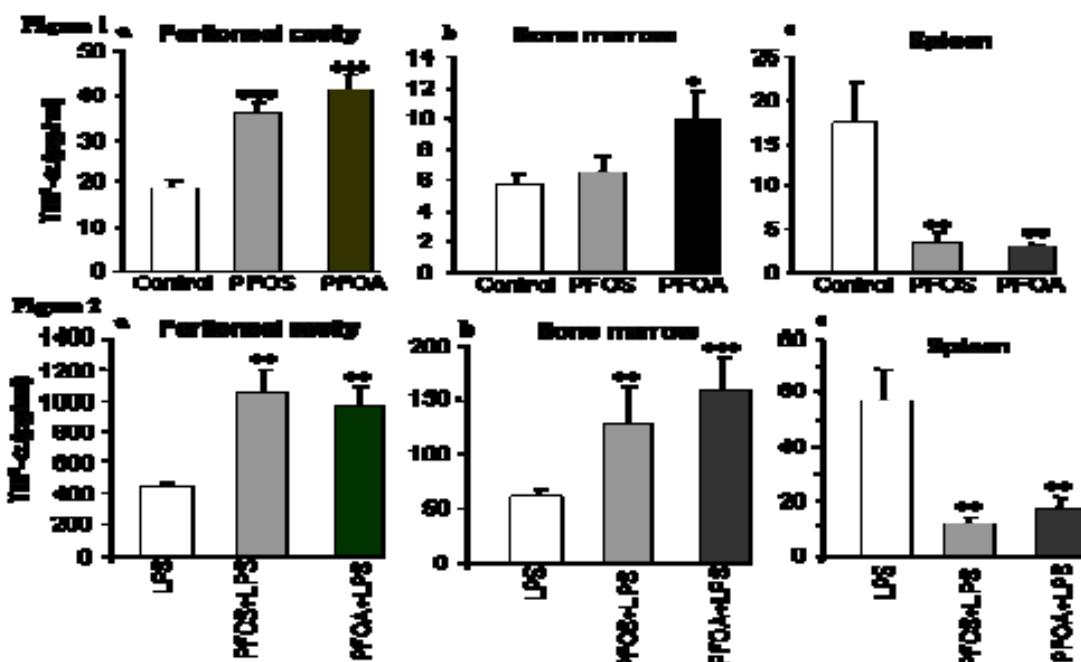
Figure 1. Pattern of OH-PCBs in polar bears

High-dose, short-term exposure of mice to perfluorooctane sulfonate (PFOS) or perfluorooctanoate (PFOA) activates certain aspects of the innate immune system and enhances inflammatory responses induced by lipopolysaccharide

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We and others have previously shown that perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) exert suppressive effects on the immune system of mice, including thymic and splenic atrophy and attenuation of adaptive immune responses (1-3). Here, we examine the effects of these compounds on the innate immune system of mice with respect to the numbers of total and different types of white blood cells (WBC), as well as *ex vivo* production of the inflammatory cytokines tumor necrosis factor- α (TNF- α) and interleukin 6 (IL-6) by peritoneal, splenic and bone marrow macrophages, with and without stimulation by lipopolysaccharide (LPS). C57BL/6 mice treated with 0.02% (w/w) PFOS or PFOA in their diet for 10 days exhibited a significant reduction in the numbers of total WBC, primarily lymphocytes, as well as certain increases in circulating levels, peritoneal and bone marrow cells production of TNF- α and IL-6, both with and without LPS stimulation, whereas the corresponding release by splenic cells was attenuated (Figure 1 and 2). Therefore, the innate immune system is not only preserved, but inflammatory responses to LPS are augmented following exposure to these xenobiotics.



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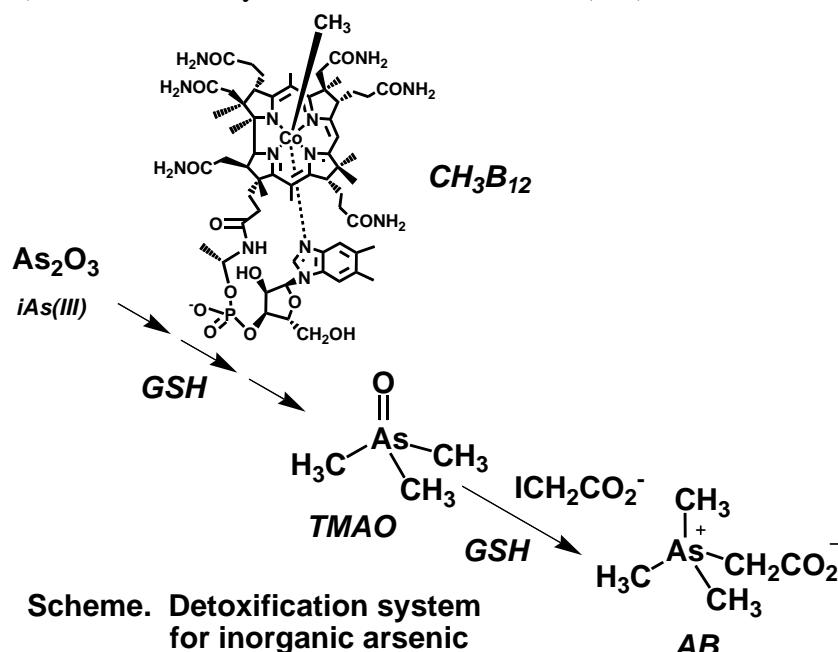
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Arsenic detoxification system: Transformation of inorganic arsenic into non-toxic arsenobetaine mediated by artificial enzyme with vitamin B₁₂ cofactor

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Detoxification processes via molecular transformation of toxic materials into non-toxic compounds are highly desirable in a new eco-friendly and safe remedial approach replacing conventional treatment, simply the removal and storage of pollutants from contaminated wastes, soils and waters. The efficient biomimetic catalysts that simulate the functions of natural enzymes with high activity and selectivity under mild conditions may play an important role in realising a low-energy-consumption and safe detoxification process. In particular, the detoxification of acutely toxic inorganic arsenic is realised by converting arsenic trioxide, As₂O₃ [iAs(III)], into essentially non-toxic arsenobetaine (AB), which occurs naturally in many types of seafood. Here, it is demonstrated that methycobalamin (CH₃B₁₂), serving as a methyl group donor, converting arsenic trioxide into TMAO as the main product in the presence of glutathione reduced (GSH) [1, 3], which followed by subsequent treatment of TMAO with iodoacetic acid and GSH to give AB with a high yield [2]. Since vitamin B₁₂ (CH₃B₁₂) and GSH are biomaterials and reactions proceed in water as an aqueous medium under mild conditions, a safe and environmentally-friendly process, conveting toxic inorganic arsenicals into non-toxic arsenobetaine, is successfully confirmed [3].



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Acknowledgments

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The impact of ionic liquids on the metabolism of ascomycota fungi

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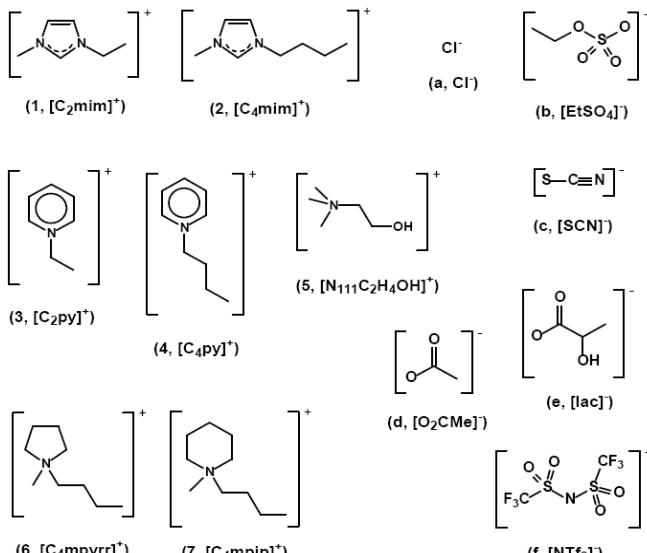
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Ionic liquids are salts, and hence completely composed of ions, that are liquid at, or near, room temperature. Their negligible vapour pressure and usual non-flammability are the basis for them sometimes being classified as “green” solvents. In addition, ionic liquids can be, by design, chemically and thermally stable, recyclable, and with tuneable physical and chemical properties. Integration of these with their outstanding solvation ability opens doors for numerous industrial applications as replacements for conventional organic solvents. Their environmental fate in aquatic and terrestrial compartments, however, is a complex equation which crosses numerous unknown abiotic and biotic factors.

Although this field is still in its infancy, significant efforts are being made to collect ecotoxicological data, and to design ionic liquids with reduced toxicity and increased biodegradability.¹ Testing a vast number of ionic liquids and organisms is rather time-consuming and costly, therefore, in this work, Ascomycota fungi were used as eukaryotic model organisms. These soil microorganisms play a central role in the carbon cycle in earth, own rich enzymatic systems and are able to adapt to extreme environments. The metabolic footprint, as investigated by electrospray ionisation mass spectrometry, revealed that fungal cultures respond to specific ionic liquids (combining different cationic head groups with different anions, see Figure) by changing their cell biochemistry, resulting in an altered pattern of secondary metabolites.² Following these observations, complementary objectives were imposed, such as design of biocompatible and/or biodegradable ionic liquids for specific applications.



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Perfluorinated compounds and gene expression profiles in middle aged women from Norway

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Perfluorinated compounds (PFCs) is a large group of compounds that have similar chemical structure; a hydrophobic fluorinated carbon tail, and a polar, hydrophilic head attached to one end of the carbon chain. PFCs act as surfactants and have been widely used in industrial products. As a result, they are also ubiquitous in the environment, biomagnifies in the food chain and have been detected in human blood around the world [1, 2]. Concerns have been raised about these compounds since the concentrations found in the environment are relatively high and currently perfluorooctane sulphonate (PFOS) and perfluorooctanoate (PFOA) are the dominating contaminants in nature and in humans. These two compounds are also potent peroxisome proliferators in rodents and as a result, alterations in fatty acid and lipid metabolism have been observed in rats exposed to these chemicals [3, 4]. PFOS and PFOA have also been detected in human cord blood in levels comparable to those found in maternal plasma, clearly indicating a transfer of PFCs to the fetus. As a result of all these findings, PFOS has voluntarily been withdrawn from production.

In our study, we have analyzed the concentration of eight PFCs in plasma from 286 postmenopausal Norwegian women. The women are participants of the Norwegian Women and Cancer Study and are randomly chosen from women born between 1943 and 1957. Most prominent PFCs in the study group were Perfluorooctane sulphonate (PFOS), Perfluorooctanoate (PFOA) and Perfluorohexane sulphonate(PFHxS). Concentrations varied between 0.2 and 50 ng/g plasma for linear PFOS, which was the dominating compound. We have also performed a full genome microarray gene expression analysis on the same blood samples, which is a technique used for evaluating which genes that are up- or down- regulated at the moment of blood draw. Differences in gene expressions responsible for a number of biochemical pathways between high and low contaminated women of PFOS, PFOA and PFHxS are currently evaluated and results will be presented.

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Perfluorinated compounds in delivering women from south central Vietnam

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As a result of many years of production and use in the industry, perfluorinated compounds (PFCs) are frequently found in the environment as well as in human blood world wide. The exposure routes of PFCs to humans are not well understood, but several different pathways are considered as important; e.g., the diet and exposure to house hold dust[1]. There is limited information about human exposures to PFCs in developing countries. Previous studies indicate that there are worldwide geographical differences in human levels of PFCs, with people in the western world generally having higher concentrations than in the developing countries [2, 3]. There are however large differences between countries within Asia for example with elevated levels reported Japan and low levels in India and Sri Lanka[2]. The only data presented from Vietnam is in breast milk where the levels were indicated to be moderate compared to other Asian countries [4]. Since Vietnam is a country of rapid development it is important to monitor background concentrations in the population to gain more information about exposure routes to humans and the global distribution of PFCs. In this study, we have investigated the concentrations of eight different PFCs in 91 pregnant women from south central Vietnam. Our main objectives were to provide more information about exposures to PFCs in South East Asia and evaluate differences in concentrations between an inland and a coastal study group.

Perfluorooctane sulphonate (PFOS), Perfluorooctanoate (PFOA) and Perfluorohexane sulphonate (PFHxS) were detected in 98-100% of all samples. Linear PFOS were the most common compound and the concentration varied between 1.0 and 8.9 ng/g plasma. The range for PFOA and PFHxS were 0.6-94 ng/g and 0.2-69 ng/g respectively. The women from the coastal city Nha Trang had higher concentrations of all investigated compounds than women from the inland district Dien Khanh. This may be explained by differences in living conditions.

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Evaluating the toxicity of flame retardant Fire Master 550 on eco-indicator organism *Daphnia magna*

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Firemaster 550 (FM550) is a chemical flame-retardant formulation used in furniture foams and fabrics. It contains four major chemical components, two of which are brominated (1), and is marketed as a safe replacement for penta brominated diphenyl ether (Penta). Penta is banned in parts of the United States and regulated in the European Union due to toxicity and persistence.

FM550 is considered safer than Penta because it has a shorter half-life, a low bioaccumulation factor and low water solubility (2). However, toxicity assays performed with FM550 show that the acute LC₅₀ of FM550 and the chronic LC₅₀ of concentrated Firemaster BZ-54 in water-dwelling eco-indicator *Daphnia magna* are 1.2mg/L and 79.3 ug/L, respectively (3,4). These numbers place FM550 in the moderately severe acute and severe chronic LC₅₀ categories for aquatic organisms.

FM550 has already been shown to leach out of consumer products like couches and into the environment (5). But, not many toxicological tests beyond those that assay for endpoints such as death or skin irritation have been performed on FM550. Assays that look for molecular responses such as changes in gene expression are especially lacking. FM550's toxic mode of action is unknown; our work seeks to determine the mechanism by which FM550 causes toxicity to *D. magna*. This will be done via differential gene expression (DGE) analysis using microarray technology. We are also investigating and validating a new method of DGE analysis using high-throughput sequencing (HTS), which could provide a faster, less expensive method for determining the molecular effects of toxicants. Preliminary results (6) show HTS and the subsequent alignment is an effective method for assembling the *D. magna* transcriptome, an important first step in the DGE analysis process.

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The effects of ruthenium(II) complex on the activity of antioxidative enzymes

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Reactive oxygen species (ROS), such as the superoxide anion ($O_2^{\cdot-}$), the hydroxyl radical (OH^{\cdot}), hydrogen peroxide (H_2O_2) and reactive nitrogen species (RNS) including nitrosyl radical (NO^{\cdot}) are known as pathogenic factors of cell damages [1]. The organism has evolved specific defenses against these ROS including superoxide dismutase (SOD), glutathione peroxidase (GPx), and catalase (CAT) whose function is to convert these reactive chemical species in less toxic molecules. As previously reported, ruthenium complexes shown antioxidative enzyme activities (SOD, CAT) and that may be responsible for the complex-induced cytotoxicity [2].

We investigated the effect of three different doses (0.4, 4.5 and 90.4 $\mu M/kg$ bw) of ruthenium(II) complex with trifluoroperazine dihydrochloride, $TFH_2[Ru(DMSO)_3Cl_3]Cl \cdot C_2H_5OH$, (synthesized and characterized in our laboratory in previously researches) on the activity of SOD and CAT, as well as influence on nitrite production (NO_2^-) and level of erythrocytes malondialdehyde (MDA) in rat blood.

The first and second doses of the complex exhibit almost the same SOD activity as control group, as like their isoenzyme SOD_1 and SOD_2 activity. The third dose significantly increased the total SOD activity ($p<0.001$) and isoenzymes, SOD_1 and SOD_2 activity. The total SOD activity in samples of rat blood treatment with 90.4 $\mu M/kg$ bw of ruthenium(II) complex is increased to 73 % of control group, as well as the isoenzyme SOD_1 and SOD_2 activity, 70 and 150 %, respectively, when compared to the control group. The CAT activity of doses I and II are slightly lower than control group, but there is unsignificant differences ($p>0.05$). The decreases of nitrite levels in samples of doses II suggest a possible interaction between the complex and nitrogen(II) oxide [2]. Very significant differences ($p<0.001$) between control group and dose III show that ruthenium(II) complex in a higher doses induced production of NO^{\cdot} or it cannot reacted with them. At last, MDA as parameter of lipid's peroxidation, shows differences between control group and all doses, with very significant difference between the third doses.

In addition, it was shown that the new ruthenium(II) complex, has possibility to capture NO^{\cdot} radicals in lower doses, doesn't increase SOD and CAT activities and it is also able to capture free radicals such as superoxide anion and hydroxyl radical.

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Uncertainty Estimation for the Determination of Trace Heavy Metals in Human Hair by Flame and Electrothermal Atomic Absorption Spectrometry

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Abstract

Human hair indeed is a suitable biomarker for determination of trace elements absorbed into the body. However, the results are reliable only if the experimental results are based on the elements deposited inside the hair and not adsorbed by it, in other words the endogenous elements. Trace metals present in the environment are adsorbed on the hair, exogenous elements and cause serious errors in determination endogenous elements. In the present work, we tried to find an efficient solution to wash adsorbed trace heavy metals from hair and make the hair samples ready for determination of cadmium, lead, copper, iron, manganese, and nickel in human hair are developed. Then, we propose uncertainty estimation for the analytical results we obtained from determination of above elements by flame and electrothermal atomic absorption spectrometry.

Eight different organic and inorganic washing solutions are tested for desorption of the above exogenous elements from hair. It was indicated that the most suitable solution for desorption of Mn, Pb, Cu, Cd, Fe, and Ni from hair samples was 1% (w/v) sodium diethyldithiocarbamate (DDTC). The hair samples were digested afterward in a mixture of HNO₃, and H₂O₂. Concentrations of exogenous and endogenous of each element were carried out by FAAS and ETAAS. To estimate the uncertainty of analytical result obtained, we propose assessing trueness by employing spiked sample. Two types of bias are calculated in the assessment of trueness: a proportional bias and a constant bias. We applied Nested design for calculating proportional bias and Youden method to calculate the constant bias. The results we obtained for proportional bias are calculated from spiked samples. In this case, the concentration found is plotted against the concentration added and the slope of standard addition curve is an estimate of the method recovery.

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Effects of MPTP, METH and FeSO4 on the formation of acrylamide measure as adducts to hemoglobin

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Acrylamide is a chemical known to be neurotoxic both to humans and animals. Recently it was reported that acrylamide is formed in heated human foods and that humans are exposed to acrylamide on daily bases. In this study adult C57 mice were treated with either 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine-hydrochloric acid (MPTP) methamphetamine (METH) or FeSO₄. At the end of the experiment, 24hrs after exposure to FeSO₄ and 72 hrs after exposure MPTP or METH, blood samples were collected and acrylamide levels measured as adducts to hemoglobin (Hb) using LC/MS-MS. A significant increased of acrylamide Hb adducts was observed after treatment with all these compounds. Since the common underlying mechanism for the neurotoxicity of, MPTP, METH or FeSO₄ is through free radical formation the finding suggests that acrylamide is probably formed endogenously as a result of oxidative stress. In a follow up study, in order to confirm the possible formation of acrylamide at 37°C and the role of oxidation, we incubated glucose and asparagine at 37°C in the presence of H₂O₂ and found that acrylamide is formed in a time depended manner. The study further suggests that oxidative stress may lead to possible endogenous formation of acrylamide. However, more studies are warranted to understand the effect of physiological conditions that are linked to chronic oxidative stress.

Cometabolic degradation kinetics of 4-chlorophenol and phenol by *Pseudomonas putida*

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Phenol and chlorophenols are toxic compounds widely used in chemical and petrochemical industries. Despite the recalcitrant nature of those pollutants, several bacteria have been shown capable of their biodegradation. In the present study, a pure pre-adapted culture of *Pseudomonas putida* CECT 4064 has been used for biological degradation of phenol and 4-chlorophenol (4-CP). Cometabolism is a well-established method to enhance the biodegradation of chlorophenolic compounds. Thus, the presence of growth substrates such as phenol not only serves to sustain biomass growth but also induces enzymes required for 4-CP degradation. The aim of this work is to study the biodegradation of either phenol or 4-CP as sole carbon sources and the cometabolic transformation of 4-CP in presence of phenol by *P. putida*. Kinetic models for simultaneous description of microbial growth and pollutants degradation are also proposed.

P. putida was propagated in a mineral salts medium containing 200 mg·L⁻¹ of phenol. Aerobic batch cultures were carried out in conical flasks with a working volume of 150 mL at 30°C, pH 6.8 and 120 rpm. Different concentrations of phenol (40-530 mg·L⁻¹) and 4-CP (5-135 mg·L⁻¹) were tested. Cometabolic studies were carried out at two 4-CP concentrations (25 and 50 mg·L⁻¹) adding a wide range of phenol concentrations (10-275 mg·L⁻¹). Biomass was determined by optical density measurements ($\lambda= 600$ nm). Phenol and 4-CP were measured by HPLC with UV-VIS detector ($\lambda= 280$ nm).

Phenol was completely degraded by *P. putida* in the entire range of concentration studied. Since the microorganisms were previously adapted to the toxic compound, the cell growth was satisfactorily described by the Monod model. The phenol consumption rate was modelled taking into account the yield of biomass on substrate. The obtained kinetic parameters were $\mu_{max}= 0.36$ h⁻¹, $K_M = 6.907$ mg·L⁻¹ and $Y_{XS} = 0.22$ mg·mg⁻¹.

No significant 4-CP removal was observed when it was treated as sole carbon source due to its high ecotoxicity. However, the presence of phenol as cometabolite led to a clear enhancement of 4-CP biodegradation. A kinetic model for the simultaneous description of microbial growth and the diauxic degradation of both pollutants was proposed. The model takes into account that phenol greatly attenuates the toxicity of 4-CP and supports the cell growth with no significant inhibition, whereas 4-CP inhibits the cell growth through the inactivation of cells. The evolution of both substrates concentrations along the process proved the occurrence of competitive inhibition. Experimental data of biomass, phenol and 4-CP concentrations were accurately predicted by the proposed model.

Acknowledgements

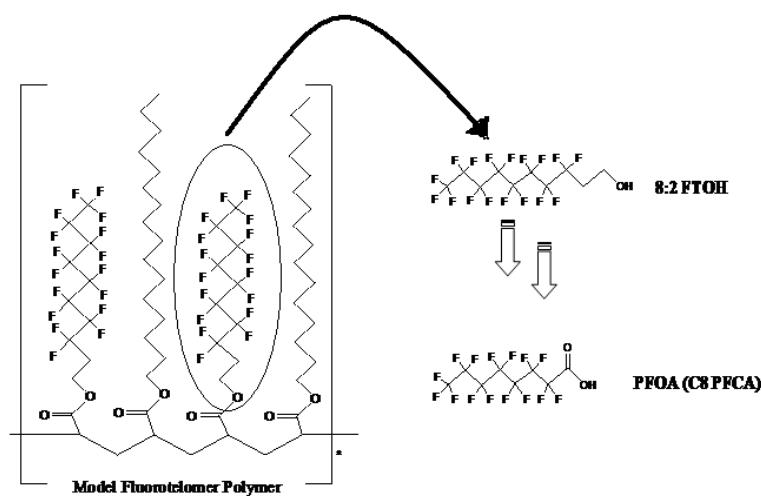
This work was supported by Comunidad de Madrid - Universidad Autónoma de Madrid through the project CCG08-UAM/AMB-4436.

Degradation of fluorotelomer-based polymers in the environment

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Fluorotelomer (FT) based polymers are widely used in textile treatments and upholstery and carpet industries as oil and water repellents. Despite their wide industrial application, current scientific studies have neither definitively supported nor dismissed fluorotelomer based polymers as potential contributors to the burden of perfluorinated compounds in the environment. The current studies explored the susceptibility of a solubilised FT acrylate polymer to hydrolytic and microbe mediated degradation. In the hydrolysis study, evolution of 8:2 FTOH in pH = 6, 8, and 10 experimental vessels followed a logarithmic trend over the 80 day duration of the hydrolysis study. pH = 4 experimental vessels showed limited 8:2 FTOH evolution. ^{19}F NMR and MALDI-ToF results suggest that complete hydrolytic degradation of the polymer occurs at pH 10, and supports the suggestion that hydrolytic degradation of the polymer is limited at pH = 4. In the wastewater mediated study, the formation of 8:2 FTOH greater than what can be attributed to hydrolysis was observed in the test vessels. In addition, significant formation of PFHxA, PFHpA, PFOA, and 8:2 FTUCA was observed in the test vessels. No formation of fluorinated compounds was observed in the control vessels. Production of PFHxA, PFHpA, and PFOA peaked at 12 ± 2 , 10 ± 2 , and 11 ± 2 days respectively into the study.; the greatest concentration of 8:2 FTUCA in the test vessels was observed at 5.5 days into the study. The results from both the hydrolysis and wastewater mediated studies suggest that FT acrylate polymers are susceptible to abiotic and biotic degradation under environmentally relevant conditions.



Competitive binding of poly- and perfluorinated compounds to the thyroid hormone transport protein transthyretin

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Due to their unique surfactant properties, poly- and perfluorinated compounds (PFCs) have been extensively used, and can be found all over the environment. Concern about their environmental fate and toxicological properties have initiated several research projects. In the present study, we investigated if PFCs can compete with thyroxin (T4, i.e. the transport form of thyroid hormone) for binding to the human thyroid hormone transport protein transthyretin (TTR). Such competitive capacity may lead to decreased thyroid hormone levels as previously reported for animals exposed to PFCs.

Twenty four PFCs, together with six structurally similar natural fatty acids, were tested for binding capacity in a radioligand binding assay. The binding potency decreased in the order: PFHxS>PFOS/PFOA>PFHpA>L-PFOSi>PFNA, with TTR binding potencies 12.5-50 times lower than the natural ligand thyroxine (T4). Some lower molecular weight compounds with structural similarity to these PFCs were >100 times less potent than T4.

Simple descriptors based on the two dimensional molecular structures of the compounds were used to visualize the chemical variation and to model the structure-activity relationship for the competitive potencies of the TTR-binding compounds. The models indicated the dependence on molecular size and functional group(s), but demanded a more detailed description of the chemical properties and data for validation and further QSAR development.

Competitive binding of PFCs to TTR as observed for human TTR in the present study, may explain altered thyroid hormone levels described for PFC-exposed rats and monkeys. Median human blood levels of the most potent TTR-binding PFCs are 1-2 orders of magnitude lower than IC50-values determined in the present study. In addition, this study contributes to the understanding of the bioaccumulation of PFCs in man and possibly in other wildlife species.

Effects of the antibiotic minocycline in the cyanobacterium *Microcystis aeruginosa* growth

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The monitoring of antibiotics in the aquatic environment has gained much interest in recent years. Such is the case of minocycline (MC), a member of the tetracycline antibiotics class, with a very broad spectrum of action. Despite not being primary targets, freshwater phytoplankton species are constantly exposed to these compounds, and most of the consequences of this exposure are still unknown. Amongst the freshwater phytoplankton, the environmental relevance of cyanobacteria is primarily related to its ability to bloom and produce a range of cyanotoxins, hazardous to many organisms, including human beings.

Aiming at gaining a better insight of this compound effects' on microbial aquatic communities, cultures of the cyanobacterium *Microcystis aeruginosa* were subjected to exposure to environmental relevant levels of MC.

Firstly, the MC concentration in culture media (from 0.02 to 15 mg L⁻¹) was monitored for 10 days, by HPLC. It was observed that the initial concentration of MC in the medium strongly conditioned the decomposition rate, which was faster for the lower MC concentrations. Toxicity towards *M. aeruginosa* was assessed (from 0.02 to 1 mg L⁻¹) through the monitoring of cell growth for 14-day periods, and it increased as the levels of MC were higher. In this case, the decomposition rate of 1 mg L⁻¹ MC in culture medium was faster in the presence of *M. aeruginosa* cells. For lower concentrations, however, no such significant difference was found. Admitting that MC decomposition products remain in the culture medium, their possible influence on *M. aeruginosa* growth is being assessed (study in progress).

This study illustrates the interactions that may occur in real environments, and highlights the need to obtain data from assessments of the stress to which non-target organisms are exposed to.

This work was partially funded by Fundação para a Ciência e a Tecnologia (FCT), Portugal, through fellowships awarded to Mafalda Baptista (SFRH/BD/16292/2004) and Teodor Stoichev (SFRH/BPD/32700/2006) and the CONC-REEQ/304/2001 re-equipment project.

Identification of androgen disrupting compounds in effect directed analysed river sediment with an LTQ-Orbitrap

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Attention regarding the presence of endocrine disrupting compounds (EDCs) in the environment has been high the last decades, especially in the aquatic system. These compounds range from natural (e.g. 17 β -estradiol) and synthetic (e.g. 17a-ethynodiol, anabolic steroids) hormones, to industrial chemicals and inorganic compounds (e.g. pesticides, organohalogen metabolites), which can mimic endogenous hormones. In areas influenced by human activity, samples can contain a complex mixture of these compounds. Effect Directed Analysis (EDA) studies employ bioassay-directed fractionation techniques to be able to identify those fractions containing active compounds, and to decrease the complexity of the sample matrix before identification of the responsible compounds. The identification of key toxicants and the final confirmation of toxicity and identity are critical for the success of EDA studies. For the identification of unknown compounds one has to deal with the handling of very large datasets.

The study in short: A sediment sample from the tributary Schijn to Western Scheldt (location close to Antwerp, Belgium) was selected after a first toxicity screening of androgenic activity (AR-CALUX® bioassay). The sediment was extracted by ASE, cleaned up by GPC, and fractionated by reversed and normal phase LC. The fractions were chemically analysed on accurate mass instrument, LTQ-Orbitrap (full scan m/z 50 to 600, 30,000 in resolution). The software SIEVE (Thermo Fisher) was used to sieve the active and the non-active fractions to discriminate the peaks of interest. The requirement of a ratio of >100 between peak intensity in non-active and active EDA fractions were set to be able to handle the large dataset.

The approach described here resulted in a clearly relevant decrease of masses that were analysed in the active fractions (Table 1), i.e from ~70 000 masses present to ~40 tentatively identified compounds. Thus, one fourth of the most intense discriminated peaks (ratio >100) were tentatively identified. e.g. flame retardants, anabolic steroids, antidepressants, musks and flavouring agents.

Table 1. The number of masses discriminated in the active fractions

Fraction	Total masses	SIEVE peaks	Ratio >100	Ratio 10-100	Tentatively identified
Agonistic active fractions (n = 2)	53000	3900	99	725	21
Antagonistic active fractions (n = 4)	20400	5100	100	220	23
Total	~70 000	~9 000	~200	~1000	44

At present, the tentatively identified compounds still need to be confirmed to be present in the fractions, as well as the inherent toxicity of the compounds. In conclusion, the results here suggest that working with an accurate mass instrument is a powerful tool in the task to identify compounds in EDA samples containing a complex mixture.

Biomarkers of exposure - Analysis of haemoglobin adducts in pregnant mothers and cord blood

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Hemoglobin (Hb) adducts have been shown useful as biomarkers for exposure to electrophilic compounds (1). Such adducts have been used to elucidate the “internal dose” from exposure to electrophilic compounds or metabolites, that is potentially genotoxic compounds. Hb has the same lifespan as the erythrocytes, about 4 months in humans, which means that Hb-adducts could be used to measure exposure a few months back in time.

A new method, the adduct FIRE-procedureTM, for determination of adducts to N-terminal valine in haemoglobin (Hb) by LC-MS/MS has been developed (2). The method is sensitive and specific, and has a high throughput compared to earlier used methods. Within the EU-project “NewGeneris” (3), the method is applied for analysis of blood samples from mothers and their foetus (cord blood) from five countries within Europe.

Hb adducts from acrylamide, glycidamide (the metabolite of acrylamide), and ethylene oxide are measured. Exposure to acrylamide from food is main focus. Ethylene oxide is formed from ethene in the normal metabolism. Both compounds are also components in tobacco smoke.

There was a good correlation between adduct levels in the cord blood and the mother’s blood. The adduct levels in the cord blood were about half of the levels found in mothers. This difference could mainly be explained by that the major part of Hb in fetus consists of F-type Hb, which has glycine as N-termini instead of valine. On this basis we conclude that the internal doses of acrylamide, glycidamide, and ethylene oxide do not differ much between the mother and her fetus. Smokers were identified, particularly through the adduct level from ethylene oxide.

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Species differences in the in vitro metabolism of carbosulfan

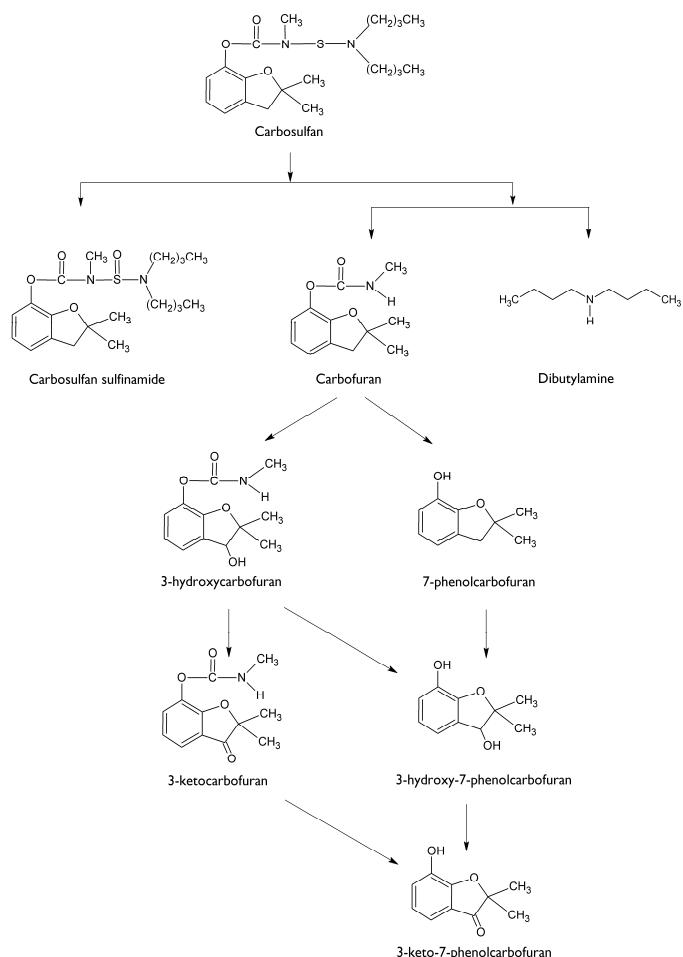
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The in vitro metabolism of carbosulfan, a widely used carbamate insecticide, by hepatic microsomes from seven mammalian species including human were studied. Altogether eight (8) phase I metabolites were detected by LC-MS; phase II metabolites were not found in human homogenates fortified with appropriate cofactors. The primary metabolic pathways were the initial oxidation of sulfur to carbosulfan sulfinamide ('sulphur oxidation pathway') and the cleavage of the nitrogen sulfur bond (N-S) to give carbofuran and dibutylamine ('carbofuran pathway').

3-hydroxycarbofuran was the main metabolite in all species, but otherwise there were interspecies differences in carbofuran pathway metabolites. Only rabbit liver microsomes were able to metabolize carbofuran via hydroxylation to 7-phenolcarbofuran. Carbofuran was not detected in dog liver microsomes due to rapid further metabolism. 3-hydroxy-7-phenolcarbofuran was not detected in both rat and mouse liver microsomes while 3-keto-7-phenolcarbofuran was not detected in rat liver microsomes. The cross-species comparisons illustrated noteworthy kinetic differences. In general, metabolite formation as a function of time and the metabolic clearance rates indicated that liver microsomes from all seven species produced the more toxic product (carbofuran) and toxic metabolites (3-hydroxy-carbofuran, 3-ketocarbofuran) more rapidly than a detoxification product (carbosulfan sulfinamide).

With human derived techniques and quantitative chemical specific data based on animal to human efficiency comparison, the chemical specific adjustment factor for animal to human differences in toxicokinetics for detected metabolites were within the usual default uncertainty/safety factors for chemical risk assessment restricted to in vitro metabolic data by human and animal liver preparations.



Exposure to biomass combustion smoke induced oxidative stress and adverse health effects

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The burning of biomass in the developing world for heating and cooking results in high indoor pollution. Long-term exposure to these pollutants has been associated with increased rates of acute respiratory infections, chronic obstructive lung disease and cancer. The mechanisms of such associations remain unclear. In this study we examine the oxidative activity of biomass smoke exposure by measuring the antioxidant levels in nasal lavages of children and observed low levels of AA, SOD and GSH/GSSG ratio in children lived in biomass used households. The study suggests that the biomass smoke has a potential to produce oxidative stress and adverse health effects in children. There is much more work needed to investigate the mechanisms underlying air pollution induced health problems would allow a more targeted approach to remove the most toxic components of air pollution, and could possibly provide a means to decrease individual sensitivity to air pollution.

Oxidative damage of human plasma proteins induced by benzene

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Benzene is a human carcinogen and an ubiquitous environmental pollutant. During the process of its biotransformation, reactive intermediary products (aryl oxides), reactive oxygen species (ROS) and reactive nitrogen species (RNS), provoke changes in the activities of antioxidant enzymes, impair the integrity of the cell membrane and induce structural changes in plasma proteins. The aim of this study is to evaluate oxidative protein damage (OPD) by investigating protein carbonyls (PCO), oxidative stress by total thiol (T-SH), nitric oxide (NO), lipid peroxidation (MDA) levels in human exposed to benzene. The investigations were done on blood samples of persons from urban environment, industrial area, (n=46, both sexes, from 20 to 48 years old). Plasma glycoproteins and lipoproteins were analyzed by native PAGE (8 %) according to the method of Laemmli. Protein oxidation was evaluated by measuring carbonyl group content in plasma proteins as a marker of free radical activity, according to Levine method by 2,4-dinitrophenylhydrazine was measured. The lipid peroxidation in terms of MDA was estimated by using TBARS method, T-SH group by measured after the reaction with dithionitrobenzoic acid using the method of Ellman.

Exposed to benzene decreased concentration of plasma proteins and albumine, and very significantly increased concentration of α_1 -, α_2 -glycoprotein and haptoglobin ($p<0.001$) compared with control group. Benzene significantly increased the level of erythrocytes malondialdehyde MDA ($p<0.001$), leading to the accumulation of heterogeneous protein modifications, classified as advanced glycation end-products (AGEs) or advanced lipidation end products (ALEs).

Benzene and their metabolites induced the formation of RNS and enhanced the expression of inducible nitric oxide synthase (iNOS), which can lead to the formation of excessive NO^\bullet . The present results showed that there were significantly changes in the level of NO_2^- in plasma of benzene exposed group. The combination of NO^\bullet and $\text{O}_2^\bullet-$ also results in the rapid generation of the highly reactive molecule ONOO^- . The marker for ONOO^- formation is nitration of tyrosine residues in proteins (Tyr (NO_2)). The main cellular target are of ONOO^- is thiol group containing molecules. There was a significant decrease in plasma protein thiol levels group ($p<0.001$). The observed alterations indicate that benzene might be involved in free radical processes and damage plasma proteins.

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Study of health impact for Fenton degradation of laboratory-scale synthetic dye containing wastewater

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In order to study the health impact of the waste effluent after using advanced oxidative degradation of CI reactive dyes (i.e. Black 5 and Reactive Blue 19) with Fenton's reagent, we firstly simulated the industrial dyeing process using pilot scale apparatus in our laboratories. The dye remains after the dyeing processes were treated with Fenton's reagent and the kinetics of the degradation processes were investigated using the optimal conditions reported in literatures, and the health impact of the treated waste effluents was tested using human cell lines. Our preliminary findings show that advanced oxidative degradation using Fenton's reagent can be achieved (>95%) within half an hour, and significant cytotoxicity was observed towards human liver SKHep-1 cell line.

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